
15th International Conference on

Condensed Matter Nuclear Science

Rome, Italy
October 5-9, 2009

Edited by Vittorio Violante and Francesca Sarto



Italian National Agency for New Technologies,
Energy and the Environment





ICCF-15

15th International Conference

on

Condensed
Matter

Nuclear
Science

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Editors

Vittorio Violante RdA, Francesca Sarto

Preface

We had the great honor to organize ICCF15 in Rome, occurring on the 20th anniversary of the announcement of Professor Martin Fleischman, our Honorary Chairman, and Prof. Stanley Pons in the spring of 1989. The 20th Anniversary is certainly giving a specific meaning to the Symposium supported by the content of the given lectures.

We had the honor and the privilege that the Conference, supported by the Italian Agency for Energy New Technologies and Sustainable Development (ENEA), was under the patronage of the Italian Physical Society (SIF), of the Italian Chemical Society (SCI) and of the Italian National Research Council (CNR). We also had the honor to have as speakers Prof. Martin Fleischmann, Dr. Renzo Tomellini (General Directorate for Research of the European Commission), Prof. Luigi Campanella (President of the Italian Chemical Society), Dr. Enzo De Sanctis (Vice-President of the Italian Chemical Society) and Prof. Robert Duncan (Research Chancellor of the Missouri University).

During the last two decades we understood that condensed matter nuclear science is an extraordinary mixing of knowledge because of the wide interdisciplinary character of such a research field and our opinion is that this aspect has characterized this event.

The letter we received from the President of the Italian National Council of Research –CNR– Prof. Luciano Maiani perfectly describes our feeling:

He said: “The high scientific value of the event on condensed matter nuclear science represents a reason of great interest for the research world involved into the many aspects of such a discipline”.

We received also appreciations and wishes for the very interesting Conference, by the Department Committee of the Mechanical Engineering Faculty of the University of Tor Vergata in Rome.

During the Conference Prof. Martin Fleischmann was awarded with the Preparata golden medal into the wonderful scenario of Castel Sant’Angelo.

The ICCF15 participants have been received by S.S. the Pope Benedetto XVI into the Vatican.

In order to draw the conclusions about the outcome of our contribution to the Conference we all need to consider the objectives and compare them with the results.

On the occasion of the anniversary of Fleischmann and Pons announcement we were due to guarantee the best success to this Conference.

The participation of prestigious Institutions, the content and the level achieved by the lectures and the increased interest concerning our discipline have been the indicators for the level of the conference as well as of the scientific importance of the matter.

The Symposium has created the appropriate conditions for a useful exchange of ideas and for an advantageous osmosis of knowledge among disciplines concerning the condensed matter nuclear science.

The material science, the enhanced screening in nuclear processes, nanoscience, interphase phenomena and other disciplines are emerging as fundamental pillars in our research field.

Now considering the question whether the F&P effect exists or not the answer is given by the results presented at the conference and on previous occasions.

Considering the question whether the full control and understanding of the effect have been achieved the

answer is given by the hard work done up to now and the harder and harder work still to be done in the future.

We personally consider that the scientific out coming of this conference be the beginning of a new scientific age for our studies

A big research work has been done during the last two decades but there is still a huge effort to be carried out in the years to come and only the involvement of the whole scientific community will make this effort possible.

Our challenge is to give priority to an easy and smooth interaction with the whole scientific community optimizing the effort mentioned above.

We have already done this in the past thanks to the programs reviewing the matter, we have continued during ICCF-15 and we will do the same in the years to come. This is our future!

First of all we wish to thank the Institutions giving their Patronage to the Conference: The Italian Physical Society, The Italian Chemical Society and the CNR.

We thank also ENEA for supporting the Event.

Thanks are due to Enenergetics Technologies since they partially sponsored the Conference and in particular the CEO Ms. Alison Godfrey.

We have also to thank Dr. G.Dattoli, and Dr. G. Hubler since they guided in a masterly manner the round table on theories.

We acknowledge the chairs of the conference sessions, for their skills and professionalism in heading the discussion.

We are very grateful to the co-chair Dr. S. Lesin, to the chair and to the co-chair of the Scientific Committee Prof. Franco Scaramuzzi and Dr. F. Frisone.

Very well deserved thanks to the president of the Kyoto Club Dr. G. Silvestrini for his lecture and to Prof. Melich and Prof. D. Nagel for their help in starting the job .

Thanks are also due to ISCMNS for supporting the Preparata Golden Medal Award.

We wish also to thank Dr. M. Polidoro, she was the Architect of the Conference, and the ENEA Staff: M. Cecchini, C. Torelli, F. Simoni, Emanuele Castagna, Stefano Lecci, Mirko Sansovini, D. Karacostas, L. Crescentini ed E. Vitale because of for their valuable effort in supporting the Event. A particular thank is for the Scientific Secretary of the Conference Francesca Sarto since her professional skill and accuracy was fundamental for the success of the Symposium.

Note about the Proceedings publication

This Book of Proceedings collects most of the papers presented at the 15th International Conference on Condensed Matter Nuclear Science (ICCF-15), held in Rome on 5-9 October 2009.

All the presenting authors have been invited to submit their paper for publication in the Proceedings and about the 90% of them accepted the invitation.

The papers have been reviewed by referees chosen from the scientific community, both inside and outside the more restricted group of scientists working in the field of “cold fusion”.

Due to skepticism of some part of the scientific community and lack of an established literature on this topic in full accredited journals, the review process was not intended to filter papers but to stimulate critical revision of his own work by each author. The aim was to get papers which could be as much as possible understandable by the open scientific community, discussing in deep the possible sources of artifacts and errors in the experimental results and clearly highlighting the working hypothesis, approximations and limits of the theoretical models.

The authors were encouraged to review their papers according to the referees' comments. In many cases this process resulted in a net improvement of the article; in a few cases the authors maintained their original version. Anyway, the only version of the papers acknowledged by the authors has been published. For such a reason, the only authors are responsible for their works' content.

Sincere thanks to all referees who voluntarily dedicated their time and expertise to improve this book.

Introductory remarks

The book should give a complete picture of what went during the Conference.

In accordance with the structure of the Conference we have organized the book following the scheme below:

- Section 1. Electrochemical experiments
- Section 2. Gas loading experiments
- Section 3. Material science aspects
- Section 4. Nuclear measurements
- Section 5. Theory

The study of Condensed Matter Nuclear Science (CMNS) has been marked through 15 past conferences (ICCF1 at Utah, USA, in 1989 to ICCF15 in Rome, Italy). The advances in this discipline are based on the scientific findings that have been obtained along two decades of research activity. Nevertheless because of the lack of information very few people know that some hundreds of researches, the majority of them belonging to some of the most prestigious scientific Institution in the world, have continued this study during the past 20 years.

Background Information

In 1989 two electro-chemists, Martin Fleischmann and Stanley Pons announced that they had produced nuclear fusion reactions between deuterium nuclei in a table-top experiment, under ordinary conditions of temperature and pressure, by using electrochemistry. The experimental evidence consisted of the production of large amounts of heat, which could not be attributed to chemical reactions. The heat excess was revealed by means of calorimetric measurements during electrochemical loading of palladium cathodes with deuterium.

The reactions were termed "cold fusion", by comparison with the high temperature of thermonuclear fusion. One of the most intriguing features of the experiment was the substantial lack of the typical nuclear emissions associated with the excess of power, produced in thermonuclear fusion experiments.

The experimental results thus were in contrast with hot fusion data and were not supported by accepted theories. Many scientists concluded that there were no nuclear reactions and that the reported experiments were in error. Cold fusion was considered as an example of wrong science. This produced a partition between the traditional scientific world and the community which continued its research in the field.

In the 20 years elapsed since then, increasing evidence was found of the reality of the phenomenon, and an extended search for nuclear products connected with cold fusion was performed. Reproducibility was improved, and recently the first examples of cross-check experiments were implemented. Fourteen International Conferences have been held in those almost 20 years, and the present is the 15th of the series.

In 2002, also in order to take into account the variety of phenomena investigated, a new name was introduced, namely "Condensed Matter Nuclear Science" (CMNS). "Condensed matter" is a term employed by the American Physical Society for the last few decades to embrace the characteristics and mechanisms of both solids and liquids. CMNS was meant to focus on the science of nuclear effects in systems involving solids and liquids. It is an appropriate description for the current and continuing science of the field.

The International Society for Condensed Matter Nuclear Science was founded in 2003. It remains the primary scientific society of the field.

At present, the name that many people are using to identify the field is the “Fleischmann-Pons Effect” (FPE). That effect is the production of heat and other products in a deuterium-in-metal system under unusual circumstances of very high densities of deuterium. The amount of heat produced per reaction can be up to several hundreds of times the energy released per known chemical reaction. The power densities (measured in watts per cubic centimeter of the metal) occasionally exceed those from fission nuclear power systems.

Preliminary measurements of 4He at levels that is consistent with the measured energy gain, as if the effect could be ascribed to a deuterium+deuterium fusion, giving helium plus heat as products in the palladium lattice, have been carried out in some Laboratories in the world.

Even though it is difficult to make forecasts on practical applications of these phenomena, there is no doubt that the observed effects are indicative of a process related with the field of clean energy.

Many Institutes and Companies in the world are involved in this study either on experimental activities or on theoretical studies. However the phenomenon is not well understood yet.

ICCF History

The ICCF conferences, which began in 1990, have been held with a three continent rotation: America, Europe and Asia. It is the primary venue for the international community of involved and interested scientists to show and discuss results concerning the Fleischmann&Pons effect. The papers are then published in the proceedings of the conference. The numbers, years and locations of the ICCF are:

No.	Year	Location	Participants	Countries	Papers
1	1990	Salt Lake City, Utah	USA 296		35
2	1991	Lake Como, Italy		57	
3	1992	Nagoya, Japan	324	18	102
4	1993	Lahaina, Maui, Hawaii, USA			12 65
5	1995	Monte Carlo, Monaco	207	15	76
6	1996	Lake Toya, Hokaido, Japan		175	17 110
7	1998	Vancouver, British Columbia, Canada			218 21 76
8	2000	Lerici, La Spezia, Italy	145	18	68
9	2002	Beijing, China	113	17	87
10	2003	Cambridge, Massachusetts, USA		135	93
11	2004	Marseilles, France		20	74
12	2005	Yokohama, Japan		63	
13	2007	Sochi, Russia	75	93	
14	2008	Washington DC, USA	180	15	97
15	2009	Rome, Italy	150	14	70

ICCF15 is the second conference in 10 years as number of participants and is confirming a positive trend.

In addition to the ICCFs, there have been many other conferences on the Fleischmann&Pons effect in Russia, Japan, Italy, USA, including dedicated sessions at various scientific society symposia, such as those of the American Physical Society (APS), American Chemical Society (ACS) and American Nuclear Society (ANS).

Topics

The evidence that identical experimental observations have been done by different Institutions by using the palladium cathodes produced by ENEA and belonging to the same lots of material increased, without any doubt, the level of attention for such a discipline. The palladium giving a significant probability to observe the effect has several features that have been identified; however the possibility to reproduce a material having those characteristics remains still an open problem. The consequence is the absence of a full reproducibility and of the control of the signals amplitude.

Materials have a crucial role in the field of low energy nuclear reactions since their characteristics, on the basis of statistical data, seem to be a necessary conditions to observe the phenomena.

Materials characterization before, during and after the experiments is essential to increase the reproducibility. Such a study points to know the composition of the materials, their structure and their characteristics at nano-scale, in order to select possible mechanisms, occurring during the effect or triggering the effect, that are consistent with the material features.

ICCF15 gave a significant role to material science because of the reasons mentioned above.

A section of the Conference has been dedicated to both dynamic and static gas loading experiments. In general the energy gain obtained by using such a technique are lower than those obtained by using the electrochemical approach. The results obtained with hydrides (deuterides) nano-particles deserves a very deep study of the interaction of the hydrogen isotopes with particles at nano-scale since literature data show a significant difference between the values of the thermodynamic functions of hydrides at nano-scale compared with those at macro-scale.

The (D-D) fusion reaction cross section at low energy represent an important aspect of the discipline. Results from Tohoku and Berlin Universities show an increasing of the (D-D) fusion reaction cross section, at the energy in the order of some KeV when the reaction takes place into some materials like palladium, palladium oxides and others. As the energy decreases the cross section increases up to some orders of magnitude compared with the values, at the same energy, into plasmas or in vacuum. Such a behavior may be explained in terms of an enhanced screening into the condensed matter that was unknown until a few years ago, even if the reaction is giving the typical products (neutrons, ^3He , protons and tritium). This is indicative of the condensed matter effect on low energy fusion reactions.

In the field of condensed matter nuclear science the nuclear measurements are investigating mainly:

D+D reaction products as expected in plasmas or in vacuum.

Possible products due to interaction of hydrogen isotopes with metal atoms (transmutations).

Emission of particles or radiations associated with the above mentioned reactions.

A proper space has been given into the Conference to talks on measurements techniques in order to give a proper frame for a critical review of the results in this field on the basis of the limits and potentialities of the used techniques.

^4He measurements have a remarkable importance in the research on F&P effect since the energy gain observed in several experiments makes a chemical process inconsistent with the resulting energy per particle that is even above 100 eV/particle. Therefore the most likely expected ash is helium four produced by a D+D reaction without emission of radiation. This is a not simple measurement since ^4He is in the atmosphere at 5.25 ppm and since this element ($m=4.0026$ a.m.u.) have to be revealed into a gas mixture containing D_2 molecules ($m=4.0282$ a.m.u.). A high resolution and high sensitivity mass spectrometer is required for such a measurement. In addition we have to consider that the experiment must be conceived in order to avoid any helium leakage from the ambient into the cell and vice versa.

The study of transmutations is a controversial field within the frame of the condensed matter nuclear and an accepted answer whether the phenomenon exists or not doesn't exist yet. The evidence of elements after the experiment that were considered to be absent at the beginning is not enough since reorganizing the contaminant concentration profiles and/or contaminant from the ambient could be the reason for such an

evidence. The most appropriate marker for transmutation processes produced by interaction, at low energy, of hydrogen atoms with metal atoms into the lattice, is the isotopic ratio measurement. As matter of fact if the “new elements” were be due to a nuclear reaction their isotopic ratio would have to be related to the one of the reacting species and then would have to differ from the natural one.

Such study may be performed with high resolution and high sensitivity mass spectrometers and cross check between different laboratories to validate the data to be appropriate.

A round table on theories was organized to give, during the conference, a further occasion to have an open discussion on the status of the theoretical work in the field. Several participants highlighted the importance of having reliable and shared experimental results free of possible experimental artifacts.

The mixing of knowledge and the interdisciplinary nature of the matter makes this task very complex but exceedingly challenging.

To enhance the exchange of ideas some review talks were given to experts in some discipliner crossing CMNS. The reviews were on:

- Material science
- Material characterizations
- Optics and photonics
- Nuclear measurements
- Mass spectrometry

The main out coming was the evidence that F&P effect is a real effect with energy gains that cannot be explained in terms of chemical processes.

Even if a reasonable transportable reproducibility has been achieved and material characteristics, that are necessary conditions to observe the effect, have been identified the start up of the effect and the amplitude of the signals are not under control yet. A complete theoretical frame defining the effect, its trigger and able to increase the reproducibility and the amplitude of the signals is not available yet.

The increasing of the knowledge and the consequent improvement of the control of the effect is the target that is getting close.

Vittorio Violante RdA, Chairman ICCF-15

ENEA – Frascati Research Center, Rome (Italy)



Foto Group, October 5, 2009

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Castel Sant'Angelo

Welcome of the Italian Physical Society (SIF)

I am pleased to extend a greeting of the Council of the Italian Physical Society to all participants to the to ICCF15-2009 symposium.

The Italian Physical Society (in the following I will use the acronym SIF, for Società Italiana di Fisica) is a non-profit, scientific association devoted to promoting and favouring the progress of physics in Italy, to increasing its understanding and applications, and to supporting physicists.

SIF represents the Italian scientific community in the research, educational and professional fields, both private and public, relevant to all areas of physics and its applications. It has an extensive membership - mainly national - and is a leading communicator of physics to all audiences, from specialists through government to the general public.

My presence here today and the SIF patronage to the meeting confirm the loyalty of SIF to its original mission and its determination to work for advancing science, while keeping the research within the border of the experimental method.

In fact, from its foundation, which dates back to 1897, SIF has been tightly bound to the Galilei's method. This strong ideal tight is shown, among other things, by the title of its own journal of physics, *Il Nuovo Cimento*, that recalls the ancient *Accademia del Cimento*, the association founded in 1657 by Prince Leopoldo de Medici and the disciples of Galileo Galilei. SIF also adopted the association logo of the *Accademia del Cimento*, shown in Fig. 1, in which are reproduced a burner, three crucibles full of melted metals, and a flying scroll with the motto "Provando e Riprovando" (trying and trying again), which refers to the experimental method. The motto can also be interpreted as "proving and reproofing", which is also very appropriate.¹ Giovanni Polvani, President of the SIF from 1947 to 1961, described in a very effective and elegant way the meaning of the logo:

"Cimento in its pregnant meaning is at the same time the trial, the test, the effort, the risk, the peril, the experiment, the comparison, the thirst for knowledge, the extent to which the metal refines in the crucible. The crucible then is the mind, and the two words (provando e riprovando) of the enterprise, mirroring each other, show the route to attain, by trying and trying again, the "beauteous truth". It is the essence of the Galilei's method."

The story of the cold fusion research is particularly hard and the link to the experimental method very appropriate.

The link to the experimental method is very appropriate for the cold fusion research, the story of which has been particularly hard.

¹) It is worth mentioning that "provando e riprovando" is found, with this latter meaning, in the first tercet of the third "canto" of the *Paradise* in the *Divine Comedy* poem by Dante Alighieri:

*"That Sun, which erst with love my bosom warmed,
Of beauteous truth had unto me discovered,
By proving and reproofing, the sweet aspect."*

translation by Henry Wadsworth Longfellow of the original:

*"Quel sol che pria d'amor mi scaldò 'l petto,
di bella verità m'avea scoperto,
provando e riprovando, il dolce aspetto."*



Fig. 1 – The logo of the Italian Physical Society

Here the beautiful truth, which Dante refers to, concerns the lunar spots and the influence of stars.

Cold fusion, first announced on March 1989, raised hopes of a cheap and abundant source of energy.

Enthusiasm turned soon to skepticism after replication failures of the original experiment. In November 1989, the majority of a review panel organized by DOE found that the evidence for the discovery of a new nuclear process was not persuasive.

In 2004, a second DOE review reached conclusions similar to the first, but with a smaller majority. Moreover, “the reviewers identified two areas (properties of deuterated metal and search for fusion events in thin deuterated foils) where additional research could address specific issues, and invited funding agencies to entertain individual, well-designed proposals”.

The interest in the field has been growing in recent years, as shown by the presence of a session on cold fusion at the APS meeting in 2007. A number of basic research areas interesting in itself and helpful in resolving some of the controversies have been identified. A number of researchers keep researching and publishing in the field. In brief, today cold fusion is back on the menu.

Since its first edition in 1990, the International Conferences on Condensed Matter Nuclear Sciences have provided a good forum for researchers to share their results and promote the understanding, development and application of the discipline. I am sure that also this edition of the Conference will be a success and hope it will pave the way for further sound developments.

I also wish everyone a pleasant stay in Rome.

Enzo De Sanctis

Italian Physical Society (SIF) - Bologna

In Memory of Andrei

Andrei Lipson was a long-time, highly respected member of the Condensed Matter Nuclear Science community. He was a member of the International advisory committee for the ICCF meeting series, representing Russia. Aside from his home base at the Institute of Physical Chemistry, Russian Academy of Sciences and the Joint Institute in Dubna, he “had suitcase and would travel” to do research. Stays elsewhere included over four years with me at the University of Illinois, time at the New Hydrogen Energy Laboratory in Sapporo and then at Tohoku University with Professor Kasagi, time in Israel at Energetics Technologies, at the US Naval Research Laboratory and the Naval Postgraduate School in CA with Michael Melich. He had just accepted a visiting position at the University of Missouri - Columbia when his unforeseen death occurred while riding a subway in Moscow. This seemed impossible to me—Andrei was in good health when I saw him months earlier at ICCF-15 in Rome, and again 2 weeks before his death when he stopped at my lab to spend several days talking about joint experiments.



Several months later I gave a presentation for him that we had been working on for the ACS meeting in San Francisco. It was my honor to represent him in this manner. Many Russian colleagues and ICCF colleagues can recount Andrei’s many contributions to the field. However, here I will simply present my personal view based on the years of close collaboration we had. Andrei was a great colleague and had a significant influence in my LENR research. It seems like only yesterday that I first met him at an ICCF meeting in Europe. He had just returned from a stay in Japan where he collaborated with Professor Kasagi on low-energy nuclear cross sections using ion beam-target experiments. I approached Andrei afterwards and asked if he would come to Illinois to join my work, if I could raise enough money. He consented. Later, in e-mails, I asked if he “believed” in cold fusion. He replied that he thought so, but wanted to keep an open mind because “experiments would determine the truth”. I told him that I shared that view.

We do continued experiments on thin film electrode concepts, we successfully applied some analysis techniques that Andrei used in Russia, such as nuclear particle detection using CR-39 film. He also contributed, in collaboration with others at the University of Illinois, developed a pioneering method for creating near metallic density hydrogen (or deuterium) states in dislocation loops in palladium. The resulting Physics Review article about superconducting properties of this state has received a number of citations.

There is not enough space to tell all I want to about Andrei’s accomplishments and our close relationship. I grew to deeply respect him as a person and as a scientist. The interested reader can find out more about him from the article by his daughter, Maria, in Infinite Energy magazine following his death. Also, I was asked to speak about some of his recent research at the March 2010 American Chemical Society meeting in San Francisco. Andrei prepared a presentation on the effect of electron beam bombardment on loaded hydrides for that meeting which can be found in the proceedings based on my presentation and my comments about Andrei’s many contributions to cold fusion research.

As all people in the field know, Andrei was extremely prolific in his range of research work, and he had numerous publications. As a result of his collaboration with me, we had coauthored along with others in my lab and his lab back home over 50 publications ranging from articles in ICCF meeting proceedings to articles in various journals. In addition, Andrei had a number of other publications that I was not involved in.

A characteristic of all this work is that the problems were attacked from a very fundamental, basic science point of view. Another characteristic of Andrei that I deeply admired and which made me so comfortable working with him was his high integrity and honesty in everything he did. He never allowed himself to become so emotionally involved that he would fail to bring out all the facts about anything he was studying. Andrei was very strong willed and hard to convince if he had already formed an opinion, but I could always have complete faith in any results that Andrei reported. And if your point of view had merit, Andrei would keep an open mind and help you get deeper insight into the physics issues. We will all sorely miss him.

George H. Miley

Professor, University of Illinois - USA

Foreword

Cold Fusion (LENR) One Perspective on the State of the Science”

M.C.H. McKubre

SRI International, Menlo Park, California.

Abstract. With recent publicity outside the CMNS field it has become increasingly important to clarify in non-specialist terms what is known and what is understood in the general field of so called Low Energy or lattice Enhanced Nuclear Reactions (LENR). It is also crucial and timely to expose and elaborate what objections or reservations exist with regard to these new understandings. In essence we are concerned with the answers to the following three questions: What do we think we know? Why do we think we know it? Why do doubts still exist in the broader scientific community?

In this Foreword to the Proceedings of ICCF15 I lean heavily on the experimental work performed at SRI by and with its close collaborators (ENEA Frascati, Energetics and MIT) with a view to define experiment-based non-traditional understandings of new physical effects in metal deuterides.

1. Introduction

I was tasked to review the state of the science: at least 1000 man-years worth of work in 30 minutes, and here on a few pages. Of course it is impossible, so what was and is presented here is a very brief and personal view of the state of the science, through time and space constraints necessarily avoiding consideration of many large and important research subtopics.

It is important to understand what we have come together to study. On March 23rd 1989 Fleischmann, Pons and Hawkins [1] reported results of:

- i. an anomalous heat effect resulting from the
- ii. extensive, electrochemical insertion of deuterium into palladium cathodes
- iii. occurring over an extended period of time.

The underlined phrases are important and often forgotten. The effect reported was a heat affect. Calorimetry is the means of studying heat effects. Please note the underlined words: extensive, electrochemical insertion for a prolonged period of time, of deuterium into palladium. The experiment is electrochemistry, with which very few in the physics community were familiar. And the process occurred with an initiation time many times longer than the time constant of diffusional insertion of deuterium in palladium.

This heat effect occurred at a level consistent with nuclear but not chemical energy or known lattice storage effects, but occurred (*mostly*) without penetrating radiation (α , β , γ , n^0) or lattice activation. A remarkable feature of the effect is that a prodigious amount of energy is produced. This energy is not only much greater than can be attributed to chemical reactions, there is no physical evidence for such reactions. We have seen this heat affect occurring at hundreds or thousands of times the energy of any chemical reaction. These are the characteristics of the Fleischmann Pons Effect (FPE) and from our present vantage point we can begin to answer some questions:

1. What do we think we know?
2. Why do we think we know it?
3. Why do doubts still exist in the broader scientific community?
4. How do we propose to make progress?

2. What do we think we know?

The existence of an excess power effect is an experimental question, independent of theoretical issues or preconceptions. A great many experiments in which positive excess power results have been presented can be found in the International Cold Fusion Conference series over the past 18 years. Of these the experiments based on those of Fleischmann and Pons are perhaps the most studied and discussed, which makes the FPE of interest to us in our present discussion.

In the studies done at SRI over the years, an effort was made to understand specifically what conditions are required for excess power to be observed in the Fleischmann-Pons experiment [1] (keeping in mind that different requirements apply to other kinds of excess power experiments). A number of such requirements were noted: (i) a cathode had to achieve a maximum loading of about $D/Pd = 0.9$ or higher; (ii) high loading needed to be sustained for 2-4 weeks; (iii) a current density above threshold was required; and (iv) relatively high loading needed to be present for a heat burst to occur. In addition, it was found that changes in the operating parameters could initiate a heat burst, which may be related to a more general correlation between excess heat and a net deuterium flux either in or out of the metal.

The research activity into the FPE at SRI has now accumulating more than 60 man-years of research. We first focused attention on the critical importance of deuterium loading, the role of chemical poisons and additives in controlling the electrochemical interface, in order to achieve and maintain high D/Pd loading. We studied the correlation of excess power production with loading and reported simultaneously with IMRA-Japan [2,3] the threshold onset of the FPE. We designed and built a novel, high-accuracy, fully automated mass flow calorimeter, and set out to perform replication studies of the Fleischmann and Pons heat effect, first to confirm the existence the effect and second to better define the physical conditions under which it can be observed.

As an interim conclusion of these activities we were able to define the parameter space in which one might expect to encounter the Fleischmann-Pons excess heat effect, evaluated as an empirical expression:

$$P_{xs} = M (x-x^o)^2 (i-i^o) |i_D| \quad [1]$$

where $x = D/Pd$, x^o is the threshold value typically ~ 0.875 , the current density threshold i^o typically falls in the range $75 < i^o < 450 \text{ mA cm}^{-2}$, the deuterium interfacial flux $i_D = 2\text{-}20 \text{ mA cm}^{-2}$. It is important also to recognize a time threshold t^o of at least 10 times the deuterium diffusional time constant.

3. Why do we think we know it?

Evaluation of the terms of equation [1] has been the subject of a number of reports and analyses, authored particularly by SRI, ENEA and Energetics but including data from a wide range of experimenters. This analysis will be discussed in more detail in reference [4] of this Proceedings volume. It can no longer be asserted rationally that there no heat effect in any of the very large number of experiments reported here and elsewhere [5], or that the effect is the result of (unknown) energy storage or (unseen) chemistry. Also, at this point, any claim that the Fleischmann-Pons Effect is “irreproducible” is not only unsound, it is unscientific. Where and when we are capable of reproducing all parameters critical to the effect, we reproduce the effect.

4. Why do doubts still exist in the broader scientific community?

It might be appropriate to think of this question in terms that apply to parenting. First there was a difficult birth in conditions that while not initially hostile rapidly became so. Second there has been a great deal of poor communication on both sides: an inability to broadcast real scientific progress uncoupled from emotion or ambition; an almost complete lack of willingness on the part of those outside the CMNS community to delve into the work

and understand what has been done, and what has changed, in 21 years. Finally, although not critical and somewhat circumvented by imagination, there has been an insufficiency of funding for such a materially complex (and I would argue potentially important) problem. The child, abused at birth and abandoned by most, that Minoru Toyoda helped rescue, now misunderstood and fiscally restrained, has just turned 21. I will not discuss the problem of fiscal constraint, in part because if we solve the issues of hostile rejection and poor communication that will not remain a problem.

Great significance was attached to early negative excess heat results reported by a small number of groups at prestigious institutions. In light of the discussion above, it is useful to see whether these experiments, as well as other early experiments, were operated in a relevant regime. Perhaps the most cited early negative result was that of Lewis *et al* [6] from CalTech in which they reported that “*D/Pd stoichiometries of 0.77, 0.79, and 0.80 obtained from these measurements were taken to be representative of the D/Pd stoichiometry for the charged cathodes used in this work.*” Also widely cited is the early negative result of Albagli *et al* [7] from MIT who discuss “*average loading ratios were found to be 0.75 ± 0.05 and 0.78 ± 0.05 for the D and H loaded cathodes, respectively.*” The CalTech and MIT negatives are noted in Figure 1 in a histogram illustrating a number of early SRI experiments producing positive excess power results as a function of loading.

Even lower loading results were estimated by Fleming *et al* [8] from Bell Labs in a negative report. In this paper the authors state “*the degree of deuterium incorporation was comparable to that for the open cells for the same time duration. The amount incorporated in longer electrolysis experiments was typically PdD_x ($0.45 < x < 0.75$).*”

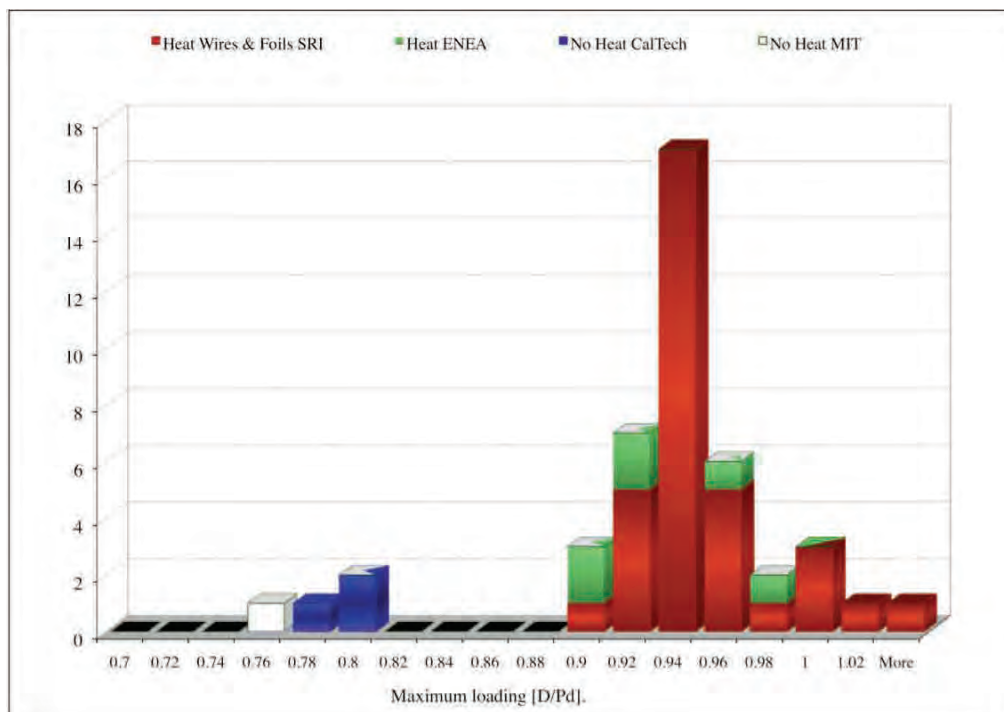


Fig. 1. - Histogram illustrating the number of early experiments at SRI and ENEA showing measurable excess power as a function of maximum cathode loading. Also illustrated are points for the MIT negative experimental result, with a stated loading of 0.75 ± 0.05 (Ref. [7]); and for the CalTech negative experimental result, with loading measurements quoted at 0.77, 0.78, and 0.80 (Ref. [6]).

From what we know today, and Figure 1 clearly illuminates, none of the cells in any of these cited studies would be expected to evidence any excess heat. Not only for the reasons of a loading deficiency (as stated explicitly): the durations of the experiments were wholly insufficient for a (typical) 300 hour initiation time; the current density stimuli were in the large part too small; the deuterium flux was not measured. None of the criteria of Equation [1] were shown to be met, at least two demonstrably were not. In hindsight it is evident that the authors were victims of “unknown unknowns”, and perhaps “indecent haste” -- but this is understandable in the circumstances of 1989. What is important is that these experiments be recognized for what they are, not what they are not. They are important members of the experimental database that teaches us under what conditions one encounters the FPE. They are not any part of a proof of nonexistence; absence of evidence is not evidence of absence.

So what are the salient criticisms today? The following attempt is made to anticipate some of the questions and at least point in the directions of resolution. Basic questions:

- *“The experiments/results are not reproducible”*:
 - Some experimental teams see no results
 - Different results are seen in different laboratories
 - Inconsistent results in the same laboratory with similar samples
- *“The results are inaccurate”*:
 - Mis-measurement of input power
 - Mis-measurement of output power
 - Excess power is not outside the measurement uncertainty
- *“The heat is real but is due to unknown or unaccounted chemical effects or lattice energy storage”*:
 - Over-accounting for electrolysis products
 - Chemistry in the electrolyte volume outside the cathode
 - Energy storage and release (small percentage integral excess energy)
 - Hydrinos or other exotic, “high-energy” chemistry
- *“Missing nuclear products”*:
 - Quantitative energetic products not seen
 - Difficulty of measuring ^4He in the presence of D_2 and ambient

“The experiments/results are not reproducible”

First the existence of an apparent irreproducibility is widely recognized and acknowledged, and several papers have been written on this topic [9-11]. What is sometimes forgotten is that the most reproducible effect by its very nature is systematic error. Irreproducibility of results far from being a proof of non-existence argues more the contrary, and simply indicates that not all conditions critical to the effect are being adequately controlled.

Early flippant and intentionally unserious, as well as other claimed serious attempts were made to correlate the appearance of positive FPE results with the record (or existence) of university football teams and with national character. Serious criticisms do exist, however, and it is well recognized that different experiments, even intentionally identical and performed simultaneously in the same laboratory, give different FPE results. These experiments also give different results of much more mundane measurements. In the early days of studying the FPE at SRI experiments were designed to probe the parameters of reproducibility. Sets of 12 cells were prepared, intentionally identically, and operated simultaneously to monitor the time evolution of electrochemical and physico-chemical parameters believed to be pertinent to the FPE.

A single length of palladium wire was used from a known source and sectioned into 13 identical lengths. These wire sections (typically 3 or 5 cm in length and 1 or 3 mm in

diameter) were machined to remove surface damage and inclusions, spot welded with 5 contacts (one cathode current and 4 wires for axial resistance measurement), annealed, surface etched (to remove surface contaminants) and mounted in 12 identical cells. These processes all were performed in the same batch and all by the same person. The twelve cells were filled with electrolyte from a single source and then operated electrically in series (*i.e.* with identical currents) in a 3×4 matrix in the same constant temperature chamber.

The variables measured were current (one measurement), cell voltage, pseudo-reference cathode potential, temperature and electrical resistance (D/Pd loading) all being monitored with the same instruments. Intermittent measurements were made of the cathode interfacial impedance. With 12 intentionally identical experiments, every one behaved differently. Not only in terms of their heat production, significant and marked differences were observed in: the current-voltage-time profile for both the cell voltage and reference potential; the ability and willingness of each electrode to absorb deuterium measured by the resistance ratio *vs.* time curve; the maximum loading achievable; the interfacial kinetic and mass transport processes reflected in the interfacial impedance. Every one of these parameters was different for each of the 12 electrodes, in every set tested!

This matrix experiment was repeated several times in an attempt to understand the origins of the irreproducibility, and therefore control it. Trace impurity differences were observed to be contributory and there were two sets: deleterious impurities (poisons) that we learned to avoid; impurities that were beneficial to high loading in controlled amounts.

We were not able to control the variability of results simply by electrochemical (and trace chemical) means. The second major factor of experiment variability is the palladium metal cathode: source and condition. Figure 2 plots as a histogram the number of cells attaining the specified loading (whether in a calorimeter or not) varying by metal source or lot #. The first material used extensively at SRI, designated as Engelhard Lot #1 (E#1 on the plot) demonstrated in an astonishing 32% of all experiments a maximum loading D/Pd >0.95, with 36% >1.0, and 14% (3 cathodes) > 1.05. An electrode capable of attaining and maintaining high loading, is an electrode that is capable of producing excess heat thus a total of 82% of all samples of E#1 material, if properly stimulated, would have been expected to demonstrate the FPE. Unfortunately this apparent success illuminates the problem. Other materials even from the same manufacturer were far inferior and none yet has been found to approach the loading ability of Engelhard Lot #1¹.

Fortunately there is some consistency of behavior within a consistent set of materials. Electrodes made from the same material lots produce similar excess heat in different calorimeters, in different laboratories. Recently we have been working collaboratively with the Violante team of ENEA (Frascati) and the Energetics team of Dardik, Lesin *et al* to conduct comparative studies on material of similar general form: Pd foils 80 mm long, 7 mm wide and 50 μm thick, designed and produced by ENEA. Figure 3 presents a comparison of results obtained in two different calorimeters, one at SRI and one at ENEA, following Energetics current protocols².

¹ Important but equally confounding, E#1 had the highest levels of impurities of any material we have ever employed in these studies, far higher in fact than the manufacturer's specification of 99.7% purity.

² The unique feature of Energetics' experiments is the use of a fractal sinusoid current stimulus designated by them as a SuperWaveTM. Alone among all of the current modulations tested at SRI, this waveform is capable simultaneously of supporting high D/Pd loading and high interfacial deuterium flux. In the terms of equation [1], both are needed for excess heat production.

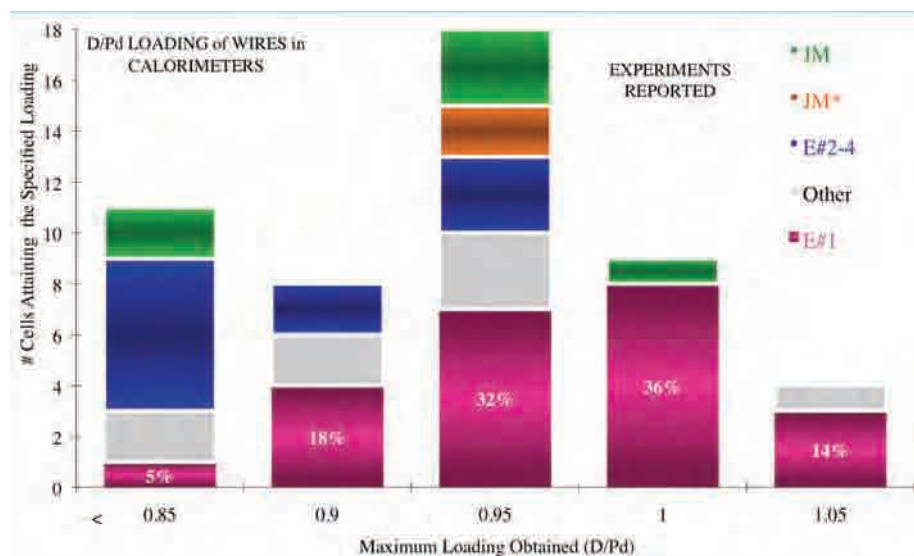


Fig. 2. - Histogram demonstrating the ability of a Pd cathode to load in 1M LiOD *versus* material source. JM = Johnson Matthey, JM* was a special lot designed to replicate pre-1989 materials, E = Engelhard.

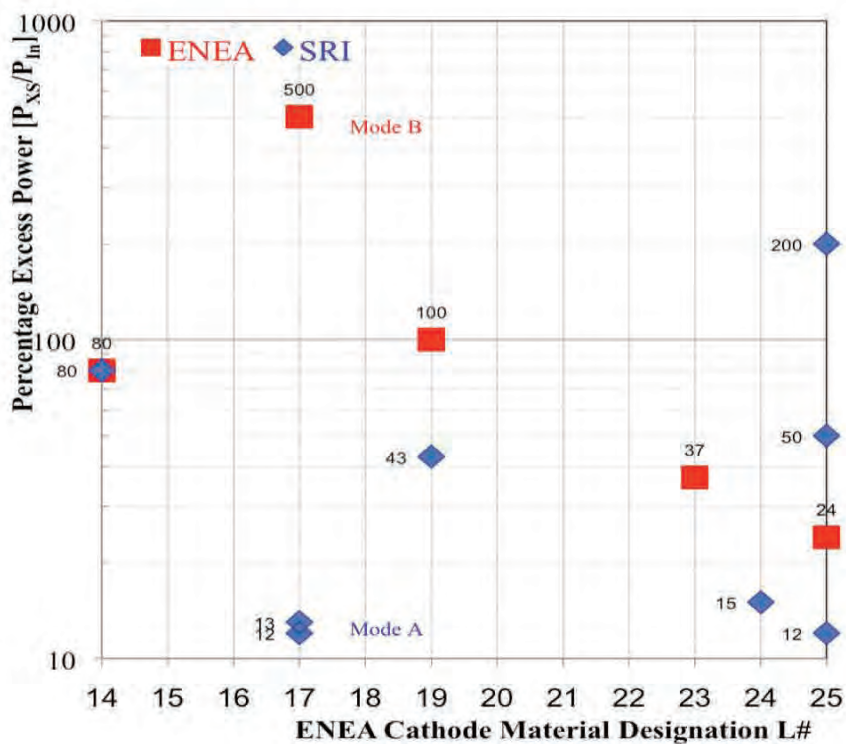


Fig. 3. - Comparison of results obtained from the same material lots performed independently at ENEA (Frascati) in a closed-cell mass flow calorimeter and SRI (Menlo Park) in an open-cell heat flow calorimeter [12,13].

The different lots of materials reflect different sources, rolling and annealing conditions and are designated by the ENEA “L” number, L14, 15, 16, 17 *etc.* on the horizontal axis. Two

experiments with a particular lot of material, L14 run at SRI and ENEA, produced completely independently of each other (without knowledge of the other's experiment) 80% excess power/input power. With another material, L17, SRI saw 13% and 12% excess power and ENEA observed 500%, but the excess heat production in the two laboratories appeared in different modes. The L19 material showed 43% at SRI and 100% at ENEA. The general point is, that the same lot type of material will give the same approximate level of excess power result in two different laboratories. There is a consistency of behavior, and that behavior varies very much with the lots; the lot numbers without points in Figure 3 produced no excess power at SRI or ENEA (although all lots were not tested at both locations).

"The results are inaccurate"

The issue of mis-measurement of input electrical power has been recently raised [14] both generally for dc current stimulus and specifically in reference to Energetics proprietary SuperWave™ modulated current waveforms. It is quite difficult to understand the basis for this criticism and how and why it persists or surfaces after 21 years. Measurement of current, voltage, resistance, and time are some of the most familiar to engineers and scientists. Industries depend on the accurate measurements of power and energy for waveforms far more complex than any used (so far) in FPE experiments. In general the electrochemical cells are operated under controlled current conditions so that only the voltage varies. Accurate determination of power is thus a scalar, not vector operation and only simple precautions are needed for accurate measurement.

The Nyquist sampling theorem states that one can perfectly reconstruct an analog signal by sampling at twice the highest frequency component. Of primary concern in such measurements therefore is ensuring that higher frequency components are not present unmeasured in the input signal. In general this is very easily arranged by constraining the power bandwidth of the current (and voltage) source. For Energetics' SuperWaves™ that contain deliberate high(er) frequency components the solution to this measurement issue is more complex, but still experimentally quite trivial. Current-Voltage pairs are sampled and multiplied at a 50 k Hz. rate and only then averaged to obtain the input power. Several experimental checks on this procedure have been applied by Energetics, SRI and ENEA [15,16]:

- a. The current and voltage measurement rate (50 k Hz.) used is 500 times higher than that of the highest SuperWaves™ frequency applied.
- b. Ten times higher measurement frequencies (500 k Hz.), have been used with no significant difference observed in the input energy.
- c. A fast commercial power meter (Yokogawa WT210/230) has been used with sampling rate of 100 kilohertz. The results were in agreement within +/- 0.5%.
- d. At SRI and ENEA high frequency oscilloscopes and spectrum analyzers have been used at times of excess power production to demonstrate that the energy of frequencies higher than the Nyquist limit could have no calorimetric consequence.
- e. Following our standard replication protocol [6], experiments set up using Energetic' data acquisition systems at SRI, were completely replaced with an entirely new data acquisition method and system with entirely consistent results [12,13].

Another obvious factor is that calorimeters measure total, absolute energy probably better than any other instrument. Most of the time, most of the calorimeters operate on the thermal baseline with output = input. If the issue were really low sample frequency one would expect to see an error at all times as a systematic effect of the input.

Since many different kinds of calorimeter have been shown to demonstrate consistent effects it seems also very unlikely that significant systematic errors are present in the

measured output power and energy. As with the evaluation of input power, the variables needed to resolve output power (mass, time, resistance, temperature difference) are some of the easiest measurements we typically make. It is very hard to sustain rationally any argument that so many people have been mis-measuring these variables consistently for 21 years, with new people entering the field learning or copying the same errors.

A final point arguing against the universal presence of systematic error measurements is the sheer magnitude of the effect. At SRI we have seen an excess power effect at 90σ , ninety times the measurement uncertainty, and have made over one hundred observations of $P_{XS} > 3\sigma$. The effect is not fleeting and persists for hours, days, weeks, in one case longer than 1 month, giving ample time to check the measurement systems. And the output power is not small compared to the power input with power ratios $P_{Out} / P_{In} > 2, 3, 5$, the highest sustained value measured being 25 [17] averaged over 17 hours!

“The effect is due to chemistry or energy storage”

Several factors are often suggested in an argument that FPE excess heat is real and measured correctly but that its cause must be other than nuclear because no such nuclear processes are known. Some of these are:

1. Over-accounting for electrolysis products
2. Chemical reactions involving species in the electrolyte volume
3. Energy storage (slow and unseen) and release (rapid)
4. Hydrinos or other “exotic” chemistry

Is the FPE due to chemistry or energy storage? Simply, it is not! Anybody who has the ability and willingness to undertake simple calculations on the energies of these two different kinds of effects – nuclear and chemical – will easily be able to ascertain that the FPE is not caused by chemistry or an energy storage effect. Furthermore, if it were, that effect would be interesting and potentially very useful. The inventories of chemical species are simply too few. A continuous error such as unwitnessed and unexpected recombination of D_2 and O_2 inside intentionally open calorimeter cells has an energy capacity of the same magnitude as some heat effects observed in them, but this argument fails on two grounds:

- i. the FPE is measured reliably and robustly in closed cells where this effect can play no role, and is similar in form and magnitude to the effect measured in open cells,
- ii. accurate account is easily (and routinely) taken for the amount of water added for electrolyte makeup due to Faradaic loss; prolonged periods of energy excess due to unmeasured recombination would result in FPE cells requiring less³ D_2O (or overfilling).

Detailed energy balance can be complicated in FPE experiments because these occur over long periods of time with no energy excess, and may have many and varied energy inputs. Although many have been accomplished with absolute statistical certainty, the early numbers were not very satisfying and (for example) do not suggest a basis for a useful energy source. This question of energy balance was put finally to rest resoundingly by the Energetics team in experiment L64 [17] about which there has been much comment [5,10,12-14]. This experiment lasted a relatively short time, there was very little time before the excess power burst was achieved, and the energy out was markedly greater than the energy in. There was no time for energy storage in this process.

³ The amount of water needed to refill an open electrochemical cell can be readily and accurately calculated using Faraday’s Law that relates the moles of species consumed by electrolysis to the total charge passed.

Energetics experiment L64 using a 7 mm × 80 mm × 50 μm Pd foil from ENEA (Frascati) and SuperWavesTM current stimulation demonstrated a maximum output power >34 W twice in the first 20 hours of the experiment, with an input electrical stimulus less than 1 W. The energetic response was even more startling with 40 kJ of input energy in that first 20-hour period, 1.14 MJ of energy out, 1.1 MJ of excess energy. A factor of 25 times more energy coming out as heat than was input electrically. For this first heat burst alone the energy was 4.8 KeV/Pd atom, thousands of times more than can be accounted for by known chemistry. A second burst produced boiling in the electrolyte and at least⁴ 3.5 MJ more energy, a total of more than 20 KeV/Pd atom. Similar but slightly less impressive results have been obtained on several other occasions by Energetics.

Missing nuclear products

Initially applied as a “*where is the beef?*” denunciation, the question “*where is the ash?*” was posed (or supposed) to refute the existence of the FPE on the grounds that the only products⁵ possible were energetic and therefore easily observed (and even hazardous). At SRI we have made efforts at varying levels to search for a very wide range of potential nuclear products and ash.

Some salient criticisms are listed below followed by comments:

1. The expected energetic radiation does not accompany heat production
2. The nuclear products claimed cannot account for the excess heat
3. The claimed quantitative product (⁴He) is:
 - a. Impossible to produce
 - b. Difficult to measure
 - c. Not found in sufficient quantity

The first question was first and most directly answered by Julian Schwinger in 1989 [18]: “*The circumstances of hot fusion are not those of cold fusion*”. By this he suggested that quantum coherent superstructure of the Pd(D) lattice might be expected to change the reaction mechanism, the rate, and the product branching ratios. At present there is no consensus among those in the field as to what physical mechanism is responsible for the effect although many propositions are under active discussion and significant progress is being made [for one proposed pathway see 19,20]. Potential products are therefore equally obscure but no rational basis exists to deny the existence of the FPE on the grounds of non-observation of a hypothetical product.

Some nuclear products of FPE reactions clearly exist sub-quantitatively with the excess heat. Tritium and ³He are produced in FPE experiments, under special circumstances, largely asynchronous with the excess energy [5]. Claims have been made for “massive transmutation” at (or above) the levels needed to account for measured excess energy [5]; these have yet to be verified.

For some time at SRI we have been performing experiments to test the hypothesis that the quantitative product of the heat producing reaction is ⁴He that evolves primarily without

⁴ This amount is under-estimated as the heat of vaporization of D₂O was not included in this energy total.

⁵ The term “ash” in “nuclear ash” is a technically inaccurate analogy to chemical ash. In chemical combustion, the ash is left-over material that does not participate in the reaction. It is the residuum of non-volatile oxidized and pre-oxidized materials. In the field of cold fusion, the term “nuclear ash” has come to mean the reaction product. This is equivalent to describing the chemical combustion products CO₂ and H₂O as “ash,” which is incorrect. Thus, in cold fusion helium is sometimes referred to as “nuclear ash” but it would be more accurate to call it a potential product of nuclear reaction.

associated energetic byproducts. This hypothesis did not originate at SRI. As early as 1991 Miles and Bush [21] developed an ingenious self-sparging helium sampling system using electrolytic evolution of D₂ and O₂ to purge out atmospheric ⁴He. They obtained a seemingly unassailable statistical correlation between heat and helium production computing a 1:750,000 chance that the correlation was random.

Miles and Bush also obtained a very impressive early quantification of a reaction Q value. Compared with the value predicted for an overall reaction of the sort $d + d \rightarrow {}^4\text{He} + 23.8 \text{ MeV}$ (*lattice*), (yielding $2.5 \times 10^{11} {}^4\text{He s}^{-1} \text{ W}^{-1}$ of energy excess), Miles and Bush measured an average value of $1.4 \pm 0.7 \times 10^{11} {}^4\text{He s}^{-1} \text{ W}^{-1}$, 54% of the hypothesized value. Later in a study to replicate this work at SRI Bush [22] measured an average $1.5 \pm 0.2 \times 10^{11} {}^4\text{He s}^{-1} \text{ W}^{-1}$ (58% of the “expected” value).

Numerous others have made measurements of gas phase ⁴He during or immediately following FPE heat excursions [5]. In general the amount of measured helium lies between ~50 and 75% of the amount⁶ predicted for a net reaction⁷ $d + d \rightarrow {}^4\text{He}$. Important experimental and theoretical issues attach to the question: “is there missing ⁴He?”, and, if so, “why”? If the net reaction were as written, and occurred in a skin layer close to but below the Pd cathode surface, then one might crudely expect ~50% of the ⁴He to leave the cathode while the rest goes deeper to be trapped. Lending some weight to this hypothesis 15 studies have found unexpected ⁴He in metal cathodes after FPE energy production [5], although in no case was the amount of ⁴He measured sufficient to account for the gas phase deficiency.

In considering the possible fate of ⁴He it is important to recall that the surface of a heat-producing FPE cathode is not well-crystallized Pd, even if it started as such. After extensive electrolysis in LiOD (for example) the cathodic surface will have incorporated significant Li, and the electro-active metallic surfaces become covered with a many-micron layer of hydrated oxy-hydroxides incorporating adventitious (as well as deliberately added) elements from the electrolyte, and leached from cell walls and parts, and from the two electrodes. In particular this “sludge” layer will act to restrain or delay ⁴He release and it is reasonable to anticipate that work must be done to disrupt this layer to approach an accurate mass balance. Since 100% of the helium can never be recovered, this balance will underestimate the total, but as recovery techniques improve it will asymptotically approach the true mass balance.

Limited resources have limited to only 2 the number of successful heat producing experiments in helium leak-tight calorimeters for which effort was extended to scavenge ⁴He held up (by whatever means) in the cell volume. Of these one performed at SRI [25] and the other at ENEA (Frascati) [15], both yielded a total mass balance of ⁴He produced within approximately $\pm 10\%$ the $2.5 \times 10^{11} {}^4\text{He s}^{-1} \text{ W}^{-1}$ value, supporting a claim for an overall reaction Q of ~24 MeV/⁴He atom produced. This is an important result that needs further verification.

⁶ One result in the early Miles Bush work measured ⁴He at greater than $2.5 \times 10^{11} {}^4\text{He s}^{-1} \text{ W}^{-1}$ but was attributed to experimental error [23]. In the published literature only the work of DeNinno and coworkers offers evidence [24] of super-quantitative ⁴He.

⁷ For reasons involving local energy and angular momentum conservation it is clear that, even if this is the net process, this reaction does not occur in a single step as written without the intimate involvement of other bodies. Since thermodynamics is path independent, however, we can calculate accurately the energy of the overall exothermic process, without knowing the pathway.

5. Summary and conclusions.

On the basis of the evidence and arguments presented here, and far more extensively and compellingly elsewhere [5,10], it is apparent that the Fleischmann-Pons effect is a new effect in physics. It requires a new mechanistic description and explanation. This new effect is very likely to be associated with a significant number of other condensed matter nuclear processes that await exposition and development.

I predict that once explained, the underlying effect will not appear strange at all. It will seem, in retrospect, that it was quite clear that we should have understood it all along. It is a heat producing reaction, consistent with nuclear but not chemical effects, both temporally and quantitatively accompanied by ^4He . This new effect, the Fleischmann Pons Effect, can be accompanied by nuclear “ash”, ^3H and ^3He being important. Strong evidence for other isotopes exists [5]; more may follow.

How do we make progress? We make progress through theory: quantitative predictive fundamental physics descriptions. We will continue to make progress best by using the scientific method. To do so we are going to have to engage the broader scientific community. We simply can't sit here secure behind our walls and talk in a closed group, we need to invoke enthusiasm in the broader scientific community. The organizers of this conference [ICCF15] are to be commended for recognizing this need and furthering that process.

Another way of making progress is by engaging in the process of creating a product. Here we might take advantage of the growing public and political interest in real alternative energy solutions. The FPE produces real and useful energy, process heat. In Energetics experiment L64, in a single burst, twenty five times more heat was produced than entered the cell as electric power. This heat was produced at temperatures sufficient to boil water. Such an effect has practical value. Obviously taking an experiment to the market as a product requires several steps that are non-trivial. This exercise however may be an effective means of gaining an engineering understanding of the effect even before the scientific.

Acknowledgements

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Part I

The “anomalous” energy production



Evolution and Progress in Material Science for Studying the Fleischmann and Pons Effect (FPE)

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Abstract. Calorimetric experiments have revealed a crucial role of the metallurgy and surface characteristics for reproducing the FPE. A material status to have an improved probability to observe the effect under electrochemical loading of deuterium in palladium has been identified by means of statistical approach. The evolution of the research approach is described in this work.

1. Introduction

The threshold effect of the deuterium concentration into the palladium lattice was identified as condition for observing the excess of power during electrolysis of palladium cathodes with LiOD electrolyte [1-2], i.e. Fleischmann&Pons effect [3].

Such an experimental evidence created a broad interest in identifying the mechanisms controlling hydrogen isotope dissolution into the palladium lattice during the loading process.

A material science study allowed to define a metallurgical treatment to have the most appropriate metallurgy to facilitate absorption and hydrogen mass transfer into the palladium lattice [4].

The most significant outcome of the study was an increasing of the loading reproducibility, near 100%, in achieving a deuterium concentration larger than 0.9 (atomic fraction), that was considered to be the threshold value to observe the effect.

The high loading reproducibility was the condition to demonstrate that the loading threshold is a necessary condition but not sufficient to have the excess of power production [5].

A research effort was performed for identifying others necessary features of the material correlated with the excess of power production and, for such a reason, the focus of the research was mainly oriented on metallurgy, crystallography, triggering, and interface - surface physics.

2. Experimental results

A mass flow calorimeter and closed electrochemical cells equipped with a catalytic fixed bed to recombine the gas produced by the electrolysis have been conceived and operated to directly measure the output power.

The calorimetric system is composed by a Memmert thermostatic box (± 0.05 °C), Haake thermostatic bath for coolant water, Bronkhorst high precision mass flow meter and controller (0.3-0.1 cc/s), read by the data acquisition system in order to have a precise measurement of the output power. Inlet and outlet temperatures of the coolant are measured with two Pt 100 thermometers (four wires measurement). The closed electrochemical cell is equipped with a recombiner. Cell power supply is an AMEL galvanostat. Output power is measured by means of the mass flow rate and coolant temperatures, R/Ro measurement is done by means of an HP- 4284 (four wires measurement). The calorimeter efficiency is 97.5% and was estimated by using LiOH electrolyte in several experiments. No excess of power production has been observed by using H₂O despite a very high loading (H/Pd=0.97) was achieved.

Palladium cathodes, loaded above the deuterium concentration threshold (D/Pd =0.9: atom. frac.) gave a different behavior:

- 1) Excess of power larger than 100% of the input power.
- 2) Excess of power lower than 20% of the input power.
- 3) No excess.

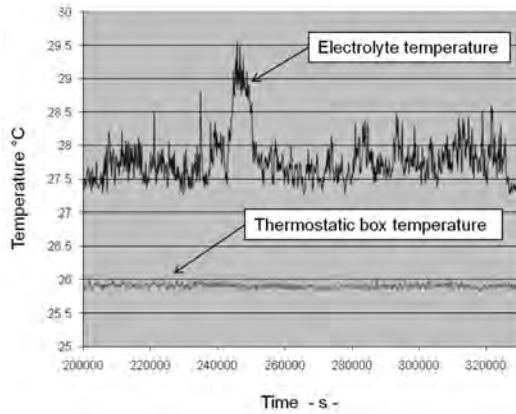


Fig. 1. – Input, output and excess power in the experiment L17.

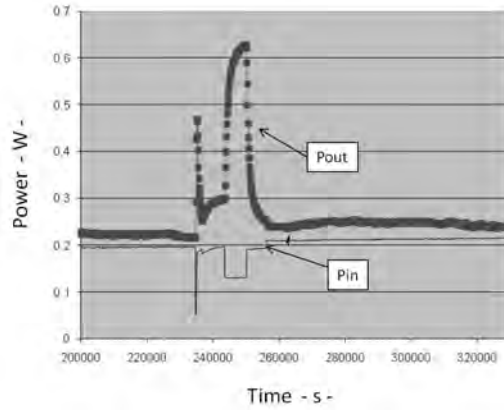


Fig. 2. – Increasing of the electrolyte temperature during the production of excess of power.

We identified some differences in two palladium lots received from the same producer. Both lots were 99.95% pure Pd. The first lot gave a reproducibility larger than 60% with signal amplitudes well above 100%. Fig.1 shows the input, output and excess power in the experiment L17 performed with a sample belonging to the first lot; Fig.2 shows the increasing of the electrolyte temperature in this experiment during the excess production. During the experimental campaign performed with the second palladium lot the reproducibility reduced below 20% and the excess amplitude was always below 20-25% of the input power.

A systematic work, to improve the knowledge about the status of the material that is required to have the effect, was conceived on the basis of such a different behavior of the two lots.

The experimental data highlighted that high loading is a necessary, but not sufficient condition to have the production of excess of heat, for such a reason the focus was moved on other features of the samples correlated with the occurrence of the excess of power production.

The most significant evidence, to be correlated to the different behavior in terms of excess of power production from these two lots, was the different spectrum of contaminants. It is well known from physics metallurgy that contaminants may have several effects on the metal characteristics; in fact, contaminants may act on grain size, crystal orientation and grain boundaries shape and depth.

The figures 3 and 4 show the typical grain size distribution of samples obtained from the first and second lot, undergone to the same metallurgical treatment. In addition samples belonging to the first and the second lot showed a different crystallographic orientation: the first lot was mainly oriented $\langle 100 \rangle$ while the second lot was $\langle 100 \rangle$ and $\langle 110 \rangle$ 50% oriented. Excess of power was mostly observed with samples having a dominant $\langle 100 \rangle$ orientation.

The difference in the spectrum of contaminants produced also a different effect of the chemical etching because of the different reactivity of the surface. The consequence was a different surface morphology between samples belonging to the two lots.

We selected the Power Spectral Density Function (PSD) as merit figure to identify the status of the surface.

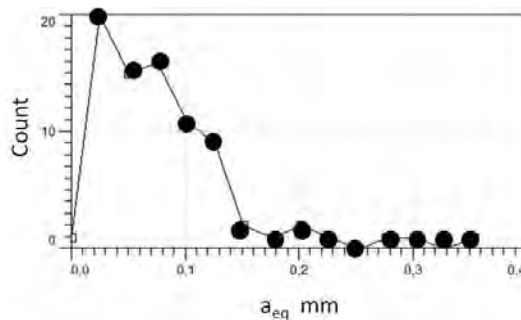


Fig. 3. – First lot grains size distribution.

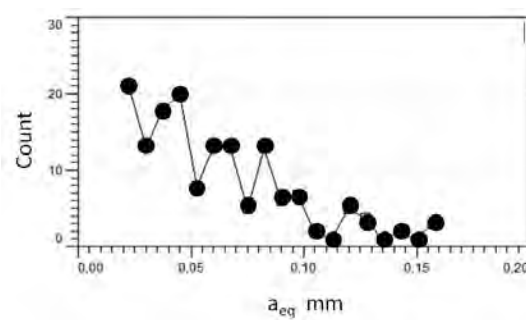


Fig. 4. – Second lot grains size distribution.



Fig. 5. - Microscopy of #64 sample surface.

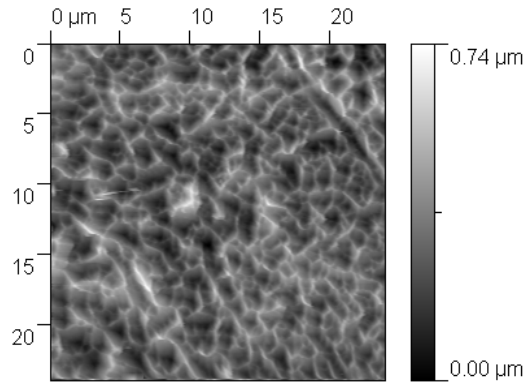


Fig. 6. - Microscopy of L25 sample surface.

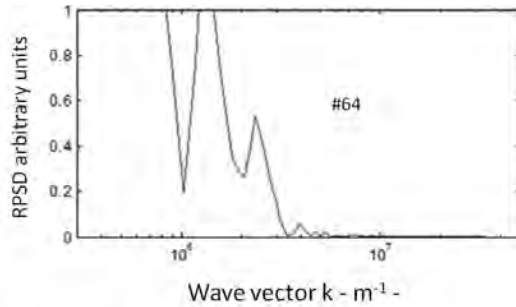


Fig. 7. - PSD of #64 sample.

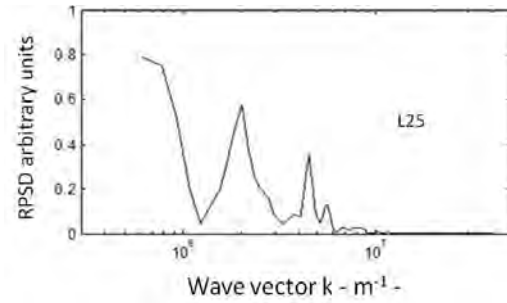


Fig. 8. - PSD of L25 sample.

Fig. 5 and Fig. 6 show the surface microscopy of samples #64 (sample #64 was produced at ENEA and experienced at Energetics) and L25 respectively; both gave a significant excess of power production but the effect was stronger for lot #64. Samples #64 and L25 gave an excess of power larger than 1000% and 200% respectively. Figures 7 and 8 show the power spectral density function for lot #64 and for lot L25 respectively. One may observe that the structure of the PSDF are quite similar but the larger the amplitude of the PSD peaks the larger the produced excess of power. This correlation, highlighting a significant role of the surface, was also found in other measurements.

3. A designed material

The experimental correlations presented in the previous paragraph led to produce a material having characteristics close to the ones described above.

A lot of Pd having a spectrum of contaminants approaching the one of lot 1 was undergone to the treatment leading to: dominant $\langle 100 \rangle$ orientation and an appropriate metallurgy.

A surface morphology quite similar to the labirintic one of sample #64 and L25 was produced by the chemical etching.

Fig. 9 shows the PSD for such a sample that results to be similar to the one of samples #64 and L25 even if the peaks amplitude is lower. A small excess was expected from such a sample. The experimental behavior gave a satisfactory agreement with the expectation. Fig. 10 show the produced excess of power up to 12% of the input.

A material designed to have excess of power production was replicated successfully by using the approach described above. Fig. 11 and 12 show the excess of power and the PSD for another designed sample.

An increased control of the effect is achieved even if not yet satisfactory, in particular if we compare the amplitude of the signals with the values observed experiencing the samples obtained from the first palladium lot. However a correlations between the amplitude of the power spectrum and the amplitude of the excess of heat turns out. This result is pointing into the direction of a crucial role of the surface status

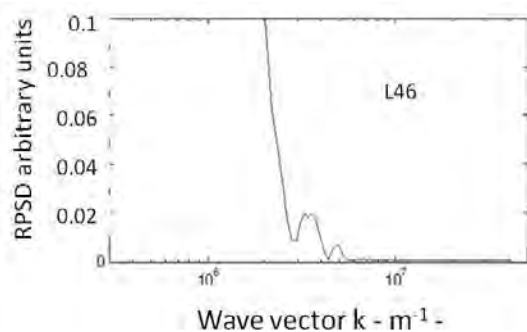


Fig. 9. – PSD of a material designed to produce excess of power.

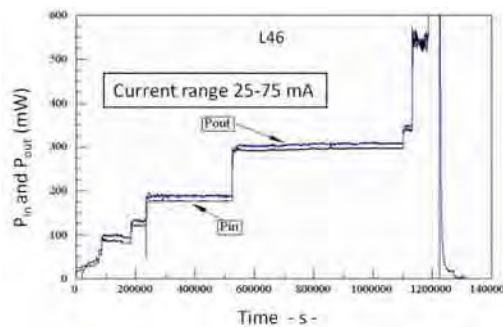


Fig. 10. – Excess of power produced by the designed material.

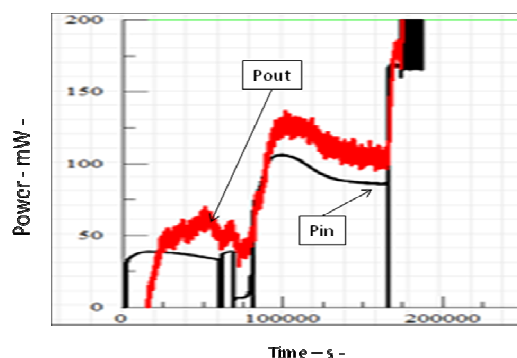


Fig. 11. – Excess of power produced by a designed sample.

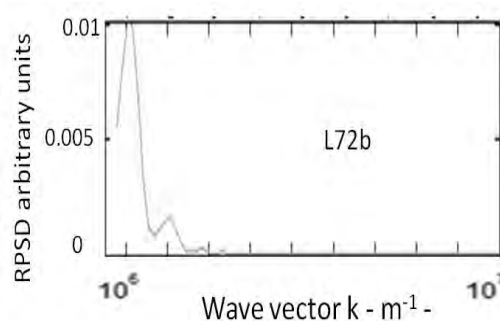


Fig. 12. – Designed material PSD.

to observe the effect; in other words an appropriate surface morphology is confirmed to be an additional condition to observe the effect. A certain reproducibility has been achieved in preparing “designed materials”; however the samples produced with the “designed material” and the ones obtained from the first lot are similar but not equal to each other. In other words the broad effort in the material science remains a crucial point for enhancing the level of knowledge in this field.

4. Conclusions

Reproducing the characteristics of the palladium cathodes that have been identified to be correlated with the excess of power production during electrochemical deuterium loading allowed to obtain the effect. This effect correlation was observed in several experiments performed with a designed material.

The enhancement of the probability to have excess of power is given by:

- 1) Easy loading at low current density due to proper metallurgy.
- 2) $\langle 100 \rangle$ mostly oriented material.
- 3) Labirintic surface giving a defined shape of the power spectral density function.

The correlation of the amplitude of the excess of power with the amplitude of the PSD is pointing in the direction of a crucial role of the surface under electrochemical conditions.

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Excess Power Observations in Electrochemical Studies of the D/Pd System; the Operating Parameter Space

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Abstract. The research activity into the Fleischmann-Pons Effect, FPE [1] at SRI has now accumulating more than 60 man-years of research. Here we focus attention on aspects of that work that lead to an improved understanding of the parameter space in which the FPE occurs.

1. Introduction

Researchers at SRI first focused attention on the critical importance of deuterium loading, the role of chemical poisons and additives in controlling the electrochemical interface, in order to achieve and maintain high D/Pd loading. We studied the correlation of excess power production with loading and reported simultaneously with IMRA-Japan [2,3] the threshold onset of the FPE reproduced as Figure 1. We designed and built a novel, high-accuracy, fully automated mass flow calorimeter, and set out to perform replication studies of the Fleischmann and Pons heat effect, first to confirm the existence the effect and second to better define the physical conditions under which it can be observed.

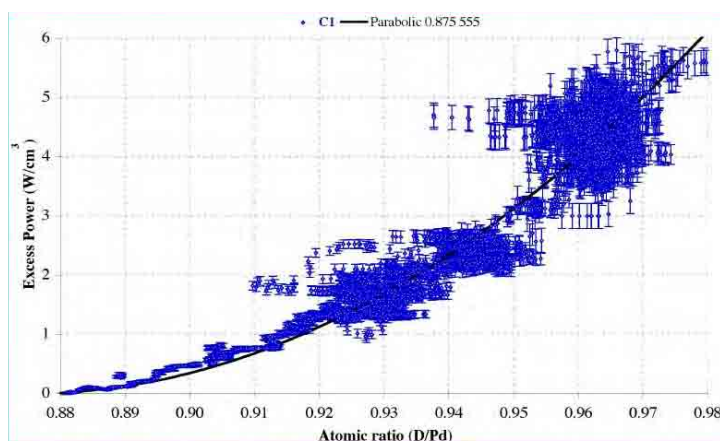


Fig. 1. - Excess power density in W/cm^3 versus average D/Pd atomic ratio measured from the axial resistance for a Johnson Matthey wire cathode 30 cm long and 1 mm diameter in 1.0 M LiOD containing 200 ppm Al.

As a second thrust of activity SRI embarked on a formal program of laboratory replication already discussed in several papers [4-7]. We successfully replicated:

- i. calorimetric evidence of the Fleischmann and Pons heat effect [8,9],
- ii. pioneering Miles/Bush FPE heat/helium correlations [4,10],
- iii. heat (and helium) results of gas loading studies reported initially by Case [10],
- iv. Arata & Zhang double structured cathode electrolysis heat (and helium) results [10],
- v. Energetics Technologies startling amplification of the power and energy gain of the FPE using innovating current (and other) modulation first elucidated by Dardik [7,11].

To accomplish these tasks the SRI team encouraged and contributed in a number of scientific partnerships. Obviously in approaching any difficult problem it is important to attract a critical mass of all the people who might contribute to the resolution of these effects. Specifically and ongoing we have a long established collaboration with Peter Hagelstein and his colleagues at MIT and over a decade of continuous, active, formal collaboration with Vittorio Violante and his group at ENEA Frascati. The Energetics team we have been collaborating actively with since about 2006, and more recently with the Naval Research Laboratory, NRL.

2. Experimental

At SRI, it was decided in early experiments to pursue excess power measurements based on flow calorimetry so that measurements of thermal power were obtained from measurements of the input and output (water) temperature, mass flow rate, and knowledge of the (water) heat capacity. In the SRI calorimetry of the early 1990s, about 95% of the thermal power was captured in the flow. The power not captured by the flow calorimetry was estimated using a Fick's law measurement, resulting in total power measurements with errors on the order of 0.5% in the case of 95% capture by the flow. In later designs, specifically the Labyrinth (L) and helium leak tight (M) calorimeter designs greater than 99% of the evolving heat was captured in the convecting fluid flow resulting in accuracies better than $\pm 0.35\%$.

To perform excess power measurements in this kind of calorimeter, closed cell operation was required, which necessitated the recombination of all gases generated in association with the electrochemistry. A further advantage of this choice is the retention of D_2O and products for analysis. It is worth noting that mass flow calorimetry and closed cell operation were not the methods adopted by Fleischmann and Pons. Much has been made of this difference but these choices reflected no disapproval of earlier principles and procedures of calorimetry. Although we were not aware of the details at the time, Fleischmann and Pons designed and built a beautiful calorimeter. It was very subtle and very sophisticated, requiring a sophisticated analysis and understanding. Unfortunately most of the people who remained skeptical in 1898 and 1990 had no means of achieving that sophisticated understanding.

In order to achieve high loading values (D/Pd ratios $\gg 0.9$) one needs to take strong control of the impurity aspects of the electrochemical cell. At SRI the various elementary constraints evolved a particular cell design shown in Figure 2. We employed mostly one molar $LiOD$, where the original work [1] employed 0.1 M. Again, no judgment is implied. We selected the electrolyte we believed best able to test our hypothesis that high D/Pd loadings prompted or promoted the excess heat effect. Most early SRI experiments were performed with 1 and 3 mm diameter wires, either 3 or 5 cm long. Loading is inferred from measurements of the resistance in the axial direction, expressed as a ratio of the unloaded resistance.

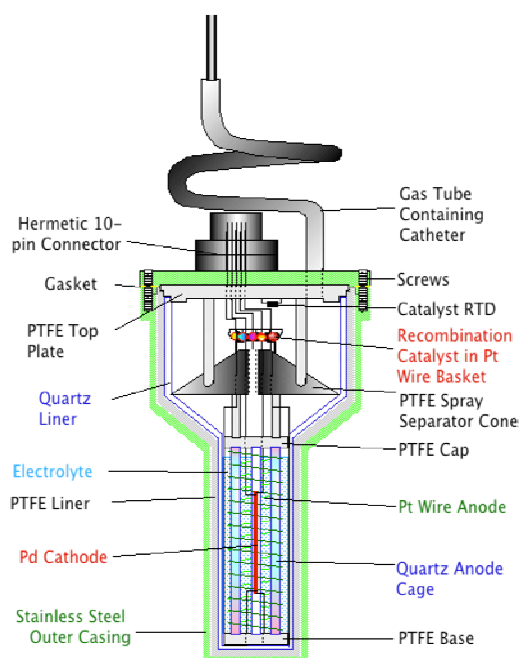


Fig. 2. - SRI Degree of Loading (DoL) electrochemical cell shown in hermetic closure.

In its calorimetric use the cell of Figure 2 is placed inside the calorimeter as shown in Figure 3. The calorimeter was submerged inside a large ($\sim 1 \text{ m}^3$), water bath that was well stirred and well regulated. This bath was placed in the center of an isolated, temperature controlled room. The mass flow fluid (water) was drawn from the bath past two inlet RTD sensors placed directly in the flow stream, past the submersed

electrochemical cell and emerges past outlet temperature sensors situated within the axial outflow channel, directly in contact with the outgoing fluid. Two outlet RTD sensors were used, identical to the two at the inlet, to provide a redundant measurement of ΔT ¹.

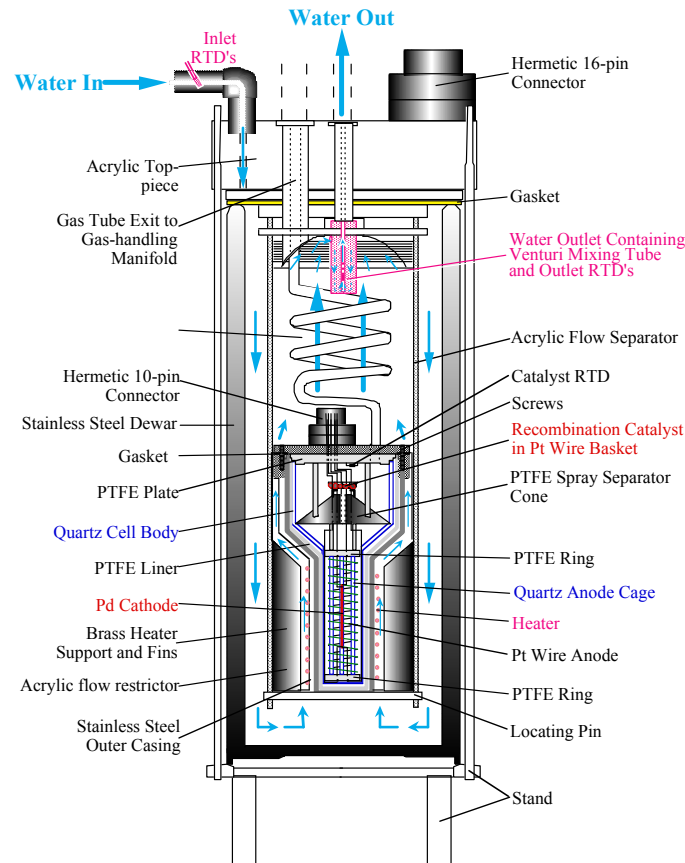


Fig. 3. - SRI Labyrinth (L) Mass Flow Calorimeter showing internal hermetically sealed electrochemical cell.

Many excess heat bursts were detected over the years in Fleischmann Pons experiments run in the SRI flow calorimeters. An example is illustrated in Figure 4, where two cells (a light water cell and a heavy water cell) were run electrically in series. Excess power was observed in heavy water cells at SRI, but not in light water cells, consistent with the results presented in this figure. In addition, the excess power effect appears to vary in response to the current density applied as shown in Figure 5. One observes a threshold in current density, where no excess power is present below 270 mA/cm^2 , and where the excess power appears to increase roughly linearly above this threshold. The appearance of a threshold in current density is typical in FPE experiments, although the specific current threshold is different for different cathodes, and depends strongly on whether the cathode is a rod or foil [12].

¹ In some experiments two additional thermistor sensors were used at the outlet to provide an alternative measurement method.

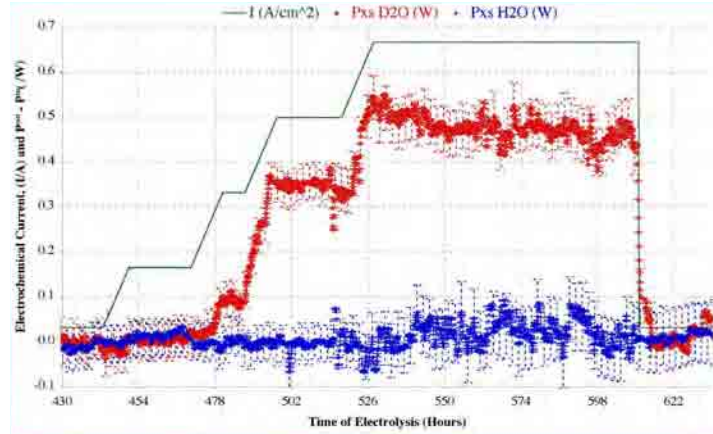


Fig. 4. - Excess power in Fleischmann-Pons experiments as a function of time in twin cells and calorimeters, driven with a common current, one with heavy water (upper data points) and one with light water (lower data points). The applied current density is shown as a solid line.

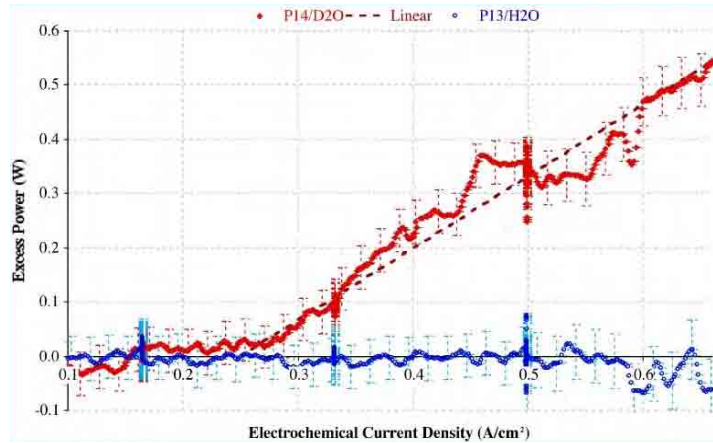


Fig. 5. - Excess power as a function of current density for Fleischmann-Pons cells with heavy water (upper data points) and with light water (lower data points).

Figure 6 presents not a typical result but a good result from later series SRI FPE experiments. With total input power² 12 W, we observe the output power increasing up to 6 W, with peak excess power of 50% with respect to the total input power. Also plotted is a pseudo-reference voltage exhibiting structure and detail reflecting extreme and at times bi-stable conditions at the electrochemical interface of the cathode, somewhat correlated to excess power. The period from ~700 hours onwards was more or less steady electrochemically, but the thermal and voltametric responses are dynamic.

It was found that changes in the operating parameters could initiate a heat burst in addition to the apparently self-stimulated dynamics of the cathode overvoltage and excess power. This observation may be related to a more general correlation between excess heat and a net deuterium flux either into or out of the metal. Figure 7 plots loading and excess power for a 24 hour period of constant electrochemical condition for (temperature and current density) a 1 mm dia. Pd wire wire cathode exhibiting variable excess power. The loading can be seen to vary in a somewhat sinusoidal “breathing” mode with ~2 hour period as the cathode apparently spontaneously absorbs and desorbs deuterium.

² Experiments were operated in pseudo-isothermal condition by holding the sum of the electrochemical and joule heater input power constant.

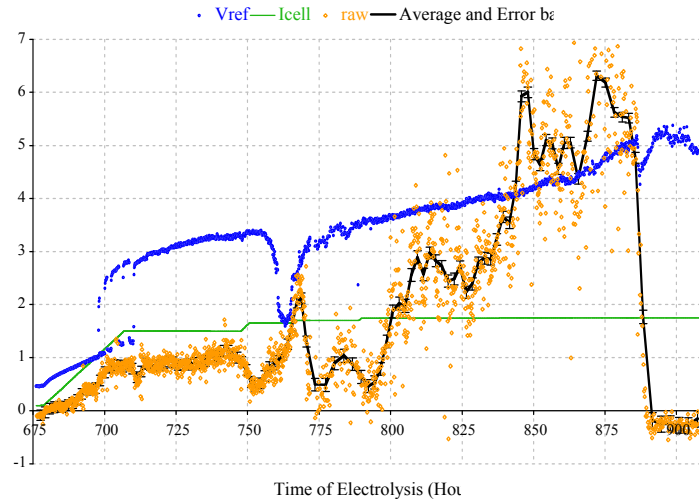


Fig. 6. - Excess power as a function of time for Fleischmann-Pons cells with LiOD electrolyte containing 200 ppm Al. The solid green line plots electrochemical current density, the square blue points are cathode voltage measured vs. proximate open-circuit Pt pseudo-reference electrode. The solid black line is the average excess power raw data points plotted in orange.

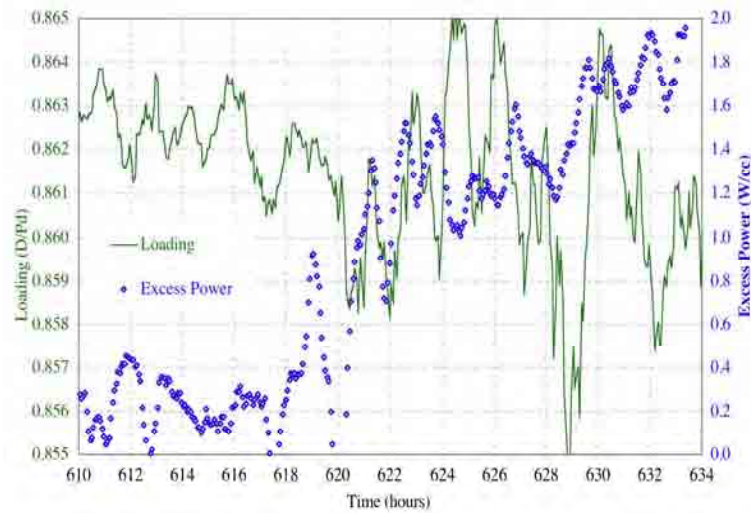


Fig. 7. - Correlation of the amplitude of loading oscillations with the magnitude of excess power in experiment M4.

While the frequency remains fixed, the amplitude of this “breathing” closely correlates with the amplitude of the excess power signal. We do not have an accurate knowledge of the diffusion coefficient of D under the prevailing loading condition but a time constant of 2 hours corresponds with a diffusion coefficient of $\sim 5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ traversing the full radius of the electrode. We do not know what caused this to occur, and all attempts to stimulate such oscillatory fluxing in the high loading condition have failed (with one notable exception discussed below).

3. Conclusions

The clear evidence of both intense and extended experimental investigation is that the FPE heat effect occurs as a consequence of four conditions in the electrochemical palladium-deuterium system:

- i. electrodes must attain and maintain D/Pd loading above a (high) threshold value, for
- ii. periods longer than an initiation time that is long compared to deuterium in-diffusion
- iii. while being subjected to a high electrochemical current that is in general larger than the current density of maximum loading
- iv. maintaining an electrode/electrolyte interface kinetically free enough to facilitate high rates of deuterium absorption/desorption (flux).

This set of observations prompted the development of an empirical expression for the simplest and most widely observed mode of excess heat production (designated by us as Mode A).

$$P_{xs} = M (x-x^{\circ})^2 (i-i^{\circ}) |i_D| \quad [1]$$

where $x = \text{D/Pd}$, x° is the threshold value typically ~ 0.875 , the current density threshold i° for wire cathodes typically falls in the range $75 < i^{\circ} < 450 \text{ mA cm}^{-2}$, the deuterium interfacial flux $i_D = 2\text{-}20 \text{ mA cm}^{-2}$.

In conclusion it should be noted that the simultaneous attainment of the above specified conditions has been found to require patient and rigorous attention to: system electrochemistry; bulk palladium metallurgy; electrode surface morphology and crystal orientation. Much, if not all of the apparent and “famous” irreproducibility of the Fleischmann-Pons heat effect can be traced directly to the failure to recognize and meet one or more of these conditions.

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Differential Thermal Analysis Calorimeter at the Naval Research Laboratory

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Abstract Differential thermal analysis (DTA) is a standard thermoanalytic technique used widely in industry and research. Drawing on this concept, DTA based calorimeters are under development at the Naval Research Laboratory (NRL) for the study of hydrogen in metals. The design goals are: high sensitivity, linear response, short time constant, tolerant to ambient temperature variations, easy to adapt to experimental constraints and low cost. In this paper we detail basic design requirements, and show a number of examples of their implementation.

1. Introduction

Since the announcement of thermal anomalies in the palladium-deuterium system reported by Fleischmann & Pons [1] in 1989, now referred by many as the Fleischmann Pons Effect (FPE), the veracity of their results have been questioned by the wider scientific community. Much of this criticism has been leveled at the calorimetry and its interpretation. Since then, the complexity of calorimeters used to confirm or refute the original isoperibolic calorimeter results has added to the confusion. One example of calorimeters applied is a first principles mass flow calorimeter, as was reviewed by McKubre et al. [2]. These are complicated systems requiring a large capital investment, and are not well suited for broad materials studies. To circumvent these limitations, we investigated commercially available calorimeters and analyzed their operating principles. None was found that met all our needs to study materials related to FPE. However, the basic operating principle for the differential thermal analysis (DTA) class of calorimeters held the promise of meeting this need. This paper describes the operating principle of DTA and our prototype implementations of DTA concepts specifically geared for the study of FPE-related materials.

2. Approach

The rejection of common mode signals is an integral part of the design of a DTA calorimeter. The technique relies on using two nearly identical thermal masses connected to a thermal reference (Fig. 1). The ability to reject common mode signals is dependent on the careful physical layout and shielding of the measurement channels. In our case, one of the thermal masses is an inert cell, while the other is the active cell. The analog electric circuit equivalent is a common mode amplifier, in this case, used to remove stray thermal signals generated by fluctuations in the ambient or reference temperature. In the ideal case

$$V_{\text{out}} = A \cdot (V_{\text{inert}} - V_{\text{active}})$$

where A is the difference gain, and V is the voltage generated by thermoelectric modules. Thermoelectric modules (TEM) monitor the flow of heat from the inert and active cells to the common thermal reference. The cell output voltages are given by

$$V = \alpha N (T_{\text{cell}} - T_{\text{ref}}) / (1 + 2r_l / l)$$

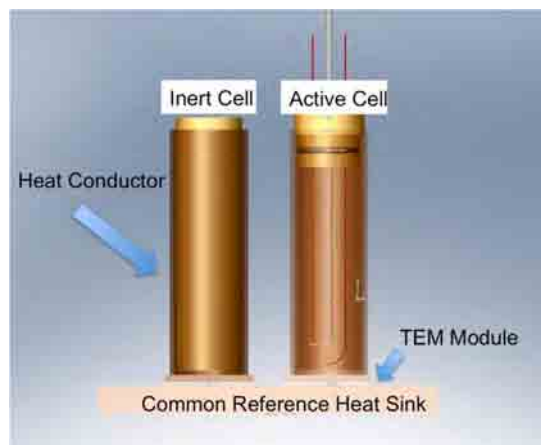


Figure 1. Conceptual drawing of a DTA calorimeter.

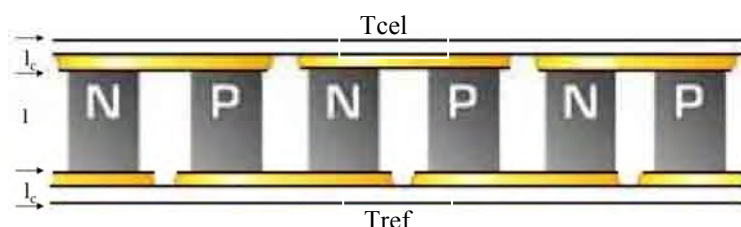


Figure 2. Graphical representation of thermoelectric module.

according to Rowe et.al. [3], where α is the Seebeck coefficient of the thermoelectric material, N the number of thermocouples, l is length of the thermoelement, l_c , the thickness of the contact layer, T_{cell} , and T_{ref} , are temperatures at the cell and reference sides of the module and $r = \lambda / \lambda_c$, where λ the thermal conductivity of the thermoelement and λ_c the contact thermal conductivity as shown in Fig. 2.

Rather than paneling the inside of a box with many TEMs as was done by Stroms [4], only two TEMs were used - one for the active cell and one for the inert cell (Fig 1). Heat flow was directed to the TEM by surrounding the active cell volume by a good heat conductor. A finite element analysis calculation was done to understand the steady state heat flow pathway for this approach. The result of this study can be seen in Fig. 3. The largest temperature gradient is across the TEM, thus, that is where the bulk of the heat flows. The time constant of the cell can be adjusted by the thermal mass and thermal properties of the cell. The cells should be surrounded by a constant temperature bath of very low thermal mass. This can be accomplished by surrounding the cell with a large thermal mass at the reference temperature, and leaving a small air gap between it and the cell. These basic principles have been used to tailor calorimetric systems to specific tasks since the invention of the thermocouple.

3. Experimental

The basic DTA concept can have nearly unlimited variations and can be tailored to satisfy specific applications. We tested two basic test tube designs. The first DTA is built around a disposable BD Falcon™ 50 ml conical tube. It can house either a simple cathode and anode assembly for electrolytic loading or a gas bottle for gas phase experiments. The heat transfer tubes were machined from two pieces of aluminum such that the 50 ml test tubes fit tightly. A large scrap piece of aluminum (26 cm x 21.6 cm * 3.81 cm) was used as the reference heat sink. The bottoms of the heat transfer tubes and the top of the reference heat sink were polished where the TEM's where to be attached. Two Custom ThermoElectric 40 mm x 40 mm TEM modules (part# 12711-5L31-03CQ) were silver printed to both the heat transfer tubes and the reference heat sink. The heat transfer tubes were then insulated using Armacel AP/Armaflex Microban 25/50 pipe insulation. Identically insulated hand wound 23 ohm nichrome wire heaters were

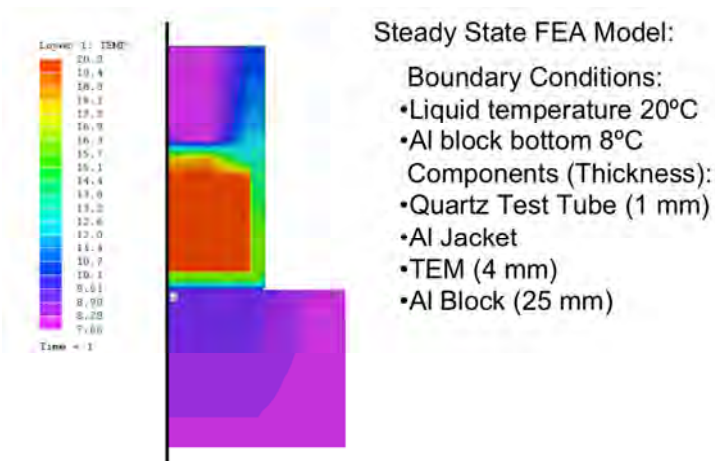


Figure 3. - Steady state FEA model of active cylindrical cell. One-half of symmetric cell is shown in cross section.

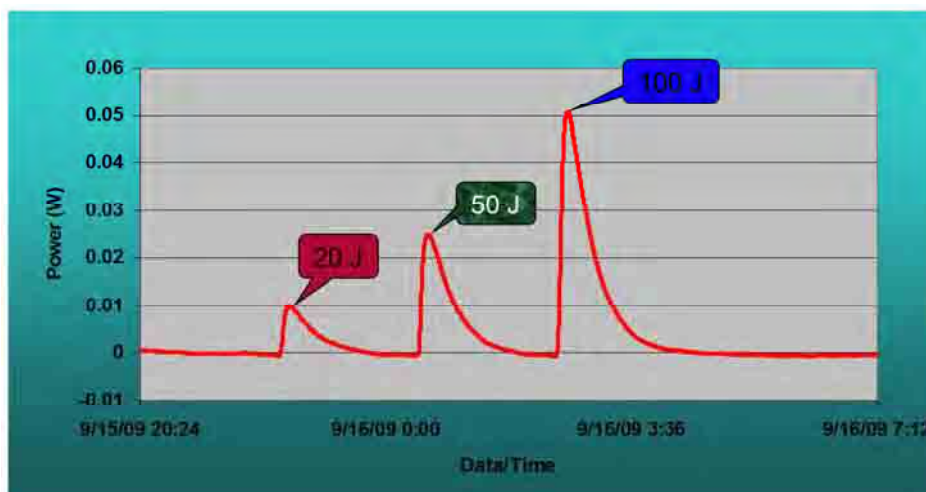


Figure 4. - DTA baseline stability and pulse response.

Table 1. - DTA response to a gas loading simulation

Impulse	Measured	Error
20 J	19.8 J	1% / 0.2 J
50 J	46.1 J	8% / 3.9 J
100 J	94.6 J	5% / 5.4 J

installed in both the reference and active cells. RTDs for temperature measurement were installed along the centerline of the cells. The completed system was then placed inside an incubator.

The DTA was tested for baseline stability and pulsed heat response to simulate our typical gas loading experiment [5]. The performance was evaluated by programming a Bio-Logic USA, LLC Model VSP potentiostat / galvanostat in constant power mode to produce 20, 50, and 100 joule pulses. Shown in figure 4 and table 1 are the results of this test. The agreement between the measured response and the delivered power is comparable to commercially produced instrumentation.



Figure 5. - Fully assembled DTA Calorimeter.

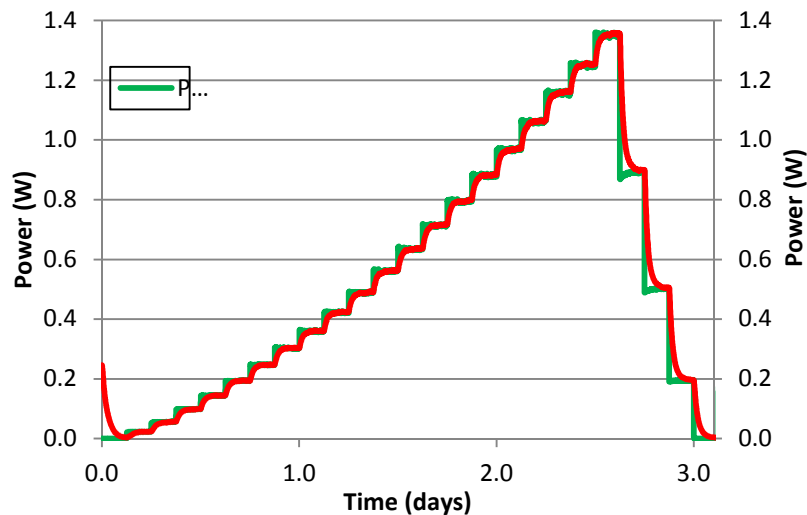


Figure 6. - Calibration run of DTA designed to match ENEA cell.

The second proof of principle DTA system was built to match the ENEA Violante closed cell design [6]. The design concept is basically the same as the first. The heat transfer tubes are built from commercially available copper pipe machined to match the outside dimension of the ENEA electrolytic cell. The fully assembled DTA is shown in Fig. 5. Results of a 3 day calibration run using light water are shown in Figure 6, where the current was stepped under galvanostatic control over a typical operating range. A single linear combination of the inert and active cell TEM voltages fit the input power of the tested range. The maximum power is limited by the heat sink's capability to transfer heat to the incubator. The inside temperature of the cell was monitored by RTDs, and also correlates with the input power as expected. Two heat sinks on either end of the thermal reference were also monitored. Their temperatures were also well correlated with the input power.

4. Conclusions

These proof of principle tests clearly demonstrate that one can build a very capable calorimeter that satisfy the needs of a rapid materials development and screening program, to gain insight underlying the requirements for the FPE. These simple systems proved to be stable (1% over 5 days) with good

sensitivity (1% absolute) comparable in many ways to our commercial Hart Heat Conduction calorimeter. The concepts can readily be modified to include, for example, external stimuli of time varying magnetic or electric fields, laser stimulation and programmable temperature ramps. This makes this design an ideal platform to test the validity of FPE claims in both liquid and gas phases. The linear response obtained over the tested operating range from a few Joules of impulse heat to long-term hours of operation at several watts DC makes the interpretation of results straightforward.

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Electrochemical models for the Fleischmann-Pons experiment

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Abstract. The loading of Pd by hydrogen isotopes in the Fleischmann-Pons experiment does not seem to be well described by the hydrogen/deuterium evolution reaction model that is commonly used for hydrogen in metals. We consider modified versions of the model that may be more relevant to the loading of deuterium in Pd.

1. Introduction

The need for high deuterium loading in Pd in the Fleischmann-Pons experiment as a prerequisite for the development of excess heat has been emphasized by McKubre and coworkers repeatedly over the years [1-3]. We are interested in modeling the cathode loading in order to understand the associated physics, and to simulate excess heat production.

The loading of deuterium in palladium can be understood simply enough in a broad sense in terms of individual reactions that constitute the hydrogen/deuterium evolution reaction model. Deuterium is brought to the surface through the Volmer reaction



Deuterium on the surface can recombine through the Tafel reaction to make D₂ gas



Adsorbed deuterium can move into the cathode to occupy more tightly bound sites associated with absorbed deuterium



Other things can happen as well (as we will discuss below). However, these three basic reactions provide a simple picture which allows for a quantitative description of the cathode loading at low current density (in the Volmer-Tafel regime).

In this reduced picture, the electrochemical current is dominated at the Pd surface by the Volmer reaction. When this occurs, one deuterium atom is deposited on the cathode surface as an adsorbed atom per charge transferred. In this regime, we can load the cathode simply by applying a current.

As deuterium accumulates on the surface (and hence in the bulk), the deuterium chemical potential increases, making D₂ gas formation more likely. The loading is determined in the Volmer-Tafel regime by matching the incoming deuterium from the Volmer reaction to the outgoing deuterium gas associated with the Tafel reaction.

Although there are technical issues, this simple picture can account for important features of cathode loading in the Fleischmann-Pons experiment at low current density. Unfortunately, at higher current density the situation becomes more complicated. One can find publications in the literature which make use of the hydrogen/deuterium evolution equations to describe the loading at higher current density [4,5]. Unfortunately, these models do not work particularly well when used systematically for different experiments. For example, Zhang et al [5] used such a model to account for a decrease in the loading at high current density observed in an experiment reported by Kunimatsu's group. In this model, the Heyrovsky mechanism



accounted for this loss of loading. The Heyrovsky mechanism decreases the loading by one deuterium per unit charge in the electrochemical current, in contrast to the Volmer mechanism that increases the loading by one deuterium per unit charge. The problem is that the kinetics rate associated with the Heyrovsky mechanism increases exponentially with loading. Hence, such a model would not predict a loading significantly higher than the maximum loading for that experiment (D/Pd of about 0.85), where there are now many reports of experiments where significantly higher loading is seen.

2. Volmer reaction kinetics model

We start with a model for the Volmer current density j_V given by

$$j_V = r j_{V0} \left(\frac{1-\theta}{1-\theta_0} \right) e^{-(1-\beta_V)f\eta} + d.b. \quad (5)$$

Here r is a roughness factor, θ is the fraction of available surface sites with adsorbed deuterium, β_V is an asymmetry factor, f is $e/k_B T = F/RT$, and η is the overpotential. The notation d.b. denotes the counter term required for detailed balance. Our notation is most closely related to that of Zhang et al [5].

There are two free model parameters here (the quantity $r j_{V0}/(1-\theta_0)$, and β_V). The asymmetry factor β_V can be obtained from experiment, and we have used 0.49 as given by Green and Britz [6] for 0.1 M LiOD. For simplicity, we have adopted $r=2$ from this work. We are able to approximately match the data given in [6] with $j_{V0} = 1.63 \times 10^{-5}$ A/cm² and $\theta_0=0.70$. This choice in our models approximately reproduces the overpotentials that are reported.

3. Tafel reaction model

In the case of the Tafel reaction, we can begin with a model for the equivalent Tafel current density j_T given by

$$j_T = r^2 j_{T0} \left(\frac{\theta}{\theta_0} \right)^2 e^{2u(\theta-\theta_0)} + d.b. \quad (6)$$

Here u is a Frumkin adsorption isotherm parameter [7], which takes into account the change in the chemical potential of the deuterium with loading. In the beta phase, we have made use of the measurements of Chun and Ra [8], which leads to $u = 20.0$ at room temperature. In the mixed phase region below a loading of about 0.60, the chemical potential does not change with loading, so that $u=0$ would be appropriate. It seems that there is one remaining free parameter, j_{T0} . It is possible to obtain a reasonable fit to different data sets in the Volmer-Tafel regime, but only if we adopt a different value for j_{T0} for each experiment separately. Individual values in this case can be different by two orders of magnitude.

For the purposes of model development here, we will adopt the point of view that the reason for this variation is that there are internal surfaces where deuterium gas can evolve via the Tafel reaction, and that this gas can subsequently find its way to the outer surface. This point of view is discussed by Storms [9]. To implement this, we will augment the Tafel reaction to read

$$j_T = r^2 [1 + a(\theta)] j_{T0} \left(\frac{\theta}{\theta_0} \right)^2 e^{2u(\theta-\theta_0)} + d.b. \quad (7)$$

where $a(\theta)$ is the ratio of the square of the internal surface area to the square of the outer geometrical surface area. In anticipation of arguments to follow, we assume that the amount of internal surface area depends on the loading.

While such a model seems to allow for a description of the effect, there is the problem that to determine j_{T0} , we require experiments carried out on cathodes that we know have no internal leaks at low loading. In this respect we draw attention to a set of experiments reported by Green and Quickenden [10] where the cathode loading was found to increase up to 0.93 for cathodes that were vacuum annealed and then etched in acid. Within the framework of the model, this pre-treatment produced a smaller value for the internal surface area. In recent experiment at ENEA Frascati with thin foils (which initially are single crystals transverse to the surface), D/Pd loadings above 1.0 have been obtained.

As a result, a low value of j_{T0} is probably appropriate. A value which seems to be in the right regime in this regard is 2.0×10^{-8} A/cm². Tafel current densities as a function of loading for different assumed internal areas are shown in Figure 1. According to this plot, the cathodes reported in Green and Britz have an internal area greater than the surface area by four orders of magnitude or so.

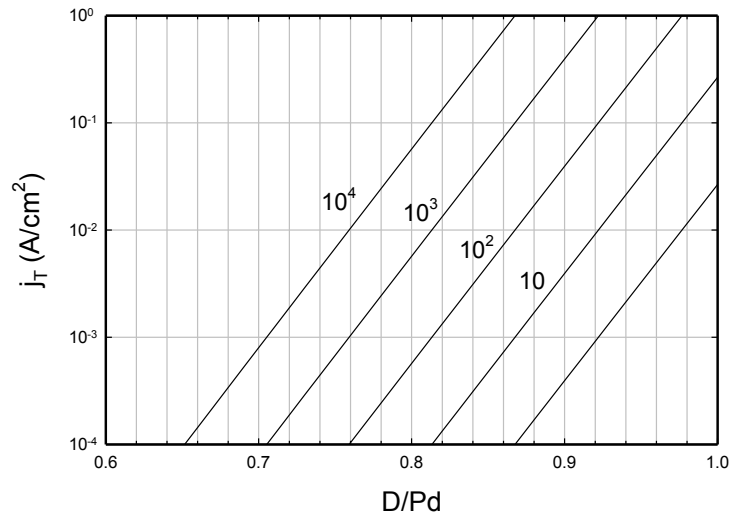


Fig. 1 – Tafel equivalent current density j_T versus loading for different values of a ; the rightmost curve is for $a=0$.

4. Lithium model

Experiments carried out in heavy water electrolytes with LiOD show that lithium enters the cathode [11,12] in significant amounts. We assume that lithium is transported to the surface through the analog of the Volmer reaction in acid



Adsorbed lithium probably comes off of the surface through a version of the lithium-water reaction



If we assume that in steady state the adsorbed lithium is determined from a balance between these reactions, then we obtain the following adsorption isotherm

$$\frac{\theta_{\text{Li}}^2}{1 - \theta - \theta_{\text{Li}}} e^{2v\theta_{\text{Li}}} = C [\text{Li}^+] e^{-(1-\beta_{\text{Li}})f\eta} \quad (10)$$

The measurements of the near-surface absorbed lithium concentrations of Yamazaki et al [11] can be fit well using this adsorption isotherm. The overpotentials in [11] are determined relative to a reference hydrogen electrode (RHE), which seems to give rather different results than the method used by Green and Britz [6]. If we substitute these overpotentials matching currents, then we can fit the near-surface absorption data using $\beta_{\text{Li}} = 0.53$ and $v = 19.4$.

5. Lattice expansion effects

As the cathode loads, the lattice constant increases. One would expect this to have an impact on the internal surface area. The loading curves of Green and Britz [6] show a reduction of loading at the higher current densities over what would be predicted from a simple Volmer-Tafel regime model (which would give the loading approximately proportional to the log of the current density). Near 0.5 mA/cm^2 , the Volmer-Tafel kinetics matches the data well, but up at 50 mA/cm^2 a pronounced reduction in loading from the Volmer-Tafel model can be seen.

There is not agreement as to why the loading should decrease with increasing current density. From the discussion above, the cathode loading is determined by a balance between incoming deuterium (which is provided by the electrochemical current via the Volmer reaction) and the outgoing deuterium (which leaves as molecular D_2 via the Tafel reaction). As the current initially increases, there is no reason to believe that the efficiency of producing adsorbed deuterium somehow decreases (which might be the case if reactions occurred via the Heyrovsky mechanism). Measurements in this regime searching for evidence of the Heyrovsky mechanism showed that it is not present [6]. It seems unlikely that some new reaction mechanism kicks in that removes deuterium more efficiently than the Tafel mechanism.

We will assume that the loading decreases because additional internal surfaces become available as the lattice expands with increased loading. This point of view seems generally consistent with Storms [8], McKubre [10], and Zhang [13].

Once we adopt this approach, then technical questions arise as to how to implement a model which works this way. Intuitively, one would expect that the surfaces and channels that open as the lattice expands constitute physical changes in the lattice that might be expected to remain if the loading is subsequently reduced. This would show up as hysteresis in the loading curve. Although there is some hysteresis present in the loading curves, it seems that the effects are largely reversible. As such, it seems reasonable to begin with a reversible model that can sensibly be parameterized. To model the initial increase in the internal area, we have found reasonable agreement with a fit of the form

$$a(\theta) = a(0.60) \left(1 + e^{w(\theta - \theta_a)^7} \right) \quad (11)$$

The idea is that the internal Tafel leak rate at the beta-phase boundary (near $\text{D/Pd}=0.60$), when large, dominates the loading curves in the Volmer-Tafel regime. The subsequent increase in the internal Tafel rate is then assumed to depend only on the loading, and not on the current density or overpotential. The experimental curves seem to show a similar shape that has an offset in θ . A more highly loaded cathode suffers a similar reduction in loading as compared to the Volmer-Tafel model as the loading increases. To capture this effect, we require a characteristic loading at which the increases start. This is accomplished most naturally within the model by defining a characteristic loading θ_a , which satisfies

$$\theta_a = \theta_0 + \frac{1}{2u} \ln \frac{j_{V0}}{rj_{T0} [1 + a(0.60)]} \quad (12)$$

With this definition, the parameter w is fitted to be 6.0×10^5 . This model seems to account well for the data of Green and Britz [6] up to 50 mA/cm^2 .

5. Effects at higher current density

The model discussed above seems to be capable of extending the hydrogen/deuterium evolution reaction model to current densities up to about 50 mA/cm^2 . To go higher in current density, we require further modifications of the model, for which there is even less consensus.

To proceed, we focus on three relevant experimental observations. The first is that the loading curves as a function of current density generally become flat with increasing current [9], and can show a decrease in

loading at current densities approaching 1 A/cm² [14]. A reversible decrease in the loading cannot be accounted for by the model above that we introduced to account for lattice expansion effects. The second observation is that the Tafel plot (overpotential as a function of current density) can show a distinct change of slope at higher current density [15]. This effect can also be seen in the data of Ref. [14]. The third observation of interest here is that the catalytic activity of Pd and other catalysts is strongly dependent on the local surface morphology, so that atoms on edges and corners are more active [16]. There is a growing literature on this issue, but we have so far not found papers yet which consider this effect specifically in the case of the Volmer reaction.

We consider first the overpotential anomaly as reported by Bockris et al [15]. In the Bockris measurement, the (negative) overpotential is seen to increase with current density at a rate of 157 mV/decade of current density between 20 μ A/cm² and 5 mA/cm². At higher current density, the slope changes to 357 mV/decade. In essence, more overpotential is required to maintain the electrochemical current density. In the data of Akita et al [14], the same effect is observed, except that the slope increases near 100 mA/cm².

What physical process is capable of changing the slope on a Tafel plot? Usually a change of slope signals the onset of a different reaction becoming important. Such an interpretation doesn't work here because the slope increases rather than decreases. If the slope had decreased instead, then a plausible explanation is that the relative strength of a different reaction increased compared to the Volmer reaction, overtaking it at more negative overpotential where the current density is higher.

For the slope to increase, we need instead some mechanism that makes it harder to get the current to flow as the current increases. Perhaps the simplest approach is to assume that sites at which the Volmer reaction occur are getting blocked, so that more overpotential is needed to support a higher current per unit site at the remaining unblocked sites.

We can show that this approach can work in principle through a simple example. Assume that whatever blocks the active sites has an adsorption isotherm something like that of lithium given above in Equation (10). In the limit that the blocking is sufficiently efficient that most of the sites are occupied, the number of unblocked sites is exponential in the overpotential

$$1 - \theta - \theta_{Li} = \frac{\theta_{Li}^2 e^{2v\theta}}{C[Li^+]} e^{(1-\beta_{Li})f\eta} \quad (13)$$

The current density of the Volmer reaction in this limit would then acquire a different dependence on the overpotential

$$j_V = rj_{V0} \left(\frac{1 - \theta - \theta_{Li}}{1 - \theta_0} \right) e^{-(1-\beta_V)f\eta} \rightarrow \frac{rj_{V0} \theta_{Li}^2 e^{2v\theta}}{(1 - \theta_0) C[Li^+]} e^{-(\beta_{Li} - \beta_V)f\eta} \quad (14)$$

In this limit, there will be an increased value for the change in overpotential per decade of current, as long as β_{Li} is greater than β_V . The increased slope in this model would be matched to the difference in asymmetry parameters

$$\beta_{Li} - \beta_V = \frac{\ln 10}{0.357f} = 0.167 \quad (15)$$

In our two-parameter fit of the Yamazaki data using the Green and Britz overpotential numbers, we obtained 0.53 for β_{Li} . But β_{Li} would need to be about 0.66 to be consistent with the measurements of Bockris et al given this interpretation. An approximate fit to the Yamazaki data is possible if such a large value for β_{Li} is assumed.

Now, the amount of lithium computed to be absorbed near the surface is in the few per cent range, so that we would not expect complete coverage. However, suppose that the Volmer reaction occurs primarily at edge or corner sites, and suppose further that these sites are also targets for adsorbed lithium, then this mechanism could account for the Bockris and Akita observation. If so, then the offset in current density where the slope changes could be related to the number of active Volmer sites.

There remains the question of why the loading is reduced at high current density. Given the picture above, one might conjecture that inhomogeneities are responsible for loss of loading at high current density. The basic problem with the Heyrovsky mechanism in this model is that the Heyrovsky current density has such a strong dependence on the loading. But if we assume that the loading is high close to a small number of active Volmer sites, then the local loading might be high, leading to the appearance of a Heyrovsky current density that is not connected with the average bulk loading.

6. Conclusions

We have described issues involved in the development of a new electrochemical model to describe the loading of Pd cathodes in the Fleischmann-Pons experiment. The basic hydrogen/deuterium evolution reaction kinetics model fails in this case, and we are working to develop a modified version of the model which works better. To account for the data, we have to assume that D_2 molecules are formed at internal surfaces inside that cathode. The loss of this gas is responsible according to the new model for the low loading observed in most cathodes in early experimental work. Lithium is adsorbed on the surface, and can be fit using an adsorption isotherm that results from a balance between Li^+ deposition and the lithium water reaction. The change in slope observed at high loading is attributed in the model to a blocking of a limited number of active Volmer sites by lithium (or perhaps by some other impurity that is adsorbed as a singly charged species). The decrease in loading is conjectured to be caused by a modified Heyrovsky current density that depends on local high loading near active Volmer sites. These modifications address the primary experimental issues, and it remains to develop connecting relations between the adsorbed and absorbed deuterium and lithium fractions.

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New approaches to isoperibolic calorimetry

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Abstract. Relatively inexpensive isoperibolic calorimeters have been designed and constructed with the goal of obtaining a constant heat transfer coefficient that is insensitive to normal changes in the electrolyte level during electrolysis. Four prototypes were constructed from copper tubing and used different insulating materials. Preliminary tests on two of these new calorimeters show excellent stability for the cell temperature measurements, stable heat transfer coefficients during electrolysis, and precise power measurements.

1. Introduction: design considerations for isoperibolic calorimeters

An important goal for isoperibolic calorimeters is a constant heat transfer coefficient that does not change as the electrolyte level decrease due to the electrolysis and evaporation. All measurements could then be evaluated with a single, predetermined value for the heat transfer coefficient. The placement of the thermistors in a secondary compartment outside the cell has been shown to minimize the cell electrolyte level effect [1-4]. This type of calorimeter can then be modeled as a fluid in which the electrochemical cell serves as a heating element for the substance in the adjacent compartment.

The size of the calorimetric system must be carefully considered in the design. Large systems give slower electrolyte level changes along with larger heat capacities and time constants. Small calorimetric cells yield faster electrolyte level changes and smaller heat capacities and time constants, but their small cell volumes require more frequent makeup of H₂O or D₂O additions. The heat transfer coefficient will also increase with the surface area of the calorimetric system. Adequate stirring of the cell contents by the electrolysis gases requires thin, tall cells where the cell diameter does not exceed 3 or 4 cm. All these factors were carefully considered in selecting design features for these new isoperibolic calorimeters.

2. Experimental details of the calorimetric design

Four prototype isoperibolic calorimeters (A, B, C, D) have been constructed from commercial copper tubing and copper end caps, and two (A, B) have been tested. Each calorimeter consisted of two completely isolated copper cylinders. The outer copper cylinder for each calorimeter had a 5.1 cm (2.0 inch) diameter and a 28 cm height. The inner copper cylinder (3.2 cm x 20 cm) was completely separated from the outer cylinder by the insulating material consisting of either pipe foam insulation (Cell A) or of tightly packed Oregon timber sawdust (Cell B). The glass electrochemical cell (2.5 cm x 20 cm) was a large commercial glass test tube (Kimax). This test tube cell was positioned inside the inner copper cylinder and filled 2/3 full using 50.0 mL of the selected electrolyte. Two thermistors were positioned on opposite sides of the outer wall of the glass tube with each thermistor level with the center of the cathode used. Thermal contact between the glass cell and the inner copper tube was provided by Mobil-1 (5W-30W) synthetic motor oil (50 mL) as the heat conducting fluid. This Mobil-1 oil has a reported density of 0.80 g/mL at 15°C and a heat capacity of 2.10 J/g.K at 80°C. This 50 mL of Mobil-1 oil filled the secondary chamber well above the cell electrolyte level. It is expected that this calorimetric design will provide for high cell operating temperatures up to the boiling point of the selected electrolyte solution. Photographs of the calorimetric cell and experimental arrangements are available electronically (http://iccf15.frascati.enea.it/ICCF15-PRESENTATIONS/S1_O9_Miles.pdf).

3. Review of equations for isoperibolic calorimetry

The mathematical equations that model isoperibolic calorimetry have been fully presented elsewhere [5-8], thus this will only be a brief review. The fundamental modeling equation is

$$P_{calor} = P_{EI} + P_H + P_X + P_C + P_R + P_{gas} + P_W \quad (1)$$

where these individual power terms have all been defined elsewhere [5-8]. Equation 1 represents a differential equation because

$$P_{calor} = C_p M dT/dt \quad (2)$$

where $C_p M$ is the heat capacity of the total calorimetric system expressed in terms of the heat capacity (C_p) and the equivalent moles (M) of H₂O or D₂O.

It is useful in initial calculations to assume that there is no anomalous excess power, $P_X=0$, thus Eq. 1 becomes

$$P_{calor} = P_{EI} + P_H + 0 + P_C' + P_R + P_{gas} + P_W \quad (3)$$

The simple subtraction of Eq. 3 from Eq. 1 yields

$$0 = P_X + P_C - P_C' = P_X - k_C \Delta T + k_C' \Delta T \quad (4)$$

or

$$P_X = (k_C - k_C') \Delta T \quad (5)$$

where $\Delta T = T - T_b$. Therefore, the difference between the true conductive heat transfer coefficient (k_C) and the pseudo heat transfer coefficient (k_C') obtained by assuming $P_X = 0$ provides for a simple calculation of the actual excess power via Eq. 5. All of the power terms in Eq. 1, however, should be considered in the determination of k_C' .

4. Initial experimental results

The use of this new isoperibolic calorimetric design requires the evaluation of the conductive heat transfer coefficient, k_C , and the heat capacity, $C_p M$, of the calorimetric system. Several experiments using H₂O control electrolytes yielded $k_C = 0.164$ W/K for Cell A and $k_C = 0.133$ W/K for Cell B. These cells differ only by the use of foam insulation in Cell A and packed sawdust insulation in Cell B.

The experimental cooling curve obtained by simply turning off the cell current provides a convenient method for determining the heat capacity, $C_p M$, of the calorimetric system. For a H₂O control experiment at zero current, Eq. 1 becomes

$$C_p M dT/dt = -k_C (T - T_b) \quad (6)$$

This differential equation can be rearranged to

$$dT/(T - T_b) = -(k_C/C_p M) dt \quad (7)$$

and then integrated to yield

$$-\ln (T - T_b) / (T_0 - T_b) = (k_C/C_p M) t \quad (8)$$

This integrated equation is of the form $y = mx$ where the slope (m) is given by $m = k_C/C_p M$.

The experimental cooling curve for Cell B using a H₂O control is present in Figure 1 where T_2 is the cell temperature measured by thermistor 2. This figure shows the expected exponential decrease of $T_2 - T_b$ with time. Figure 2 shows the same data using the integrated Eq. 8. The slope $m = 0.01752 \text{ min}^{-1} = 2.920 \times 10^{-4} \text{ s}^{-1}$. Therefore $C_p M = k_C/m = 456 \text{ J/K}$. The heat capacity of the system can also be calculated using the differential equation (Eq. 6) directly, but this is considerably less accurate because of the estimate of dT/dt . From Eq. 6, $C_p M = -k_C (T - T_b) / dT/dt$. Table 1 presents the value for $C_p M$ obtained directly from Figure 1 at 10, 30, and 65 minutes. The three values calculated for $C_p M$ range from 427 J/K to 485 J/K with a mean of $457 \pm 29 \text{ J/K}$. It is obvious that more

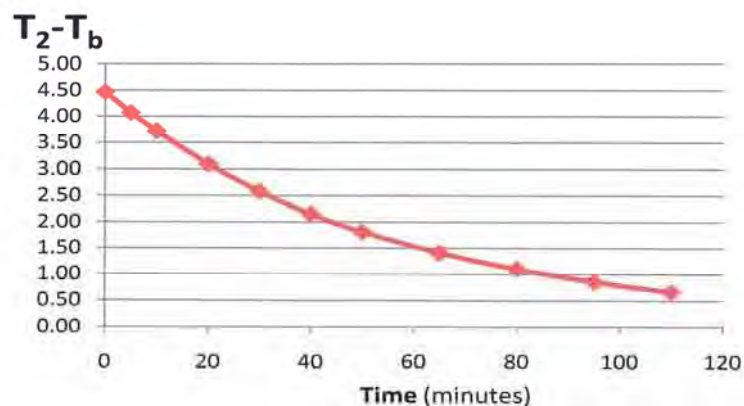


Fig. 1. - Experimental cooling curve for Cell B.

Table 1. Heat capacity (C_pM) for Cell B calculated from the cooling Curve of Fig. 1 using the differential equation (Eq. 8).

T (minutes)	dT_{cell} / dt (K/min)	$T - T_b$ (K)	C_pM (J/K)
10	-10.8×10^{-4}	3.72	458
30	-8.03×10^{-4}	2.58	427
65	-3.87×10^{-4}	1.41	485
Mean $C_pM = 457 \pm 29$ J/K			

accurate results for C_pM are obtained by use of the integrated equation (Eq. 8) where the results can be displayed in a straight line form (Fig. 2). The same is true for all isoperibolic calorimetric results using Eq. 1. Numerical integration of the experimental calorimetric data along with casting them into the straight line form, $y=mx+b$, gives the most accurate results as previously reported [6-9].

The heat capacity of the cell can also be estimated by considering the heat capacity of all materials in the cell or in contact with the cell that undergo the same temperature changes. These calculations give 200 J/K for the 50.0 mL of H_2O used, 133 J/K for the 344 g of the inner copper cylinder, 84 J/K for 50 mL of Mobil-1 oil, 38 J/K for 52 g of the glass cell, and 3 J/K for the copper cathode, platinum wire, palladium and nickel present. The calculated total of 458 J/K is close to the measured value for C_pM .

The time constants for Cells A and B can be readily calculated once k_C and C_pM are known because $\tau = C_pM/k_C$. This yields $\tau = 3420$ s or 57 minutes for Cell B and 46 minutes for Cell A.

It should be noted that cooling curves such as Fig. 1 and 2 provide a useful method for determining lingering excess power effects or “heat-after-death” when electrolysis ceases in active D_2O/Pd experiments. Cell cooling that departs from Eq. 8 or Fig. 2 would be readily apparent. Such studies of cooling curve behavior is planned for future D_2O/Pd experiments. A previous study of $Pd-B/D_2O$ in a Dewar type cell showed marked deviations from the expected cooling curve behavior (see pp. 22-23 and Figs. A.23 and A.24 of Ref. 6).

Although potassium nitrate (KNO_3) has been widely used for years by electrochemists as an inert supporting electrolyte, it has been proposed that shuttle reactions involving nitrates may give false excess power effects [10]. Theoretically, the nitrate ion may be reduced at the cathode to form various gaseous nitrogen oxides, nitrite ions (NO_2^-), or even N_2 or NH_4^+ . With the use of special electrocatalysts and conditions, some electrochemical reduction of nitrates is possible [11]. In molten nitrates ($LiNO_3-KNO_3$) at elevated temperatures ($250^\circ C$), there exists a large 4.5 V electrostability region between the reduction of lithium ions and the oxidation of nitrate ions [12, 13]. This demonstrates the stability of the nitrate ion even at high temperatures. This extreme anodic limit for the nitrate melt is the oxidation of the nitrate ion, $NO_3^- \rightarrow NO + O_2 + e^-$, followed by the further reaction of NO with oxygen to form brown NO_2 gas [12].

Because of the proposed shuttle reactions involving nitrates [10], an initial study using this new isoperibolic calorimeter was the investigation of 0.154 M KNO_3 in Cell B. This study used a platinum wire cathode

(1mm x 15mm) and a platinum coil anode. The $\text{H}_2\text{O} + 0.154 \text{ M KNO}_3 / \text{Pt}$ system was investigated over several days of electrolysis at currents of 80, 100, and 150 mA. These were no measurable excess power effects. The correct value of $k_C' = 0.133 \text{ W/K}$ was obtained using Cell B and assuming $P_X = 0$. Therefore $k_C - k_C' = 0$ and $P_X = 0$ from Eq. 5. Recent cyclic voltammetric studies on $\text{KNO}_3 + \text{NaNO}_2$ have confirmed that there are no reversible reactions involving nitrates or nitrites that could act as shuttle reactions.

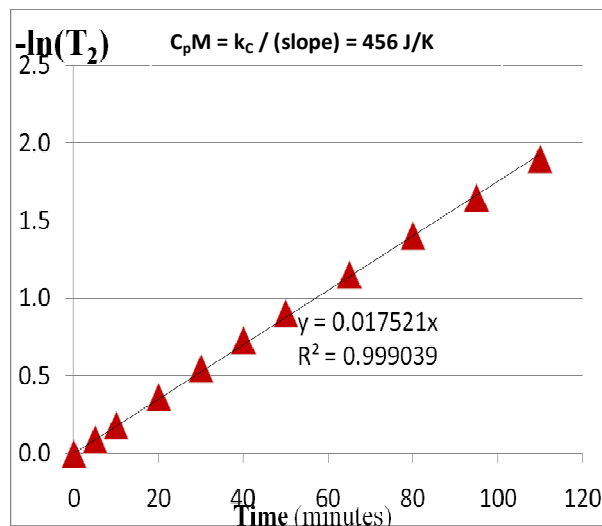


Fig. 2. - Cooling curve data of Fig. 1 using the integrated equation where $-\ln(T_2)$ represents the left-hand side of Eq. 8.

The measured pH of the 0.154 M KNO_3 solution, however, changed from near neutral initially ($\text{pH} = 7.02$) to $\text{pH} = 10.24$ at the end of this study. Any electrochemical reaction of a NO_3^- ion to form a neutral product such as N_2H_2 or N_2 results in the production of OH^- ion to maintain electroneutrality. For the total of 27,626 coulombs used in this study, the observed pH change could be explained by 0.003% of the current being consumed by the reaction of NO_3^- . Therefore, 99.997% of the current was consumed by the expected H_2O electrolysis. The electrochemical reaction of nitrates would, therefore, change the thermoneutral potential (E_H) by only $4.4 \times 10^{-5} \text{ V}$. At the highest current used (150 mA), this nitrate reaction would give a calorimetric error of $(4.4 \times 10^{-5} \text{ V})(0.150 \text{ A}) = 6.6 \times 10^{-6} \text{ W}$ or less than 0.007 mW. Therefore, based on this study of 0.154 M KNO_3/Pt , the use of KNO_3 as an inert electrolyte in calorimetric studies would be justified. In a related experiment using 0.158 M $\text{KNO}_3 + 0.0577 \text{ M NaNO}_2$, 99.992% of the current (90,720 coulombs) was consumed by H_2O electrolysis. There are no shuttle reactions involving nitrates or nitrites that would give a false excess power effect. In both experiments, the volume of H_2O consumed was larger than the theoretical amount based on Faraday's Law.

This new calorimeter was also used to study the 0.15 M $\text{NH}_4\text{Cl} + 0.15 \text{ M NH}_4\text{OH} + 0.025 \text{ M PdCl}_2$ co-deposition system in H_2O . Complete results are given elsewhere [14]. In this case, a chemical excess power effect was detected early in the experiment due to the solution becoming acidic ($\text{pH} = 1.25$) resulting in chlorine evolution and the formation of nitrogen trichloride (NCl_3). Similar excess power effects were measured by NRL for this same system using a Seebeck calorimeter [15]. With further electrolysis, the solution becomes more basic, chlorine evolution ceases, the NCl_3 dissipates, and normal calorimetric results are observed [14].

In a new study, $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH} + \text{PdCl}_2$ co-deposition was repeated, but following the palladium co-deposition onto a copper cathode, sufficient LiOH was added to maintain a basic pH. This provided a very stable electrolysis system with no chlorine or NCl_3 formation. The electrolysis of this system using a high current of 400 mA gave evidence for a stable cell constant that was independent of the electrolyte level. The results for this study in Cell B is given in Table 2. The mean cell constant over almost five hours of electrolysis was $\langle k_C \rangle = 0.1324 \pm 0.000069 \text{ W/K}$. The cell constant never varied by more than $\pm 0.0001 \text{ W/K}$ from the mean value. This is the best evidence to date for an isoperibolic calorimetric cell where the electrolyte level does not affect the cell constant. We were, therefore, successful in attaining our major goal for this new isoperibolic calorimeter.

Table 2. Calorimetric data summary for Cell B with I = 400 mA using the PdCl₂ + NH₄Cl + NH₄OH + LiOH electrolyte.

Time	-E _{cell} (V)	P _{El} (W)	ΔT ₂ (K)	k ₂ (W/K)
2:29	5.122	1.4564	11.000	0.1324
2:44	5.121	1.4560	10.995	0.1324
4:01	5.110	1.4516	10.970	0.1323
4:53	5.103	1.4488	10.935	0.1325
5:51	5.094	1.4452	10.915	0.1324
6:46	5.088	1.4428	10.900	0.1324
7:19	5.083	1.4408	10.890	0.1323

$$\langle k_2 \rangle = 0.1324 \pm 0.000069 (\pm 0.052\%)$$

5. Summary of results

New isoperibolic calorimeters that are relatively inexpensive have been designed, constructed, and tested using several different electrolyte systems. These calorimeters show stable heat transfer coefficients that do not change during electrolysis at high cell currents over long time periods.

Acknowledgements

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Characteristics of Excess Heat in Pd|D₂O+D₂SO₄ Electrolytic Cells Measured by Seebeck Envelope Calorimetry

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Abstract. Pre-electrolysis at the boiling point in open Pd|D₂O cells is an effective method to activate a palladium cathode, which can produce excess power in subsequent electrolysis in closed systems for several months. The reproducibility is 23/45. Another characteristic of excess heat is the apparent resistance of electrolytic cell changes irreversibly with temperature.

1. Introduction

In previous works [1–3], anomalous excess thermal power in Pd|D₂O cells was observed using Seebeck Envelope Calorimetry (SEC). Two phenomena were found for reproducibility of excess heat. One is that the temperature increment during electrolysis must be high enough; otherwise no excess heat will be produced [2]. Another is that the second run always gives more excess heat than in the first under the same condition as shown in Table V in Ref. [2]. After reviewing the data of past experiments, it is found that the samples Pd-A and Pd-E in Ref. [2], which gave the maximum excess power (~ 1 W, about one order greater than others), have the same histories. Both of them had been electrolyzed at the boiling point in open cells due to mistakes (Exp. #041110 for Pd-A and Exp. #050829 for Pd-E). After that, these two samples become active in excess heat production in electrolysis. All these phenomena inspire the author to intentionally use pre-electrolysis at the boiling point in open cells to activate samples. Experimental results show that this procedure is effective to some extent as reported below. At the same time, it is found that the apparent cell resistance changes irreversibly with temperature when excess heat occurs.

2. Experimental set-up

Electrolytic cells used in most experiments described in this paper are modified versions of pervious experiments [3]. Copper tube leads were replaced with platinum wires to avoid contamination, and H₂SO₄ is replaced with D₂SO₄ for a similar reason. A schematic and a photo of the electrolytic cell are shown in Figs. 1(a) and 2(a), respectively. The cell is a cylinder of borosilicate glass ($\phi_{in} 42 \times \phi_{out} 45 \times 142$ mm³, capacity ~ 190 ml). A PTFE male cap has three parts: the top part is $\phi 41 \times 4$ mm² for fixing the cell by a metal frame as shown in Figs. 1(b) and 2(b); the middle part is a hexagonal prism with side length 32 mm and thickness 13 mm; the bottom part is $\phi 41 \times 24$ mm² with a groove of 4 mm width and 2.5 mm depth in the middle for O-ring. The O-ring ($\phi_{in} = 31.5$ mm, width = 3.55 mm) made of nitrile butadiene rubber (NBR, resistant to acid) is used to seal the cap against the inner wall of glass cylinder. The cap has two holes, 1 mm diameter each and 20 mm apart, for the electrode lead wires. A PTFE plate ($\phi 41 \times 8$ mm²) is used to suspend the recombination catalyst. It has 57 holes of $\phi 2$ mm to pass gases (D₂ and O₂) and vapors (D₂O). A PTFE rod ($\phi 6 \times 40$ mm²) is fastened to the perforated plate and the cap. This ensures that the perforated plate being at a fixed distance above the electrolyte. Before and after every electrolysis, the cell was weighed with a Mettler balance (PM1200, 0.001 g readability) since June 06, 2009 (Exp#090605). Before that time, cells were weighed only with chemical balances.

The metal frame is used to clamp the PTFE cap into the cell as shown in Figs. 1(b) and 2(b). These arrangements ensure that the electrolytic cell is a closed system. The metal frame and cell is partly embedded in a Styrofoam base ($\phi 15 \times 12$ cm²), which is placed in an enamel jar ($\phi 15 \times 16$ cm²). The enamel jar can weaken the impact of cell explosions in the calorimeter and prevent corrosion caused by

3. Experimental results

3.1. Calibration of calorimeter and contrast experiments

The calibration was conducted with a 3.6 Ω electric heater, starting on May 19, 2009 (Exp. #090519). The heater is made of Tophet® alloy A wire (ϕ 0.3 mm) wound around cylindrical heat sink fins, which are located at the center of the measuring vessel of the calorimeter. The calorimeter was calibrated from 2 to 50 W (55 sets of data) 16 times in 13 months. It gives good stability and linearity between thermal powers and responses, as shown in Fig. 3(a) and the simulation equation (1) below:

$$P = -0.0355 \pm 0.0161 + (5.8961 \pm 0.0118)E - (0.0020 \pm 0.0016)E^2 \quad (1)$$

with $\chi^2 = 0.1661$, $R^2 = 0.9997$, mean square = 0.0031. P is the input power in Watts and E is the output electromotive force of the SEC in Volts. This equation gives less accuracy than in Ref. [3] because the period is more than one year. Fluctuations of room temperature at different seasons affect the long term precision; however this calorimeter is calibrated every 2 to 3 weeks during experiments and it is enough accurate to give the real signal of excess power within the error of 20 mW for every calorimetry.

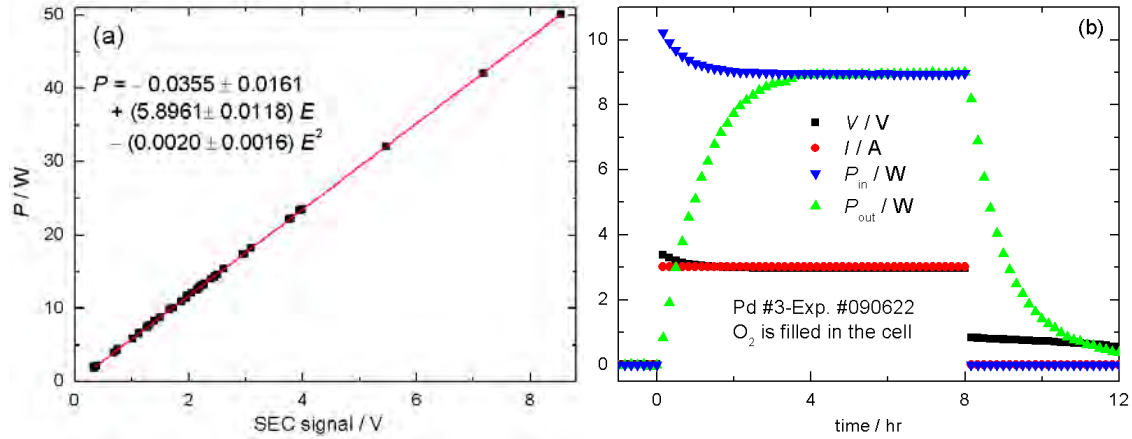


Fig. 3. - (a) Calibration of the calorimeter from 2 to 50 W, 55 sets of data, in 13 months; (b) Comparison of input electrolytic power with output thermal power of a Pd-D₂O cell. The fan's power is deducted from the total power.

Before presentation of anomalous excess heat, sample experiments are introduced to demonstrate the accuracy of the calorimetry and the reality of excess heat afterwards. Three types of experiments, i.e. Pt-D₂O, Pd-H₂O and dead Pd-D₂O electrolytic systems, were carried out. Each of them has only one component, i.e. cathode or electrolyte, being replaced with that in the active cell. All of Pt-D₂O (Pt cathode is a foil of 22 × 28 × 0.02 mm³) and Pd-H₂O systems were designed for contrast and did not give excess heat as shown in table 2. The inactive Pd cathodes also did not give excess heat especially for Pd #3 and #4.

Table 2. Parameters of different sample experiments carried out at 25 °C, 3 A.

Pd#-Exp#	system	t / hr	P_{in} / W^*	P_{ex} / mW	Q_{in} / kJ^*	Q_{ex} / kJ	$\Delta m / g$	$Q_{ex} + \Delta H / kJ$
Pt-090824	Pt-D ₂ O	7	10.819(7)	1±24	278.20(6)	-0.29±1.25	0.084	0.95±1.26
1-091002	Pd-H ₂ O	9	8.824(4)	6±29	287.98(6)	-0.51±1.16	0.038	0.06±1.17
3-090622	Pd-D ₂ O	8	8.956(3)	0.4±26	262.38(5)	-0.55±0.90	0.022	-0.22±0.90

* The number in one set parentheses is the uncertainty of the last figure of the quantity before the parentheses.

Fig. 3(b) shows an example of calorimetric results for dead-Pd-D₂O electrolysis. The input and output powers are $P_{in} = 8.9556 \pm 0.0029$ and $P_{out} = 8.9552 \pm 0.0264$ W, respectively, during the steady state (5 to 8 hours of electrolysis time). They are consistent with each other within 0.004% although the calorimetric error is 0.29%. The input, output and excess energies are $Q_{in} = 262.38 \pm 0.05$, $Q_{out} = 261.83 \pm 0.88$ and $Q_{ex} = -0.55 \pm 0.90$ kJ, respectively. The mass loss of the cell in this run is $\Delta m = 0.022$ g. If this loss was caused by poor catalytic recombination, the corresponding energy correction (enthalpy change) is $\Delta H = 0.33 \pm 0.03$ kJ. The output energy after correction is $Q_{out} + \Delta H = 262.16 \pm 0.90$ kJ; the resulting excess energy is $Q_{ex} + \Delta H = -0.22 \pm 0.90$ kJ, corresponding to $(-0.08 \pm 0.34)\%$ of the input energy. It means

there was no excess heat produced in the electrolytic cell and this calorimeter gave good accuracy (better than 0.1%) at power around 9 W running for 8 hours. Because this calorimeter is designed for power measurement, it gives higher precision for power than for energy, as shown in table 2.

3.2. Excess heat

As mentioned in the Introduction, effects of pre-electrolysis on excess heat are the main objective of this work. Seven runs with pre-electrolysis were carried out for 4 samples as shown in table 3. An example is shown in Fig. 4; this experiment was conducted at the end of 2008 using the cell described in Ref. [3]. Pd #1 was activated by pre-electrolysis on Dec. 20, 2008. The applied current was increased step by step: firstly 3.5 A for 2 hr, then 3.7 A for 1.5 hr and 3.9 A for 1 hr, 4 A for 0.5 hr at the end, as shown in Fig. 4(a). During the pre-electrolysis, the cell temperature was increasing and the electrolyte was boiling. The electrolyte level was lowering and the cathode surface was becoming exposed to the air. On the second day (Exp. #081221), more heavy water was added, and the cell was closed and electrolyzed. However, the excess heat was uncertain because of a poor seal and a great mass loss of 17.3 g. Two days later (Exp. #081223), the system was tested again and excess power was produced, as shown in Fig. 4(b). After electrolysis for 3 hr at 3 A, the calorimeter showed excess heat and its amplitude reached the maximum value of $P_{ex,max} = 220 \pm 16$ mW in 4.5 to 5 hr. After 5 hr electrolysis, P_{ex} keep the steady value of 120 ± 18 mW till the end of this experiment. In this experiment, there was no mass loss, within the error of measurement.

Another example for sample Pd #2 is shown in Fig. 5. The current applied during pre-electrolysis was: firstly 3.5 A for 3 hr, then 3.7 A for 1 hr, 3.9 A for 1.3 hr, 4 A for 2.7 hr at the end, as illustrated in Fig. 5(a). Four days later, calorimetry with a closed cell was carried out. This sample gave excess power of $P_{ex} = 0.120 \pm 0.020$ W during 5 to 6 hr of electrolysis, as shown in Fig. 5(b).

Table 3. Summary of pre-electrolysis and subsequent excess heats.

Pd #	pre-electrolysis			excess heats			total reproducibility
	Exp. #	I_{max} / A	T_{max} / °C	Exp. #	$P_{ex,max}$ / mW	reproducibility	
1	081220	4	110	081223	220 ± 16	8/15	17/35
	090808	4.5	97	090810	146 ± 24	4/4	
	090814	3	98	090828	66 ± 24	3/8	
	090915	4.5	108	090916	17 ± 22	0/1	
	090917	4.5	145	090919	31 ± 22	0/2	
	090921	4.5	127	090922	20 ± 15	0/1	
	090923	4.2	114	090927	152 ± 24	2/5	
2	090521	4	99	090525	120 ± 20	6/10	6/10
3	090620	3	97	090621	5 ± 24	0/3	0/3
4	090629	3	99	090721	3 ± 13	0/3	0/3

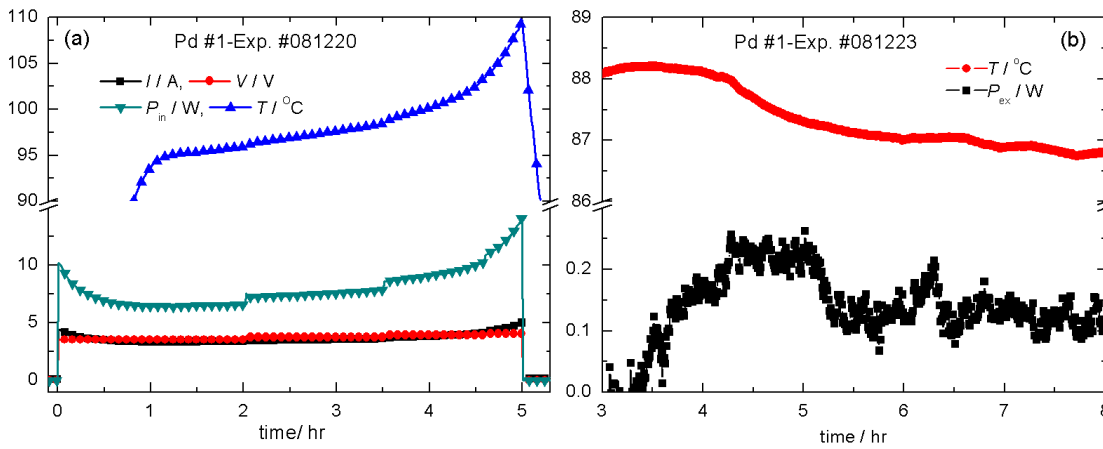


Fig. 4. - Example of effects of pre-electrolysis in an open cell in the first run on the excess heat production on the subsequent run in a closed cell. (a) Pre-electrolysis; (b) Excess power after activation. Parameters: $T_{SEC} = 25$ °C, 3 A $\times$ 8 hr, $P_{ex,max} = 220 \pm 16$ mW (4.5 to 5 hr); $P_{ex,stable} = 120 \pm 18$ mW (7 to 8 hr), $Q_{ex} = 2.46 \pm 0.33$ kJ. The mass loss during electrolysis $\Delta m = 0.0 \pm 0.2$ g.

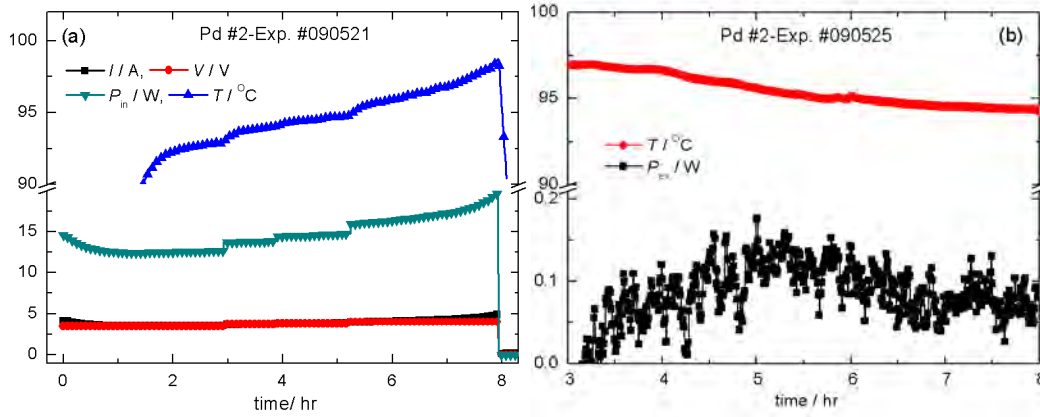


Fig. 5. - Another example of effects of pre-electrolysis in an open cell in the first run on the excess heat production in a closed cell in the subsequent run. (a) Pre-electrolysis; (b) Excess power after activation. Parameters: $T_{\text{SEC}} = 25^\circ\text{C}$, $3\text{ A} \times 8\text{ hr}$, $P_{\text{ex}} = 120 \pm 20\text{ mW}$ (5 to 6 hr). The mass loss $\Delta m = 0.05 \pm 0.02\text{ g}$ is not included in calculation of excess power.

Not every pre-electrolysis for every sample can stimulate excess power in subsequent experiments, as shown in table 3. For sample Pd #1, the effective ratio of pre-electrolysis is 4/7. For the other 3 samples, only one pre-electrolysis was tested and only one sample gave excess power; therefore, further research is necessary to determine other unknown factors which affect reproducibility.

Besides pre-electrolysis, other methods were used in attempts to stimulate increased excess heat production. These include reverse current activation in pre-electrolysis (Exp. #090814, 090915, 090921 for Pd #1), modifying cell temperature through changing the thickness of Styrofoam layers shown in Fig. 1(b) (85 to 102°C , Exp. #090725 to #090731), stepwise increasing (ladder-like) current (Exp. #090825) were also tested to stimulate excess heat production as done before [1–3]; however, all these methods did not show clear evidence of positive effects. More work is needed.

From the history of Pd #1 shown in table 3, it seems excess heat from boiling-point electrolysis can be switched on or off like a light bulb. Another question is the lifetime of excess heat activity after pre-electrolysis. Pd #1 kept the activity for at least 7 months (Exp. #081220 to 090807). Sample Pd-A had kept the activity for at least 2 months (Exp. #041110 to #050111) and Pd-E kept the activity for at least 10 months (Exp. #050829 to #060706) in Ref. [2]. Therefore, pre-electrolysis should be an effective way to activate a Pd sample for several months.

3.2. Irreversible change of cell's resistance with temperature

During the emergence of excess heat, it was noticed that P_{ex} and cell temperature T approach to their maximum amplitudes and then decrease to the stable values as shown in Figs. 4(b) and 5(b). It means that

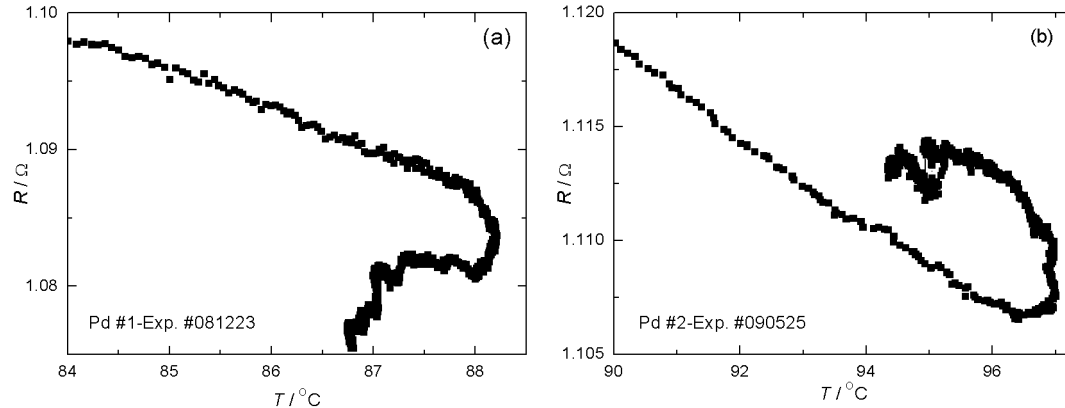


Fig. 6. - Apparent cell resistance R vs. temperature T for experiments in which excess power was produced.

increment of excess power is suppressed in electrolysis due to a changing cell parameter. This parameter is the apparent cell resistance R . R vs. T with excess heat is shown in Fig. 6 and without excess heat in Fig. 7. It is found that there is obvious irreversible change of R vs. T when excess heats occur. These results indicate this change can be a collateral evidence of excess heat besides the calorimetry. However, this irreversible change is not fully understandable and predictable at present; it may be negative or positive as shown in Fig. 6(a) and (b), respectively.

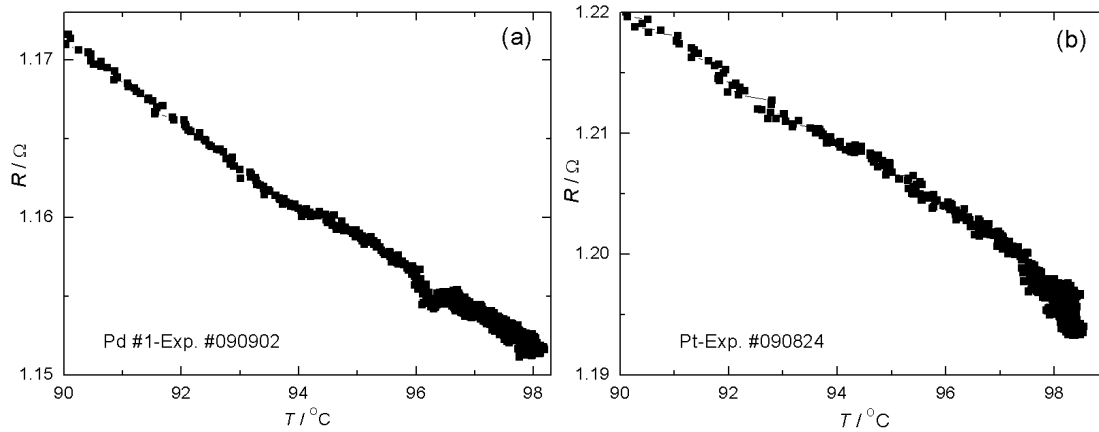


Fig. 7. - Apparent cell resistance R vs. temperature T without excess power.

4. Discussion

Pre-electrolysis activation of excess heat production reported here is similar to the heat-after-death effect observed by Fleischmann and Pons [6]; both situations work at the boiling point of the electrolyte. This phenomenon must be explainable by some mechanism which is activated by the high temperature. As concerns the irreversible change of cell resistance, it should be the intrinsic nature of excess heat because the state of cathode polarization must change in excess heat production at the cathode hot spots observed by Mosier-Boss and Szpak [7], and positive feedback of voltage and temperature observed by Fleischmann et al [8]. The author will study all these interesting phenomena in future work.

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Investigations of co-deposition systems

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Abstract. Electrochemical studies of co-deposition show that the palladium deposited onto a copper substrate produces very high capacitance values (370 Farads/g) equal to those of supercapacitor materials. This large electrode capacitance causes a collapsing and tilting of the cyclic voltammograms that approaches Ohm's Law behavior. Results for the electrochemistry, chemistry, and calorimetry of the 0.025 M PdCl₂+0.15 M NH₄Cl+0.15 M NH₄OH system and its deuterium analog are reported.

1. Introduction: selection of co-deposition systems

The observation of Fleischmann-Pons effects (FPE) for co-deposition systems was first reported by Szpak and Mosier-Boss using the PdCl₂+LiCl/D₂O system [1, 2]. Improved reproducibility of the excess power effect was obtained with the PdCl₂+ND₄Cl+ND₄OD/D₂O system [3-5]. In fact, all three initial experiments using this ammonia-based system produced large excess power effects [3]. This system was selected because the H₂O analog is commonly used for commercial palladium plating [6]. However, the extended electrolysis at the higher currents required for FPE studies leads to a black dendritic hydride deposit, large pH changes, chlorine evolution, and other unknown processes in this ammonia-based co-deposition system.

2. Experimental methods used for investigations of co-deposition systems

Electrochemical studies included cyclic voltammetry (CVA), electrochemical impedance spectroscopy (EIS) and various galvanostatic methods. The solution pH was periodically measured using a pH meter (± 0.01 pH units). Commercial chlorine detectors were used to monitor the gases escaping from the cell. A new isoperibolic calorimeter was used to determine any excess power produced by the electrochemical cell [7].

3. High capacitance produced by co-deposited palladium

The 0.025M PdCl₂+0.15M NH₄Cl+0.15M NH₄OH/H₂O system was investigated at various stages of the co-deposition onto a copper cathode. Figure 1 shows the cyclic voltammogram after the initial co-deposition at -6.00 mA for two hours (43 coulombs). This trace shows the normal features of a palladium surface with PdO formation at 0.25V and PdO reduction at -0.48V along with probable palladium deposition at -0.90V. Hydrogen and oxygen evolution occurs at the negative and positive vertexes, respectively.

Further electrolysis at -6.00 mA for 28.45 hours, I= -20 mA for 22.70 hours, then I= -50 mA for 22.95 hours (6423 coulombs total) gradually gave the completely tilted and collapsed cyclic voltammogram presented in Figure 2. Furthermore, the pH changed from pH=8.87 for the initial solution to pH=1.25, and chlorine evolution was readily detected at this electrolysis stage.

The striking contrast between Figure 1 and 2 has been previously observed for supercapacitor materials [8]. As shown in the Appendix, the exact equation for cyclic voltammetric studies yields Ohm's Law, $I \approx E/R_s$, for extremely high electrode capacitances ($R_s C_d \gg t$). From the EIS measured cell resistance ($R_s=0.9945 \Omega$) and

the time for a single scan in Figure 2 ($t=38$ s), it is estimated that the electrode capacitance (C_d) must be at least 50 Farads (F) or about 370 F/g for the deposited palladium. Typically, electrode capacitances are about $50 \mu\text{F}/\text{cm}^2$, thus the deposited palladium has an effective surface area of 10^6 cm^2 . Chronopotentiometry was used to confirm the unusually large RC time constant for the palladium deposited onto the copper cathode [8]. Similar experiments were conducted on the $\text{PdCl}_2+\text{LiCl}/\text{H}_2\text{O}$ co-deposition system and similar high capacitance values were observed. The electrochemical literature today relating to supercapacitor materials does not generally realize how large RC time constants distort cyclic voltammograms as shown in Figure 2 and explained in the Appendix.

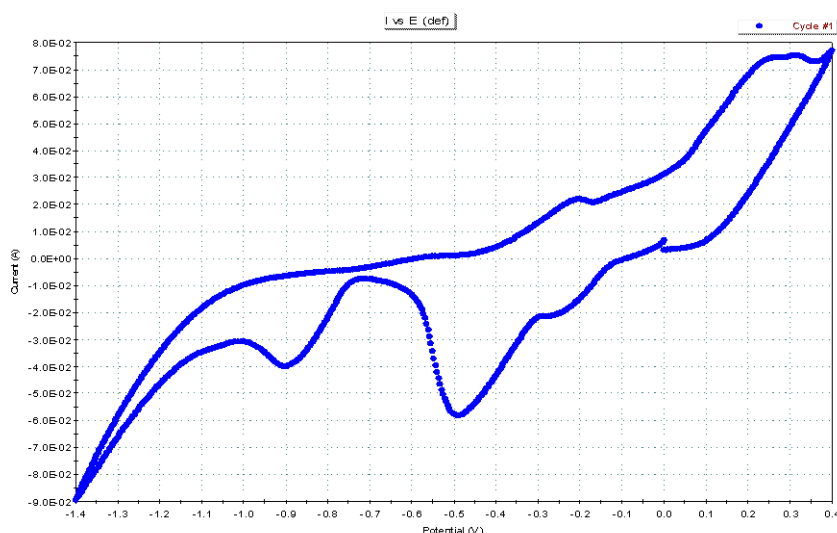


Fig. 1 - Early cyclic voltammetric study of co-deposition ($v = 50$ mV/s).

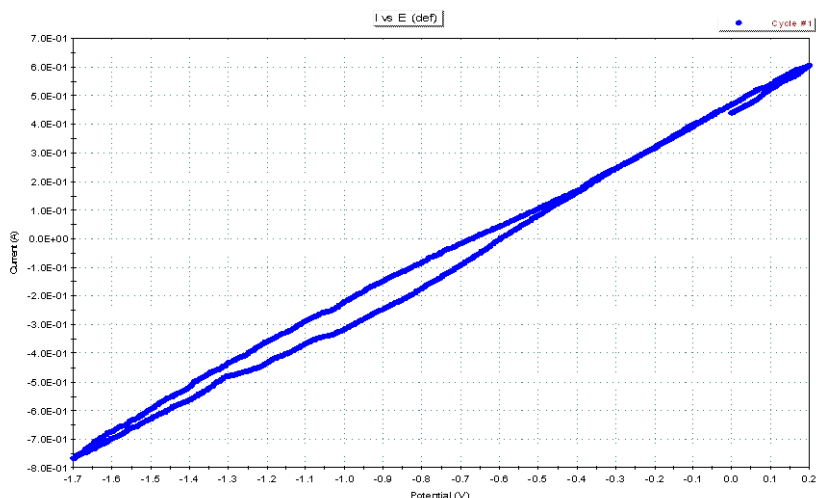


Fig. 2 - Later cyclic voltammetric study of co-deposition ($v = 50$ mV/s).

4. Complex chemistry of ammonia co-deposition system

Solution pH measurements were the key to unraveling the complex chemistry of the 0.025 M PdCl₂+0.15 M NH₄Cl+0.15 M NH₄OH co-deposition system. The electroneutrality expression for molar (M) ionic concentrations

$$[\text{NH}_4^+] + 2[\text{Pd}^{++}] + [\text{H}^+] = [\text{Cl}^-] + [\text{OH}^-] \quad (1)$$

along with the equilibrium $\text{NH}_4\text{OH} = \text{NH}_4^+ + \text{OH}^-$, $K_b = 1.81 \times 10^{-5}$ M, were also very useful. The reaction of palladium ions with NH₄OH produces insoluble palladium hydroxide



thus Pd⁺⁺ ions are initially replaced by additional ammonium ions (Eq. 1). The resulting low activity of palladium ions explains the stability of the copper cathode and other metals towards displacement reactions such as $\text{Cu} + \text{Pd}^{++} \rightarrow \text{Cu}^{++} + \text{Pd}$ in this initial solution. The cell reaction for the palladium deposition can be expressed as



with the solution remaining basic as observed experimentally. However, the generated electrolysis gases (H₂, O₂) gradually drive off the ammonia by the net reaction $\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+$ and the solution becomes acidic, $[\text{H}^+] = 0.050$ M, pH = 1.30 from Eq. 1. Acidic solutions make chlorine evolution thermodynamically more feasible, and a portion of the cell reaction becomes



instead of H₂O electrolysis. A readily observable decrease in the cell voltage magnitude clearly defines when the solution becomes acidic and chlorine evolution commences as also shown by chlorine detectors.

The introduction of chlorine into an acidic NH₄Cl solution is known to produce nitrogen trichloride, $\text{NH}_4\text{Cl} + 3 \text{Cl}_2 \rightarrow \text{NCl}_3 + 4 \text{HCl}$. The net electrochemical cell reaction for this NCl₃ production is



with hydrogen formed at the cathode. The enthalpy change for this reaction is 864 kJ/mol, thus the thermoneutral potential for Eq. 5 is nearly the same as for water electrolysis (1.49 V vs. 1.48 V). The consumption of acidic HCl by both Eqs. 4 and 5 produces an increase in the pH and an end to the Cl₂ and NCl₃ production. Therefore, only normal water electrolysis occurs after the first few days, and this is marked by a significant increase in the solution pH and an observable increase in the cell voltage as well as the end of any chlorine detection. In previous experiments, most of the excess power was observed after the third day when the chlorine evolution and NCl₃ production had ceased [3-5].

5. Calorimetric measurements of co-deposition systems

The PdCl₂ + NHCl + NH₄OH system was developed for palladium plating [6] and was not designed for the extended electrolysis at high currents required for the Fleischmann-Pons effect (FPE). However, this ammonia system can readily be converted to a very stable electrolysis system with no Cl₂ or NCl₃ formation if sufficient LiOH is added following the palladium co-deposition to maintain a basic pH. The required amount of LiOH or LiOD is given by $[\text{LiOH}] > [\text{NH}_4\text{Cl}] + 2[\text{PdCl}_2]$, or a LiOH concentration greater than 0.20 M in these experiments. Following the LiOH addition, all NH₃ is driven off by the electrolysis gases, and the solution consists of only LiCl + LiOH. Initial studies of the PdCl₂ + NH₄Cl + NH₄OH system with the LiOH

addition produced a very stable electrolysis process that was used in calibration of a new isoperibolic calorimeter [7].

Two calorimetric experiments have been completed using $\text{PdCl}_2 + \text{ND}_4\text{Cl} + \text{ND}_4\text{OD}/\text{D}_2\text{O}$ with LiOD addition following the completion of palladium deposition. Both experiments initially gave excess power effects of 70 to 100 mW at $I = -100$ mA. However, the excess power gradually diminished to near zero with further electrolysis. In both experiments, almost all of the deposited palladium somehow became detached from the cathode and settled to the cell bottom where it was electrochemically inactive. Further experiments are needed to determine if the LiOD addition destabilizes the palladium deposit.

Calorimetric studies of $\text{PdCl}_2 + \text{NH}_4\text{Cl} + \text{NH}_4\text{OH}/\text{H}_2\text{O}$ without the LiOH addition gave a chemical excess power effect reaching 50 mW during the acidic period of Cl_2 and NCl_3 formation. Nitrogen trichloride is a volatile, yellow oily liquid of high density (1.653 g/cm^3) and explosive in pure form. It could be observed experimentally as a small yellow pool at the cell bottom and as a yellow solution coloration during the Cl_2 evolution period. This NCl_3 substance is only slightly soluble in water, but this dissolved NCl_3 would readily react with the hydrogen generated by electrolysis to produce a chemical excess power effect by the reverse of Eq. 5. Because of the NCl_3 formation, it is recommended to keep the cell behind a safety shield with adequate ventilation and to wait until the chlorine evolution ceases and the yellow color clears before performing calorimetric measurements.

6. Investigations of chlorates, nitrates and nitrites

Chlorates, nitrates and nitrites are possible electrochemical products from the oxidation of chloride and ammonium ions. Therefore, effects of these substances on the electrochemistry and calorimetry were investigated. Cyclic voltammetric studies of 0.1505 M NaClO_3 using a platinum electrode showed only water electrolysis and no reversible reactions involving chlorates. The EIS studies showed that any chlorate reactions would be very slow with an exchange current density of $i_o = 10^{-6} \text{ A/cm}^2$. Constant current pulse methods proved that any electrochemical reactions of chlorates could not sustain currents above 0.5 mA/cm^2 in 0.1505 M NaClO_3 . A calorimetric study of the 0.1505 M NaClO_3 in H_2O gave no measureable excess power effects. Based on pH measurements, it is estimated that more than 99.999% of the total current (48474 coulombs) was consumed by H_2O electrolysis. The volume of H_2O consumed in this chlorate calorimetric experiment was larger than calculated from Faraday's Law (6.5 mL vs. 4.5 mL). These studies all rule out any measurable shuttle reactions involving chlorates. Related investigations involving KNO_3 and NaNO_2 showed that there were no shuttle reactions involving nitrates or nitrites that would give false excess power effects [7].

7. Evidence for a palladium volume effect

Based on the measured capacitance of the deposited palladium, the effective surface area increased by a factor of 10^6 during co-deposition. The presence of H^+ or D^+ within the deposited palladium likely contributes to these high capacitance values. Because the excess power observed in co-deposition experiments scales much more closely with the palladium volume, it appears that the FPE is a volume effect in co-deposition systems. A secondary double layer consisting of D^+ within the deposited palladium is likely a region rich in both electrons and deuterons and a prime location for near surface fusion reactions.

Acknowledgments

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8. Appendix

The exact equation for a voltage scan for an electrical circuit of a resistor, R_s , and a capacitor, C_d , is given by

$$I = \nu C_d + (E_i/R_s - \nu C_d) \exp(-t/R_s C_d) \quad (\text{A.1})$$

where I is the current (A), ν is the voltage scan rate (V/s), and E_i is the initial scan voltage at $t=0$ seconds [9]. Generally $R_s = 1 \Omega$ and $C_d = 50 \mu\text{F}$ (approximately) for electrochemical studies, thus the exponential term falls to zero within about 250 μs , and Eq. A.1 becomes $I = \nu C_d$. This simplified equation is generally used in cyclic voltammetric studies of supercapacitor materials [8]. However, $R_s C_d \gg t$ for high capacitance materials, thus $\exp(-t/R_s C_d) \approx 1 - t/R_s C_d$, and Eq. A.1 becomes

$$I \approx \nu C_d + (E_i/R_s - \nu C_d)(1 - t/R_s C_d) \quad (\text{A.2})$$

or

$$I \approx E_i/R_s - E_i t/R_s^2 C_d + \nu t/R_s \quad (\text{A.3})$$

Introducing $\nu t = E - E_i$ for a potential scan yields

$$I \approx E/R_s - (E_i/R_s)(t/R_s C_d) \quad (\text{A.4})$$

but $E > E_i$ and $R_s C_d \gg t$, hence $I \approx E/R_s$ which is Ohm's Law as observed experimentally in Figure 2.

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Anomalous Silver on the Cathode Surface after Aqueous Electrolysis

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Abstract. The presence of localized concentrations of anomalous elements (gold and silver) on the surfaces of palladium cathodes after electrolysis in either light water or heavy water electrolyte was first reported in 1994 [1]. Similarly, anomalous elements in surface pits were reported for titanium cathodes after electrolysis in heavy water electrolyte [2]. More recently, off-the-shelf battery fluid (Sp.G. 1.26) was substituted for analytical-grade H_2SO_4 (Sp.G. 1.84) in the electrolyte. Silver was found in localized concentrations on palladium cathodes after electrolysis. These results are consistent with a thermal neutron mechanism proposed previously [1].

1. Introduction

A demonstration of our excess heat experiment was performed in Salt Lake City (SLC) at an American Chemical Society conference on March 23, 2009, the 20th anniversary of the announcement by Fleischmann and Pons that they had achieved nuclear fusion in a bottle. The apparatus for this demonstration was shipped from our Portland State University (PSU) laboratory. The electrolyte, containing sulfuric acid, a hazardous chemical, was to be shipped separately, with required precautions. However, the electrolyte did not arrive in SLC in time for the demonstration. Rather than cancelling the demonstration, commercial battery fluid was substituted for our electrolyte.

2. Experimental methods and Results

The battery fluid contained dilute sulfuric acid (Sp.G. 1.265). This was further diluted with tap water. Therefore, the diluted electrolyte contained no heavy water. This was the electrolyte for the control cell (C cell). This cell contained a Pt foil anode, a Pd foil cathode, and hydrogen and sulfate ions in the electrolyte. The experimental cell (E cell) was identical except that it contained the same commercial battery fluid diluted with heavy water instead of tap water. This cell also contained a Pt foil anode and a Pd foil cathode, but the electrolyte contained both hydrogen ions and deuterium ions, in addition to sulfate ions. The cell components are given in Table 1.

The two cells were connected in series to a direct current power supply which supplied constant current to both cells at almost the same voltage. Thus, the power input was almost identical for the two cells (about 14 watts), but the power output was at least one watt higher for the C cell compared with the E cell. This result was totally unexpected. The experiment in SLC was repeated, and the result was the same, i.e. the C cell produced more than one watt greater thermal power than the E cell.

Our previous experiments used deionized water and pure sulfuric acid (Sp.G. 1.84) for the C cell electrolyte, and pure heavy water and the same sulfuric acid for the E cell electrolyte. A typical excess heat result was about 0.8 watt higher power output from the E cell. This was the result which we demonstrated at ICCF10 in Cambridge, MA in 2003.

After electrolysis for about two hours, the demonstration was stopped, the electrolyte was removed, and the apparatus was shipped back to PSU. The C cell cathode was removed from the cell and examined. Whereas it originally was a flat, silvery foil, it is now black and bent lengthwise to a curved surface which was concave to the anode during electrolysis. It was then examined with a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). Fig. 1 shows the pitted topography on the concave side of a Pd cathode after electrolysis for about two hours in light water electrolyte. A characteristic x-ray spectrum was taken by scanning the electron beam over the entire area of Fig. 1. The only elements detected in this spectrum were C, O, Al, Pd, and Pt. The origin of C is not known, O, Al, and Pt are thought to result from the $\text{Pt-Al}_2\text{O}_3$ recombination catalyst suspended above the electrolyte. Pt could also be produced by electroplating Pt dissolved from the anode.

Table 1. Cell components for experiment on 3-23-09 in SLC.

	E-cell	C-cell
	50ml D2O (99.9%, 151882-250g, Aldrich)	75ml H2O (tap water)
	50ml H2SO4 (Battery Fluid, S.G. 1.265, UN2796)	25ml H2SO4 (Battery Fluid, S.G. 1.265, UN2796)
Anode	Pt=1.2798g (25mm*24mm*0.1mmm)	Pt=1.3503g(25mm*24mm*0.1mm)
	Stock #11509 Lot # C25Q28	Stock #11509 Lot # C25Q28
Cathode	Pd=0.5355g cold rolled (29mm*8mm*0.2mm)	Pd=0.6167g cold rolled (29mm*8mm*0.2mm)
	Stock #11514 Lot # IO5S014	Stock #11514 Lot # IO5S014
Catalyst	20ml	20ml
	Alfa Aesar 0.5% Pt on alumina	Alfa Aesar 0.5% Pt on alumina

In Fig. 1 the gray areas contain mostly Pd, the white areas contain mostly electroplated Pt , and the black holes contain mostly Pd with statistically significant Ag. The ratio Ag/Pd averages 0.06 for 9 black holes. This Pd/Ag ratio for each of these nine black holes is given in Table 2.

The area shown in Fig. 1 was chosen for intensive study because it is highly pitted. One possible explanation for the pitting is that localized melting and vaporization occurred. Such events seem unlikely with only 14 watts input energy. Another possibility is that chemical dissolution occurred. If so, a more uniform topography would be expected instead of the pitted surface shown in Fig. 1. In previous research localized concentrations of anomalous elements were found on surface asperities [1] and in pits [2] The SEM electron beam, less than 1 μ m diameter, was focused on the asperity or pit. This resulted in the emission of characteristic x-rays from all of the elements present. The x-rays were detected and processed to produce a spectrum from each pit. Carbon, atomic number 6, and all elements of higher atomic numbers, could be detected and quantified by this method.

Table 2. Silver content at various locations in the black pits shown in Fig. 1. Statistically significant (>3 sigma) amounts of Ag were found in nine of 14 pits which were analyzed. The spectrum obtained by scanning the electron beam over the whole area of Fig. 1 (wa) did not contain Ag.

Atomic %-041409	Pd	Ag	Ag/Pd
Shu-SLC-C-Cell-Pd-CC-0.5k-wa		0.0	
Shu-SLC-C-Cell-Pd-CC-0.5k-s1	94.8	5.2	0.06
Shu-SLC-C-Cell-Pd-CC-0.5k-s2	95.3	4.7	0.05
Shu-SLC-C-Cell-Pd-CC-0.5k-s3	90.6	9.4	0.10
Shu-SLC-C-Cell-Pd-CC-0.5k-s4	92.7	7.3	0.08
Shu-SLC-C-Cell-Pd-CC-0.5k-s5	94.8	5.2	0.05
Shu-SLC-C-Cell-Pd-CC-0.5k-s7	95.8	4.2	0.04
Shu-SLC-C-Cell-Pd-CC-0.5k-s8	94.7	5.3	0.06
Shu-SLC-C-Cell-Pd-CC-0.5k-s10	95.4	4.6	0.05
Shu-SLC-C-Cell-Pd-CC-0.5k-s11	92.2	7.8	0.08

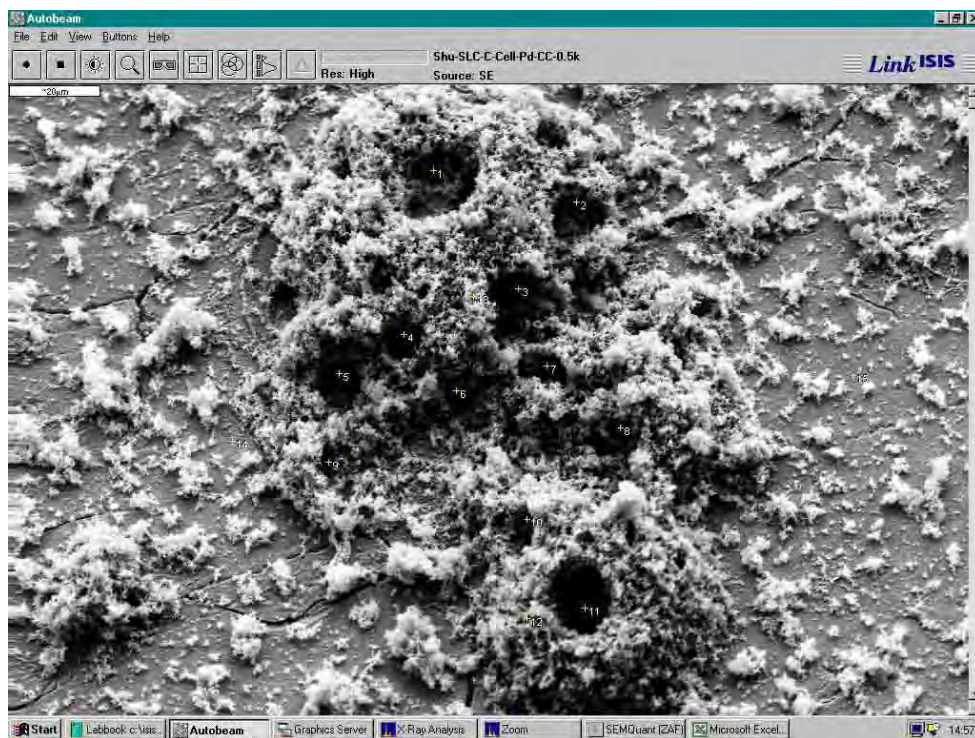


Fig. 1 - Micrograph of the concave side of the Pd cathode after about two hours electrolysis in light water electrolyte.

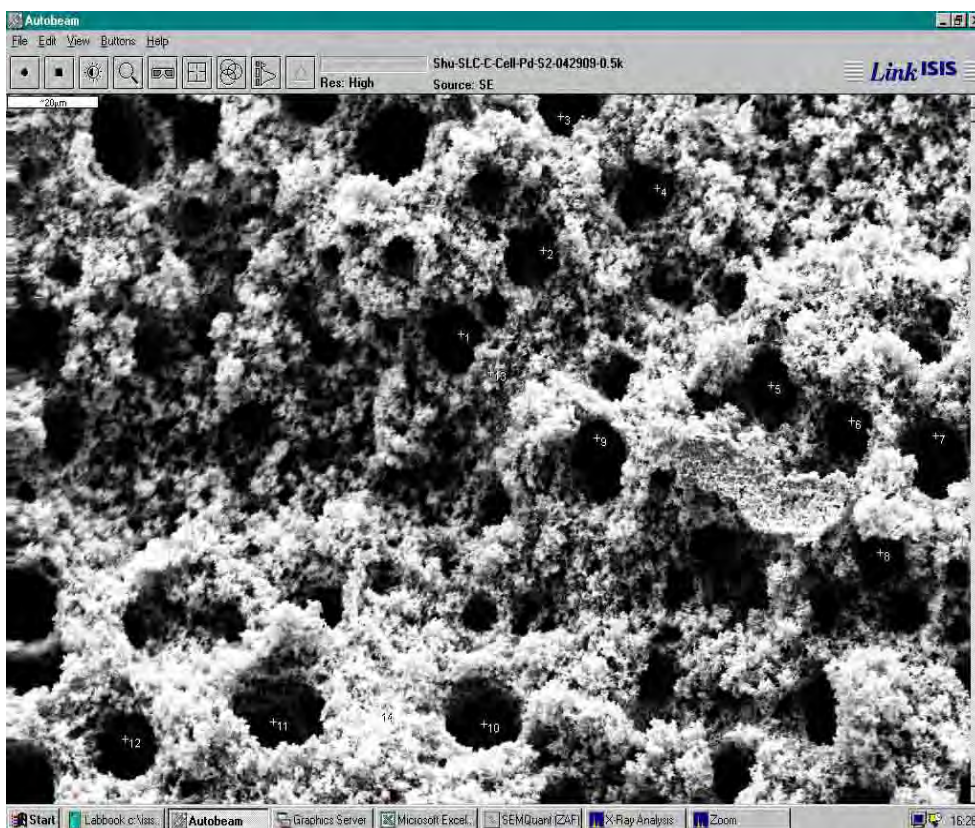


Fig. 2 - Topography of a hotspot on the convex side of a Pd cathode after electrolysis for about two hours in light water electrolyte, SLC 3-23-09. Twelve of 14 black holes contained statistically significant Ag (>3 sigma). The average ratio Ag/Pd was 0.09, and the range was 0.06 to 0.14.

3. Discussion

We now examine the possibility that the silver detected in the black holes originated from environmental contamination, such as impurities from the tap water. This seems unlikely because deposition occurs preferentially on asperities, not in pits. The black holes in figures 1 and 2 are rimmed with white particles which are almost pure platinum. We suggest that miniature explosions occurred, leaving behind pits containing Ag, which resulted from thermal neutrons absorbed by Pd. The unstable Pd isotopes then beta decayed to form Ag and heat sufficient to form a localized pit. Pt then electroplated from the electrolyte onto the rims, which were elevated above the original surface.

EDS measurements were also performed on the cathode from the E cell. Topography was similar to that found on the C cell cathode, and anomalous Ag was found in the pits. Our efforts were concentrated on the light water C cell cathode because it produced more heat than the heavy water E cell.

We are currently using secondary ion mass spectrometry (SIMS) before and after electrolysis to determine if there are changes in Pd isotopic abundance in our cathodes.

4. Conclusions

Excess heat was obtained from electrolysis with palladium cathodes in cells containing acidified H₂O electrolyte compared with cells containing palladium cathodes and acidified D₂O electrolyte.

Statistically significant, localized concentrations of silver were found in pits on the surfaces of palladium cathodes after electrolysis.

The results for the light water cells were obtained using commercial battery acid diluted with tap water, suggesting that highly purified chemicals are not necessary for LENR.

Acknowledgements

Our research began in April 1989. It was performed with the assistance of 36 high school apprentices and nine graduate students (seven M.S. theses and two doctoral dissertations).

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Calorimetry Of Pulse Electro-Melting of PdD_x Wires

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Abstract. Several groups have reported anomalous effects (heat and nuclear products) in thin PdD_x materials stimulated by different forms of electro-diffusion. We have designed and tested a calorimeter utilizes an “exploding wire” technique to examine the effect of a destructive electro-diffusion on a highly loaded PdD_x wire. We have shown that highly loaded PdD_x wires can be formed using high voltage electrolysis of very high purity D₂O with a very thin Pd wire cathode and a thin Pt wire anode. The addition a partial monolayer of a recombination poison yields a highly loaded PdD_x cathode. Following that step with the addition of a larger amount of that same poison seals the loaded wire and allows transfer to a cryogenic calorimeter. Our liquid nitrogen boil-off cryogenic calorimeter has been shown to have an accuracy of less than 0.4J.

1. Introduction

Several groups[1, 2] have reported anomalous effects (heat and nuclear products) in thin PdD_x materials stimulated by different forms of electro-diffusion. The ultimate extrapolation of this technology is the electrical heating of thin PdD_x wires resulting in destructive high-speed melting - “exploding wires”. Exploding wire technology has been used for over 150 years to make fine metal particles[3]. Celani *et al*[4-5] have reported loading thin Pd wires electrochemically up to high loading and sealing their surface electrochemically. Tripodi[6] reported that such sealed wires can be immersed in liquid nitrogen (LN) and analyzed for anomalous effects at those temperatures or soon after warming up. As such, electrically exploding such loaded wires while immersed in LN should release the deuterium and cause the evolution of gaseous N₂ equal to the electrical energy passed through the wire due to the heat capacity and enthalpy of vaporization of LN.

Since considerable attention has been directed toward demonstrating a correlation between the rates of excess heat and ³He and ⁴He production [7, 8], we will analyze the off gases for excess He and non-natural isotopic He ratios.

2. Experimental

Although some experiments have been performed, the primary effort during this year has been to design, build, and test the equipment necessary to load deuterium into palladium, seal the deuterium inside, measure the energy released during electrical stimulations, and measure He-4 products produced both in the electrolytic cell and during the stimulated energy release.

We have adapted the original H₂O high loading/sealed cathode technique to D₂O. This is not a trivial effort since the loading process requires ultra-clean materials and ultra-pure reagents. Unfortunately, most available D₂O is chemically impure when compared to 18 MΩ-cm de-ionized H₂O. We have been using high-purity D₂O (Sigma-Aldrich #P192341), which also provides the high isotopic purity necessary to yield high D loading. In order to maintain this isotopic purity all transfers are performed under dry N₂ or Ar.

5 x 10⁻⁵ M SrSO₄ in D₂O is prepared under dry conditions. Approximately 5 ml of Hg₂SO₄ saturated D₂O is similarly prepared and stirred overnight. After cleaning all components are rinsed with deionized H₂O, followed by pure ethanol before drying. ~ 5 cm length of 0.050 mm diameter Pd wire (Alfa # 40730) is

attached to 4 lengths of 0.25 mm Pt wire and attached to the cell shown diagrammatically in Fig. 1. This allows for *in situ* accurate 4-wire resistance measurements of the Pd cathode. This cell is closed with its silica quartz vessel and the Pd resistance measured.

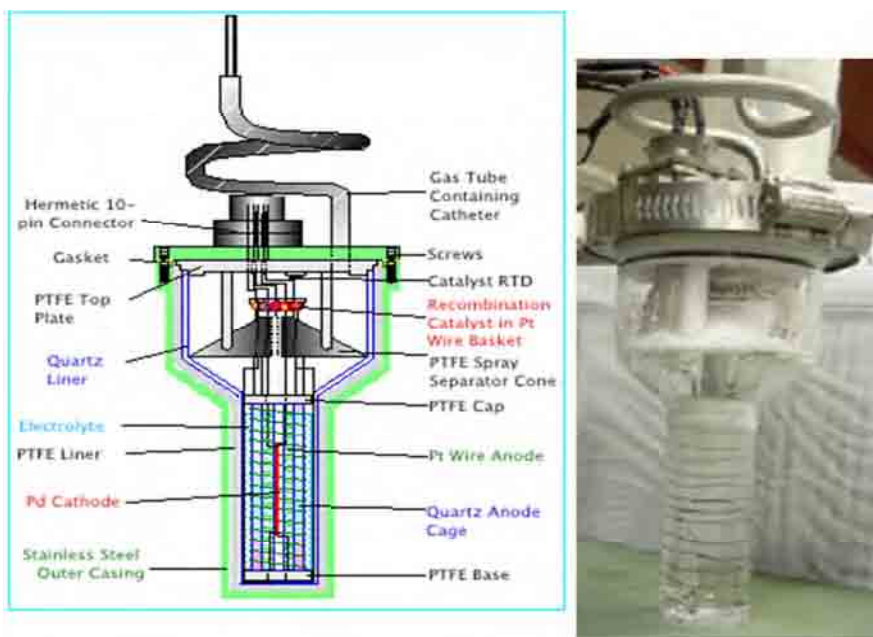


Fig. 1 - Degree of loading cell used to load and seal thin wires.

A current is passed along the length of the Pd to resistively heat the wire and anneal it in place. The current is raised slowly to $\sim 0.75\text{A}$ where the wire glows a bright orange color. Experience has shown this to be adequate to properly anneal the wire. The current is then lowered slowly to 0A at room temperature where the resistance is again measured. This procedure is repeated until the Pd resistance does not change upon annealing. This final resistance is considered R_0 .

After a stable resistance is obtained, the cell assembly is again rinsed with DI water and ethanol and dried. Then $\sim 20\text{ ml}$ of $5 \times 10^{-4}\text{ M}$ $\text{SrSO}_4/\text{D}_2\text{O}$ is added to the cell. After measuring a stable resistance with electrolyte present, $\sim 2.5\text{ mA}$ is applied across the cell. After a stable resistance value is obtained, the current is doubled to 5.0 mA . After the resistance has stopped coming down on the right side of the maximum (see the R/R_0 versus $H(D)$ loading curve in Fig.4), $\sim 1\text{ ml}$ of $\sim 5 \times 10^{-5}\text{ M}$ Hg_2SO_4 is added to the cell. R/R_0 is often reduced at this point possibly due to the partial recombination poisoning of the Pd surface. Hg_2SO_4 solution is added, one ml at a time, until the resistance stops coming down. The electrolytic current is then reduced in steps to see if the resistance stabilizes at a value below $R/R_0=1.6$. If not, more Hg_2SO_4 is added. When R/R_0 is unchanged and below 1.6, the electrolysis is stopped, the Pd cathode removed and moved to the calorimeter.

The wires are then immersed in liquid nitrogen in a cryogenic nitrogen boil-off calorimeter, shown in Fig. 2. The measured input energy from the pulse boils off a known amount of nitrogen, which is measured by a calibrated thermal mass flow meter (MFM). By using different length pulses into a current shunt immersed in the LN calorimeter we calibrated the volume of N_2 evolved at different input energies. In the case of PdD_x , the energy from the input pulse and any excess energy produced from the extremely fast electro-migration inside the PdD_x will boil off a known given volume of nitrogen. Fig. 2 also shows the cathode connection blocks to be immersed in the LN. The copper probes hold the sample via a set-screw in each probe. This probe is then immersed in the LN, sealed with a low temperature O-ring, and held tight with two clamps. All of the vaporized gas is measured using an electronic mass flowmeter. The calorimeter is calibrated using a 50 watt 1 ohm resistor. The voltage, current, and time are measured using a high-speed data acquisition system and transferred digitally to the computer. The analog output of the MFM is also measured by the high-speed data acquisition systems.



Fig. 2 - Photographs of the cryogenic calorimeter and its cathode connection blocks.

3. Results

The data collected and a photograph of the Pd wire during this annealing process are shown in Fig. 3. The blue line shows the voltage, the blue the current steps and the green line shows the R/R_0 measured

Low while the current is off. molarity Pd/SrO₄/D₂O electrolysis experiments have been performed using 50 μ m wires. These wires were then sealed electrolytically using Hg₂SO₄. A typical cell response to current steps and Hg₂SO₄ additions is shown in Fig. 4. R/R_0 goes through a maximum very quickly as you would expect for such a thin wire. Then small amounts of Hg₂SO₄ are added to enhance the loading and seal the wire. Finally the current is reduced in step with little or no loss of loading. These wires have been successfully transferred to a liquid nitrogen (LN) vessel without loss of loading. Calibration of the cryogenic calorimeter is shown in Fig. 5 as joules electrical input versus N₂ volume evolved. The red dot at ~ 0.4 J represents exploding wire results from a 50 μ m diameter pure Pd wire.

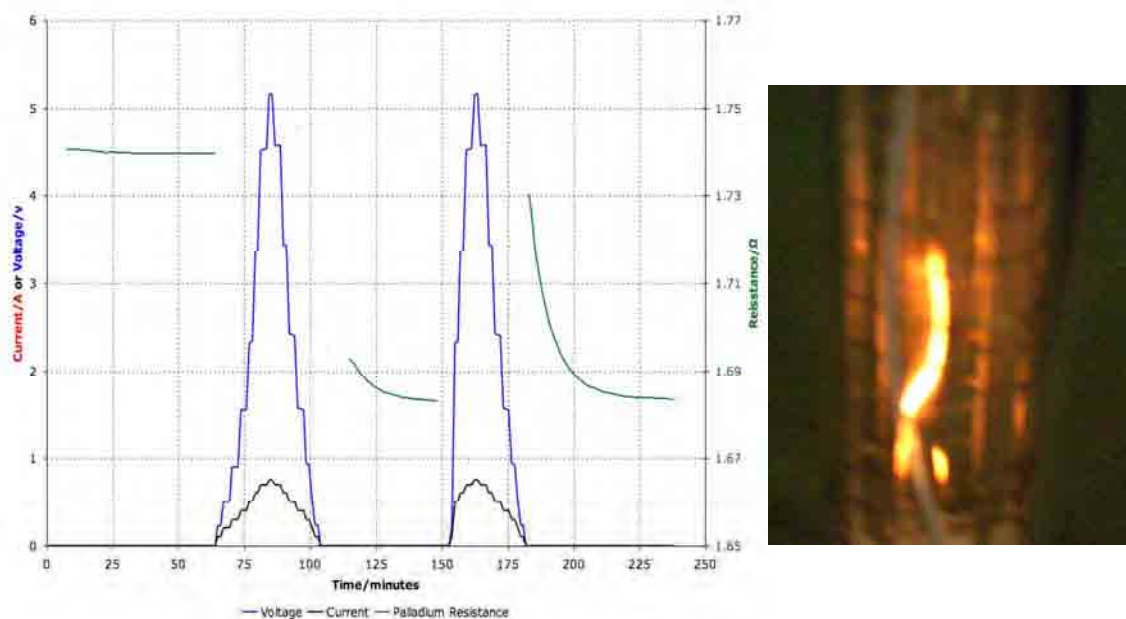


Fig. 3 - Plot of R/R_0 , current and voltage and photograph during Pd wire annealing.

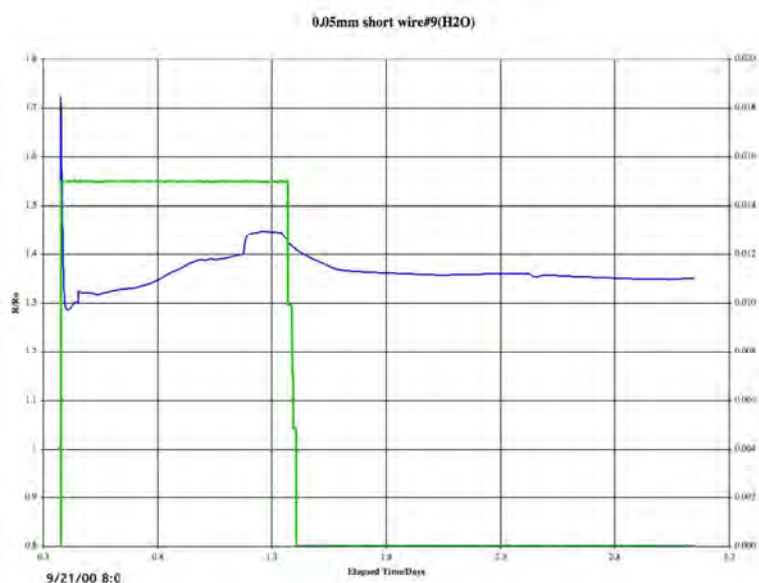


Fig. 4 - Plot of R/R_0 (blue) and Current (green) for H loading of Pd wire.

In addition to the input pulse the gas volume measured may be affected by the enthalpy of melting/volatilizing the wire as well as the gas evolution from the desorption of any hydrogen/deuterium. For these reasons, the results from PdD_x wires will be compared the energy released from pure Pd or Pt wires as well as the results from PdH_x .

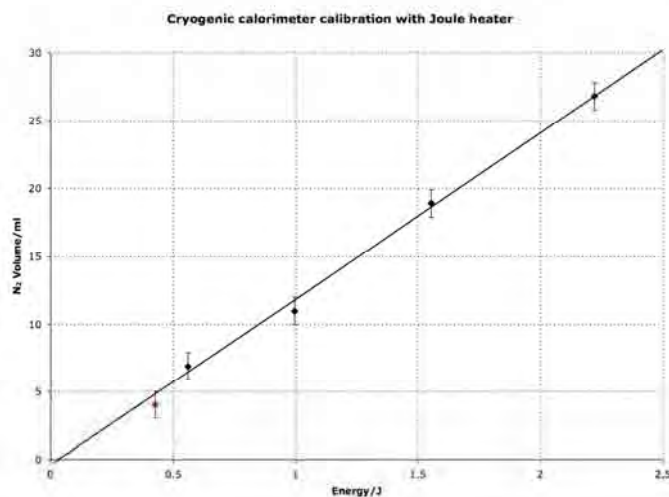


Fig. 5 - Calibration of cryogenic calorimeter and exploding pure Pd wire result (red dot)

4. Conclusions and Future Work

We have shown that we can load and seal 50 μm diameter PdH_x and PdD_x wires electrolytically. We have shown that we can transfer those wires to a cryogenic calorimeter without loss of loading. We have shown that we can measure as little as 400 mJ of input energy in the cryogenic calorimeter.

We have performed gas phase measurement of He isotopes from the headspace of various cells and are planning to perform this on most electrolysis cells' headspace gas and low-temperature stimulated wire effluent. We will also use a metal vaporization inlet to the He isotope mass spectrometer to analyze any Pd fragments for anomalous He isotopic ratio.

He insertion will be done by heating the Pd (or other wire) resistively in a tube to appropriate temperatures using sealed feed-throughs and selected pressures of He for a selected time. He insertion will be used to form defects in the Pd cathodes, which may facilitate anomalous effects.

Acknowledgements

We gratefully acknowledge the support of the Basic Research Program of Defense Threat Reduction Agency.

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Confirmation of Heat Generation during Hydrogenation of Oil

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Abstract The study was devoted to replicating and controlling that excess heat effect during hydrogenation of hydrocarbon. The reactant is phenanthrene, a heavy oil fraction, which is reacted with H₂ gas of high pressure and high temperature in the presence of a metal catalyst. This results in the production of excess heat and radiation. After the reaction, an analysis of residual gas reveals a variety of hydrocarbons, but it seems unlikely that these products can explain the excess heat. Most of them form endothermically, and furthermore heat production reached 60 W. Overall heat production exceeded any conceivable chemical reaction by two orders of magnitude.

1. Introduction

This study was stimulated by a liquefying reaction to change the heavy oil to light oil. Abnormal heat generation was observed during the hydrogenation experiments when heated in high-pressure hydrogen gas. The amount of heat generated was abnormally large considering the expected chemical reaction between a few drops of heavy oil and a little hydrogen gas. Based on their estimate, they concluded the heat generated had not come from a conventional chemical reaction.

2. Experimental

2.1 Cell

Figure 1 shows a schematic of the reaction cell and the experimental set up. The reaction chamber is cylindrical. It is constructed from Inconel 625. It has a 16-mm outer diameter, a 10-mm inner diameter, a 300-mm height, and has a 0.01-l capacity. It can sustain a pressure of 500 atm, and it can be heated to 850°C. The reactor has a plug for the hydrogen inlet and outlet, and housing for an internal temperature sensor. A platinum catalyst is placed inside the cell. The temperature inside the cell is measured with an R-type thermocouple, 1.6 mm in diameter, 30 cm long, which is enveloped in a 0.3 mm thick SS314 stainless steel shield and grounded to reduce noise. The thermocouple range is from -200 to 1,300°C. Moreover, another thermocouple of the same type is inserted between the outer reactor wall and the inner wall of the electric furnace, to measure the temperature of the outside wall of the reactor cylinder. Thermocouple data is collected by a data logger (Hewlett Packard HP3497A), with a temperature sensitivity of 0.1°C. The error ranges of the temperature measurement system is determined by the resistivity of the thermocouples (4 Ω), the insulation (100 M Ω), and the data logger (100 M Ω). In this case, the error works out to be 0.03% of the instrument reading. At a temperature of 800°C the error is 0.03°C.

2.2 Measurement system

As shown in Fig. 1, the cell is placed in the electric furnace, and hydrogen gas is introduced into the cell through a 6 mm diameters stainless steel pipe. The pipe is fitted with high pressure Swagelok valves which are used to introduce gas into the cell, or to evacuate it. Hydrogen is stored in a tank at 135 atm. It passes through a piezoelectric pressure transducer (Kyowa P-100KA) and amplifier (Shinko Tsushin 603F) and the flow rate is recorded in the data logger. Gas purity is more than 99.999%. The gas line is connected to the vacuum pump and mass spectrometer (ULVAC REGA201) that detects mass numbers up to 400.

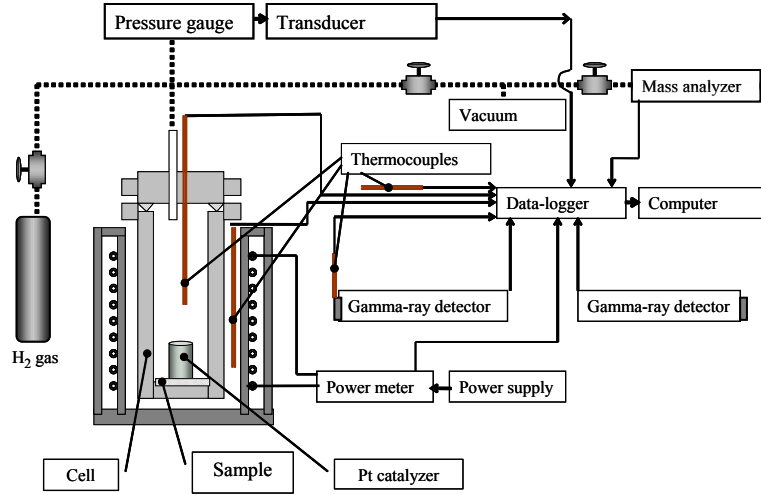


Fig. 1 - Cell and experiment configuration.

The electric furnace is custom made (Tokyo Technical Lab. PH, Mo13763A1). It is 200 mm outside diameter, 65 mm inside diameter and 200 mm high. A direct current regulated power supply is used (Takasago Electric EX-1500H), that produces up to 240 V at 6 A (1.5 kW). The heater power is monitored with high precision meter (Yokogawa PZ4000), which measures amperage and voltage every millisecond, sending averaged data to the data logger at 5-second intervals. The combined error for amperage and voltage is 0.0015%.

Radiation emissions are detected by a γ -ray detector (Aloka ICS-311) that is located 15 cm from the reactor. Its output is recorded continuously by the computer through a digital multimeter (Advantest TR-6845). The ionization chamber has a 14 cm long electrode, a correction plate 1 cm long, a window 0.5 cm thick, and it is pressurized with air at 1 atm. This detector can detect x-rays, γ -rays and β -rays. It can detect x-rays and γ -rays in the range of 30 keV $\sim$ 2 MeV with an efficiency of 0.85 $\sim$ 1.15 calibrated with ^{137}Cs .

This output is sent to the data logger and recorded in the computer. The detection of radiation emission employed a gamma-ray detector, which was calibrated by a 3.7×10^5 Bq ^{226}Ra check source that was positioned at various distances from the gamma-ray detector. Before the experiment, the check source was placed inside the reactor cylinder to obtain a gamma-ray reading. The background radiation level surrounding the system was 0.05 ± 0.008 $\mu\text{Sv/h}$.

The radiation data was further processed with OriginPro software (OriginLab) to analyze multiple peaks. A Gaussian distribution analysis was performed to fit of multiple peaks, with the following equation:

$$y = y_0 + A(w(\pi/2)^{-1/2})\exp(-2(x-x_0)^2/w^2)$$

where, y_0 = Baseline offset, A = Total area from baseline to curve, X_0 = Midpoint of peak, $W = 2\sigma$. Full width at half maximum ≈ 0.849

The midpoint X_0 is the average, where $w/2$ is the standard deviation. To reduce the difference between the fitted curve and original data, additional peaks were plotted, and the following peak analysis was performed. To analyze multiple peaks, a function with multiple dependent variables and independent variables was defined in the following equations:

$$y_1 = f(x_1, x_2, \dots, a, b, c, \dots)$$

$$y_2 = f(x_1, x_2, \dots, d, e, f, \dots)$$

$$\dots$$

$$y_n = f(x_1, x_2, \dots, o, p, q, \dots)$$

Here, x_1, x_2 are independent variable and $a, b, c, \dots, o, p, q$ are coefficient for the variables.

The Gaussian peaks derived with these functions are closest to the original data.

2.3 Materials

Fluorescent grade (98.0% pure) phenanthrene ($C_{14}H_{10}$; MW 178.23) was used in this study. It was supplied by the Kanto Chemical Co. LTD. The Pt catalyst was a high purity (99.99%) Pt mesh (Tanaka Noble Metal Co. LTD.) The catalyst is rectangular and is 5-cm high, is 10-cm wide, and weighs 50 g. Before the experiment, the Pt catalyst was activated once in an atmosphere of hydrogen gas for 1 hour at 850°C.

2.4 Experimental procedures

One gram of phenanthrene and the Pt catalyst were put in the reactor; the reactor cell was then sealed with the lid, which was secured in place with bolts. The reactor was connected to the vacuum system and evacuated to 10^{-3} mmHg. The vacuum system exhaust valve was left open for several minutes to remove the residual air from the reactor. The exhaust valve was then closed, and the gas was supplied to the reactor at the set pressure. After gas filled the reactor, the gas supply valve was closed. The temperature of the gas in the reactor then was increased to the starting temperature. Calibration of temperature versus pressure was performed by changing the hydrogen gas pressure from a vacuum to 80 atm.

2.5 Temperature calibration

The amount of excess heat is determined by comparing input heater power to a stable temperature in the cell on a calibration curve.

3. Results

3.1 Excess heat generation

Figure 2 shows an example of anomalous excess heat. In this test, 1 g of phenanthrene was exposed to a 70 atm of hydrogen gas. Furnace heater power was set for 60 W. The furnace heater temperature rose faster than the cell temperature. As shown in the calibration curve when there is no anomalous heat, by 10 ks both temperatures stabilize at around 640°C. However, in this test they both soon begin to rise above the stabilization point. After 5 ks, large perturbations begin and the temperatures continue rising. Also, at this point the cell temperature exceeds the furnace heater temperature. This temperature reversal is proof that heat was being produced inside the cell. The cell temperature reaches 800°C, which is 200°C higher than the calibration curve predicts. Since input power is 60 W, we extrapolate that roughly 60 W of anomalous heat is being produced. Because of the extreme fluctuation in heat, total energy is more difficult to estimate than power, but because the excess power persisted for 10 ks it was at least 120 kJ in this test.

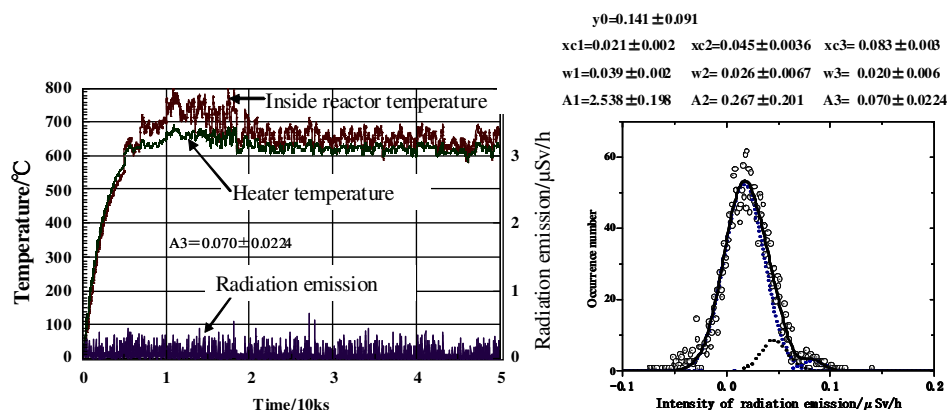


Fig. 2 - An example of anomalous heat. Fig. 3 - Intensity spectrum of radiation emission from Fig. 2.

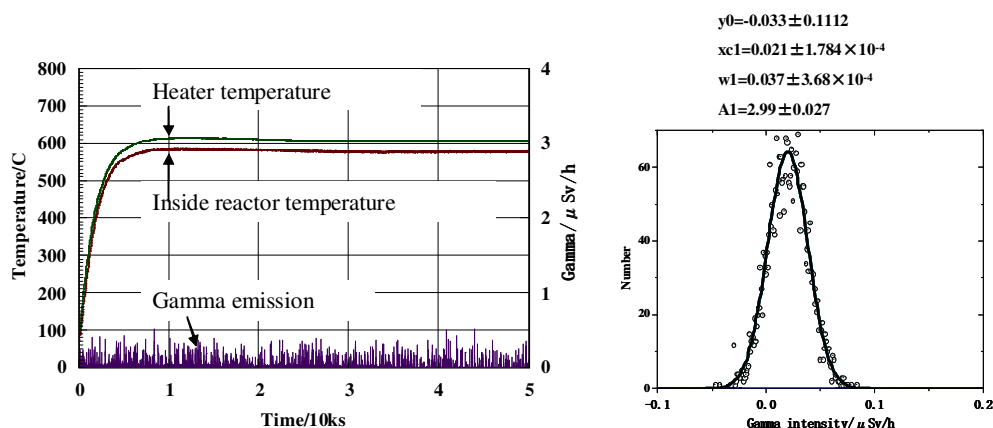


Fig. 4 - An example with no anomalous heat.

Fig. 5 - Intensity spectrum of radiation emission from Fig. 4.

Total heat production can be estimated from the calibration curve and total duration of excess heat production which started around 18 ks and continued to 50 ks. Over this period, the average temperature was 50°C above the calibration point continuing for 40 ks. Based on the calibration point of 600°C (in Fig 3) the excess was roughly 5 W on average, so total heat production was roughly 160 kJ for the entire run.

Figure 3 shows the intensity distribution of gamma-ray emission from the ionization chamber detector. Two peaks are shown, 0.05 μSv/h and 0.09 μSv/h of the background by calculated peak analysis. These are clearly differentiated from the background of 0.02 μSv/h. Gamma-ray emissions were weak but they were clearly observed when intense excess heat was generated.

Figure 4 shows an example of a test with no excess heat. As in the test shown in Fig. 2, 1 g of phenanthrene was exposed to a 70 atm of hydrogen gas, and furnace heater power was set for 60 W. However, the Pt catalyst was not placed in the cell. By 10 ks, the temperature stabilized at about 600°C. After that the temperature remained stable and settled.

Figure 5 shows the intensity distribution of gamma-ray emission for the test shown in Fig. 4. Only the background peak is observed. Calculated peak analysis reveals no other peaks.

4. Discussion

In these experiments, a 1 g sample of phenanthrene was used, which is 5.6×10^{-3} moles. Oxidation, reduction and other chemical reactions can produce at most a few kilojoules from this much material, whereas this reaction produced on the order of 100 kJ of heat. That is roughly 100 times larger than a chemical reaction. Therefore, a chemical reaction as the source of this heat is conclusively ruled out. Furthermore, during the experiment weak radioactivity was observed, probably γ or x-rays. If these are γ -rays that is proof this is a nuclear reaction; if they are x-rays then they were generated by some other mechanism. The detector used in this study can detect an energy range starting from 20 keV up to high levels. The cell wall is 3 mm thick stainless steel. The x-ray mass absorbent coefficient for 20 keV x-rays is 100 cm²/g, so most of the radiation would not penetrate the cell wall. However, if these are γ -rays at around 1 MeV, 80% of the radiation would pass through the cell wall. Therefore, although we cannot be certain it is very likely these are γ -rays

The excess heat and radiation were not strongly correlated, but they both indicate that some sort of nuclear reaction occurred. With additional research to understand the mechanism of the reaction, this reaction might possibly become a practical source of energy.

5. Conclusions

The anomalous energy generation cannot be the product of a conventional chemical reaction for the following reasons:

- At these temperatures, hydrogenation reactions are endothermic, not exothermic.
- Based on this massive reaction and the mass of the reactants, the total heat release far exceeded any known chemical reaction.
- There was no chemical fuel in the reactor cells.
- There were no chemical reaction products. Except the platinum screen that was coated with carbon, the components and chemical species in the cell, including phenanthrene and hydrogen gas, remained essentially as they were when the experiment began,
- Gamma-ray emissions were detected. These emissions are characteristic of a nuclear reaction. These emissions might have been x-rays but this is unlikely.

The reaction is reliably triggered by raising temperatures above the threshold temperature of $\sim 580^{\circ}\text{C}$ and hydrogen pressures above 60 atm. The reaction can be quenched by lowering the temperature inside the cell to below $\sim 500^{\circ}\text{C}$. When the required conditions are satisfied excess heat is generated with high reproducibility, but the rate of heat production is not stable. There is only a small amount of reactant in the cell, and it is likely that the accompanying ordinary chemical reactions that occur in the cell soon consume it all.

Acknowledgements

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Abnormal excess heat measured during Mizuno-type experiments: a possible artefact?

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« Anyone who has never made a mistake has never tried anything new » A. Einstein

Abstract. Recently performed Mizuno-type experiments confirmed generation of excess heat but not at the rate reported in ref. 2 (Sotchi -ICCF13). The main reason for the discrepancy is now clear; the bandwidth of our Unigor wattmeter, used in old experiments, was insufficient for correcting measurements of highly fluctuating electric energies.

1. Introduction

Using the boiling water calorimeter, described in reference 2, we measured excess heat generated during high voltage electrolysis. The experimental setup is shown in Figure 1. The input electric energy was measured with a D6000 Norma Goerz wattmeter, rather than with simple Unigor instrument. Note that the frequency bandwidth of the Goerz wattmeter is significantly wider than that of the Unigor wattmeter (see below). The new setup, containing the boiling water calorimeter, allowed us to eliminate two additional artifacts that could possibly be responsible for systematic errors:

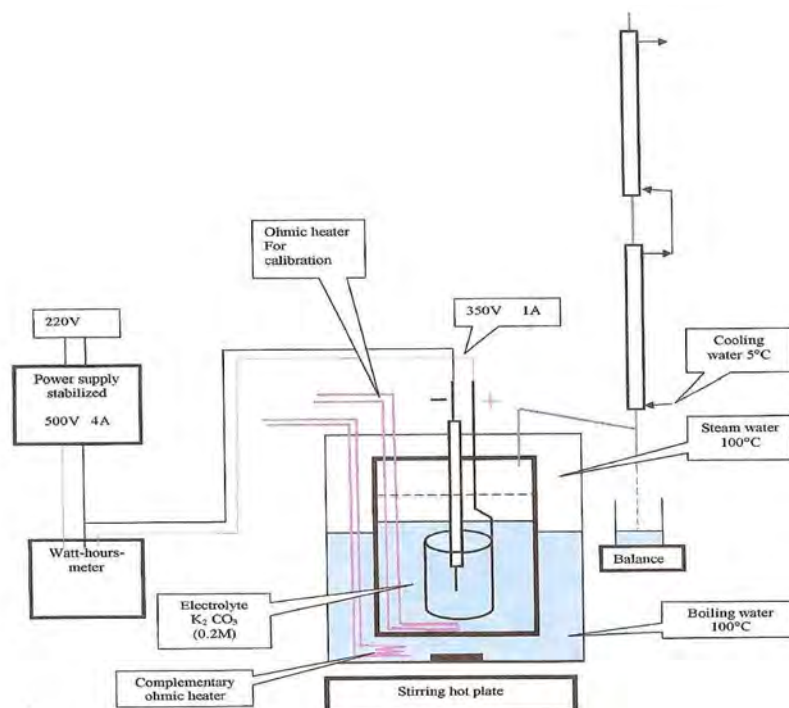


Fig. 1 - Experimental setup.

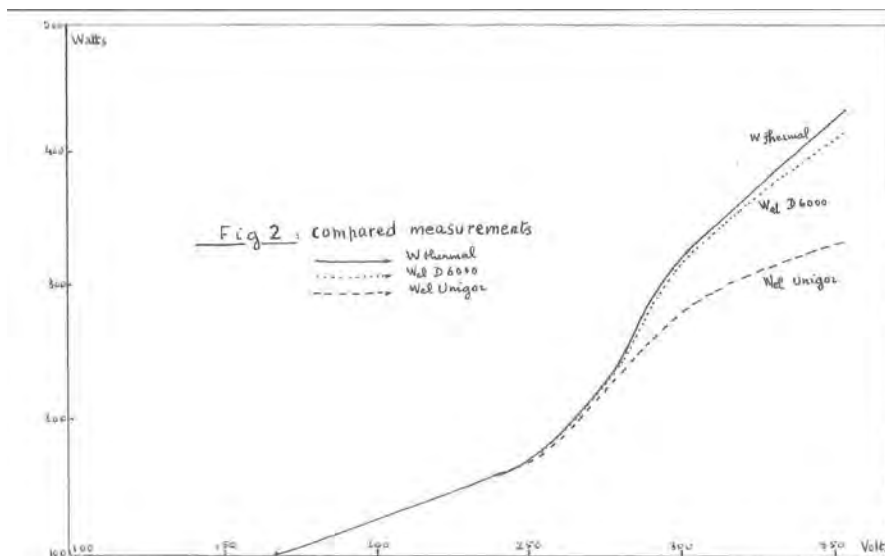


Fig. 2 – Comparison of power measurements

- storage and destorage (the internal reactor temperature remains always at 100°C and then do not allow any stored heat)
- electrolyte droplets losses (the condensed steam gives an easy chemical way to check up if electrolyte droplets are carried on)

Let us elaborate on the issue of electric power measurements. In the early experiments, they were performed by using the Unigor wattmeter. Its readings were shown to be reliable when the electrolytic cell was replaced by an ohmic resistor, that is when the current was constant. But the current in the electrolytic cell rapidly fluctuated between zero and approximately ten amperes. Wide fluctuations of the current, observed with the oscilloscope, were responsible for wide fluctuations of the voltage between the anode and the cathode. Unlike the Unigor 390M (bandwidth up to 0.1 MHz), the Goerz D6000 instrument (bandwidth up to 2 MHz) is designed to function properly at such fluctuations.

As seen in Fig. 2 (curves normalized at 200 volts), the measurements made with the D6000 wattmeter were very close to the thermal values. On the contrary, the Unigor values did not agree with the D6000 values, specially in the 280-300 volts region. This explains the discrepancy between our now results and results reported in (2). Oscilloscopic measurements of electric energy were essentially the same as those performed by using the D6000 wattmeter (even at 300 V, where arcing was very intense). The previously-reported excess heat was not observed in our new experiments.

2. Return to our Yokohama type experiments (ref. 1)

Therefore, we tried to understand why the abnormal excess heat seemed to have disappeared. We have then thought that the reactor in our boiling water calorimeter, was not large enough (only 1 liter) for the electrolysis to be made in and that violent moves of the electrolyte consequently disrupted the plasma around the cathode. Thus, we suspect that this phenomenon is responsible for the disappearance of the abnormal excess heat.

We decided to return to the experimental set-up presented in ref.1 (Yokohama - ICCF12), in which the volume of the beaker was 5 times larger for the electrolysis, but we replaced this 5 liters beaker by a Dewar flask of the same volume. See fig 3.



Fig. 3 - Experimental Yokohama (ICCF12) set up.

Essential parameters of experiments described in ref. 1 and ref. 2 were as follows:

- a Sartorius balance, measuring up to 6 kg at an accuracy of 0.1 g
- a continuous current electricity supply (500 volts, 4 amperes)
- a tungsten cathode of 2.4 mm
- a wire in platinized titanium for anode
- an electrolyte made with K_2CO_3 at 0.2 M

Calibration tests, made with a thermal resistance (~ 150 ohm), showed that in the range of 250 w to 700 w the thermal losses (escaping heat) were very small and constant.

Our first electrolysis experiments were perturbed by the storage and destorage problem. We found out that the problem was due to non uniform temperature distribution (not 100°C everywhere) inside the Dewar flask due to electrolyte stratification. We solved this problem by leaving inside the Dewar flask a thermal resistance giving a continuous power at about 300 watts. Convection of hot electrolyte inside the Dewar flask is sufficient to establish the uniform temperature distribution (100°C) within the flask. Of course, we have to take into account the continuous loss of water due to this 300 watt extra power.

Thanks to our quite deep Dewar and also to a well arranged perforated Teflon screen just above the electrodes, we did not notice any electrolyte droplets losses. Moreover, the storage and destorage problem was solved and verified by measurements made with an auxiliary thermal resistance.

3. Results obtained:

First, we will give an example of our experimental procedure, as done in our run of July 17th 2008.

Voltage applied was 300 Volts.

Duration of the run : 25 minutes.

T minutes (min)

M: water mass (g) .

Wh : Electric energy furnished (Wh).

(Water loss due to the auxiliary thermal heater for 2.5 minutes : 22g)

Table 1.

T	M	Wh
0	-150	545
2.5	-183	560.6
5.0	-240	575.1
7.5	-276	589.6
10.0	-328	602.8
12.5	-375	615.9
15	-416	628.9
17.5	-447	641.8
20	-493	654.7
22.5	-530	667.3
25	-585	679.7

The mean **COP** (coefficient of productivity) during this run may be obtained as following :

Mean thermal energy produced by electrolysis for **2.5 minutes** between 2.5 and 25 minutes (9 intervals of 2.5 minutes):

$(585-183)/9 = 22.7$ g , that is to say : $22.7 \times 2260 = 51302$ joules.

Electric energy furnished for **2.5 minutes** between 2.5 and 25 minutes :

$(679.7-560.6)/9 = 13.2$ Wh, that is to say : $13.2 \times 3600 = 47520$ joules

Mean COP value: $51302/47520 = 1.08$

The preliminary results obtained by the end of July 2008, tests that, up to now, we were not able to pursue due to the lengthy reorganization of our society are the following:

Table 2.

Voltage applied	COP values			
200 V	1.00			
250 V	1.09	1.00	1.10	0.97
300 V	1.06	1.08	1.04	1.01

The accuracy of our measurements is fairly good (2 to 3 % max. error margin), as we have a measurement made every 2.5 minute during about 20 to 30 minutes duration for a given test. On the other hand, in this type of experiment, it is difficult to imagine to have negative thermal losses (destorage problem has been solved) and usually, the COP values are under 1.00. One can however notice that the positive COP values larger than one are not very large and that they are not as reproducible as formerly announced in ref.2.

4. Conclusion

After a severe doubt due to the use of a wattmeter without a sufficiently large bandwidth, we were able to find again values for the ratio of outlet thermal energy to inlet electric energy (COP) larger than 1.00 . We think that these values are meaningful. For the time being, these values are not very large and do not occur as often as we wrote in ref. 2. We may add that we get an hypothesis for the disappearance of the excess heat : the size of the reactor in our boiling water calorimeter was too small and the violent moves of the electrolyte inside disrupted the plasma around the cathode and the abnormal excess heat disappeared.

However, although we think that these results are quite encouraging, they need to be confirmed and we need a bigger involvement of new sponsors in the future studies because the hope of a clean, cheap and abundant energy deserves it, even if some uncertainties cannot be completely avoided.

Acknowledgements

We want to thank Didier NOËL (EDF – Etudes et recherches) very much for his advice and his lent of the D6000 Norma Goerz wattmeter. We also thank Jean-Louis NAUDIN very much for his advice during our work.

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Sonofusion Produces Tritium That Decays to Helium Three

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Abstract. Three main points are covered that are unique to Ti sonofusion target foils. These are surface modification to TiO_x shown by photos and scanning electron microscope, SEM, photos, and the decay measurement of tritium, T, by mass spectrum analysis, MS, to ^3He , the Ti target foils, and the unexplained production of 1 μm Ti hollow tubes shown in SEM photos.

1. Introduction

A collection of D^+ implanted Ti sonofusion data, $\text{D}_2\text{O} \rightarrow 2\text{D}^+ \rightarrow \text{T} + \text{H} + 17 \text{ MeV}$, are measured and described as $\text{T} \rightarrow ^3\text{He}$. The cavitation bubble jet implants into a Ti target foil producing fusion and heat. Along with T some ^4He was also detected but will not be covered here. This work was spread over several years of sonofusion laboratory work. All experiments described here used 100 μm Ti target foils in M II and M III reactors. Experiments show some fusion products, the observed small but high temperature events in the foil, ejecta sites, and induced MHz acoustic standing waves in the target foils. The Ti foil behaves differently than most other target foils in that it forms a bonded hydride that stops the deep loading found in mobile D^+ lattices. The Ti shows very colorful markings due to thin film build-up of TiO_x on its surface. The unique formation of hollow Ti 1 μm tubes, atoms thick, were observable by SEM photos.

2. Experimental and data

Two Ti target foils are described, one exposed to 20 KHz, foil Ti 3A (4-2) and the other to 46 KHz, foil Ti 17. Ti 3A was run at Los Alamos National Lab., LANL. The other foil, Ti 17, was run at the EQuest laboratory on 2/09/95. The Ti 3A run in the MII reactor was a dual cavitation system, Fig. 1,2,3. The configuration of the dual concentric cavitation reactors was powered by a 5cm diameter Ti horn. The top reactor circulated D_2O ; the bottom reactor H_2O . The reactors were separated by 0.6 cm thick x 7 cm diameter stainless steel reactor volume. The acoustic energy was transferred through the disk producing the transient cavitation bubbles that implanted plasma jets into these foils. The experiments were run with the assistance of Tom Claytor, Dale Tuggle, and Russ George, The gas sample was collected from over the circulating D_2O in the MII reactor by gas transfer to an evacuated 50 cc sample volume on 4/29/94. Fig. 2.

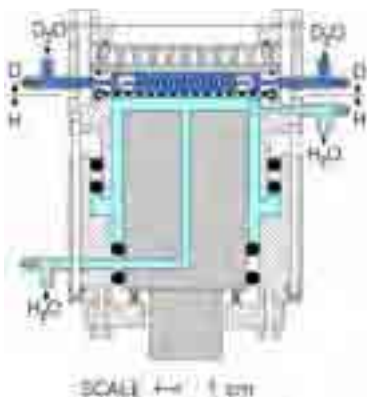


Fig.1- MII, reactor 20 KHz was used in the tritium and ^3He experiment with a heater for calibration.



Fig.2 - 50 cc sample volume was used for MS analysis.



Fig.3 - MIII, 46 KHz reactor, had two opposing piezos with a calibration heater.

Table 1. The table of mass spectral, MS, data produced by Brian Oliver. Days represent days after gas collection.

Sample Volume 4-2.	Analysis Date.	Days.	T in Volume, atoms.	³ He in Volume, atoms.
2-0	4/29/94	0	Leak ?	0+
2A	9/14/94	139	1.13E+15	1.71E+13
2B	9/14/94	139	1.10E+15	1.67E+13
2C	9/14/94	139	1.08E+15	1.63E+13
2D	2/06/95	285	1.03E+15	3.89E+13
2E	2/06/95	285	1.00E+15	3.80E +13
2F	2/08/95	287	9.76E+14	3.73E+13

Shown in table 1 is the experimental sonofusion data, Ti 3A (4-2) tritium, analyzed for T via the evolution of ³He that was identified by mass spectrometry, MS. From this experiment at LANL, the 4-2 sample was chosen. The exposed Ti target foil, 5x5x0.01 cm, in a controlled flow of D₂O and Ar at 200 ml/min was cavitated for 18 hours. The 200-watt acoustic input into a 35 cc reactor volume was driven at 20 KHz by a Heat Systems 5 cm diameter Ti horn. The steady state temperature was 61°C, the external pressure of Ar at 30 psig. The lower H₂O reactor was pressurized by N₂ gas to reduce the population of cavitation bubbles (high pressure stops the formation of cavitation bubbles). The dual sonofusion reactor MII was vacuum tight. The gas samples were collected by vacuum transfer in evacuated 50 cc stainless steel sample volumes. Sample 4-2 was collected at the end of the run on 4/28/94. All these dates are very important for measurements as $T \rightarrow {}^3\text{He} + \beta + \nu$ at a decreasing rate of ³He production in the sample volume. T has a half-life of 4475 days and $\lambda = 1.56 \times 10^{-4}$ /days. The MS data is shown in column 5 in atoms. Brian Oliver of the DOE using his tested methodology for ³He analysis performed the mass spectrometry. Column 2 shows 3 dates and column 3 shows days between measurements. These measurements show a disintegration constant that was consistent with the decay of T to ³He. A plot of this data shows the T decay rate in the sample volume to be $\Delta(T_0 - {}^3\text{He})/\Delta t$ is λ and $T_0 - {}^3\text{He} = T$, where T_0 is initial tritium. The calculated decay of T is shown as circles in Fig. 4 a,b (4b shows expanded scales).

In the experiment the hypothetical addition of less than 0.66×10^{13} atoms to the initial ³He alters the T_0 , initial titanium atoms, and corrects the data for a possible storage leak. The data in the graph shows that there is a good fit that incorporates the day the gas sample was collected, See table 1. The date produced by the uncorrected data was 30 days later and is shown by the squares in Fig. 4a. With this correction there is a good fit to Brian Oliver's data (in Fig. 4b the circles are calculated data). Brian's data has the right slope but the wrong intercept. Correction for a leak remedies that problem.

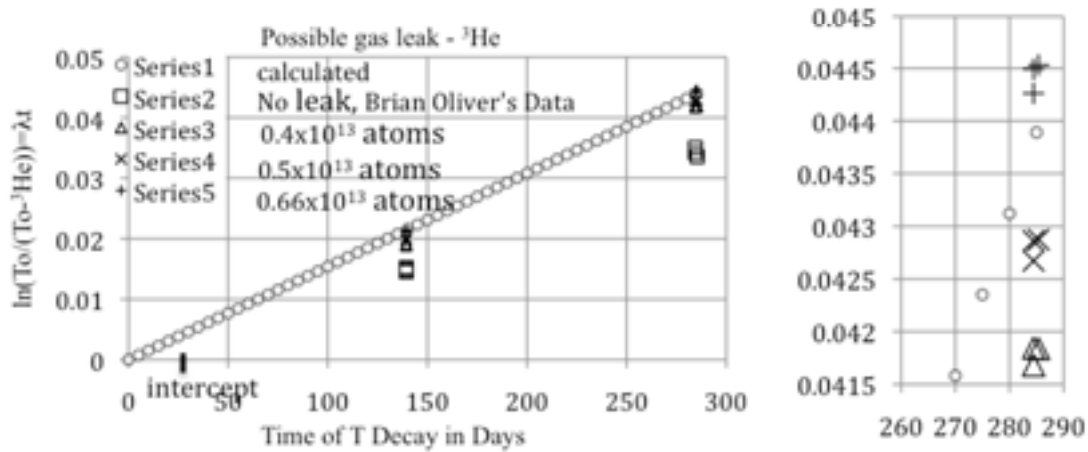


Fig. 4a,b - Graph of the MS data. Leak of gas during storage of 139 days (leaked atoms of ³He corrects the data)

The 50 cc sample volume shown in Fig. 2 may have had a slow leak in its valve, a Nupro (SS 4BK TW-VA), during its storage.

Ti target foil Ti 17 was run at EQuest Laboratory in Mountain View, CA, USA at 46 KHz. The reactor MIII consisting of opposing dual piezo ceramic disks produced smaller cavitation bubbles, same energy density, in circulating D₂O. The configuration of the concentric dual piezo stacks bonded to opposing stainless steel disks held about 0.5 cm gap with 5x5x.01 cm Ti target foil centered in the 6 cm diameter reactor. A controlled flow of D₂O passed through the 14 ml reactor volume at a rate 60 ml/min. Cavitation bubbles formed at the target foil surface were implanted via the plasma jets of deuterons and electrons into the target lattice. The MIII reactor run was pressurized with 3 atmospheres of Ar. The calorimetry was a flow through type calibrated by a variable resistance heater and measured at steady state temperatures and D₂O flow rates. Most of the acoustic activity occurred in the center 50% of the target foil.

3. Discussion

The graph, Fig. 4a, of the MS data was gathered over a period of 284 days with an assumed 0 atoms of ³He on the day the 50 cc gas cylinder 4-2 was filled via vacuum transfer with the gas from the reactor. This transfer effectively removed 50% of the reactor gas. The gas in the sample volume was flown from LANL to the EQuest laboratory where it spent most of the 139 days in storage. The sample volume was mailed to Brian Oliver at the Rocketdyne DOE facility for the 4-2 mass spectrum analyses. Table 1 of the data from the MS of Brian's gas analysis from sample volume Ti 3A (4-2) was on the 9/14/94 for samples A, B, and C and was repeated 145 days later on the 2/06/95 for samples D, E, and F. The intercept of these two points with the timeline in Fig. 4a should be the time the sample was collected, 4/27/94. However, this is not the case. Brian Oliver's calculated sample volume collection date shows an intercept 30 days later; data shown by squares, Fig. 4a. The intercept should be moved to the earlier collection date, 0 days, not 30 days later. The initial storage time was 139 days. This can be done if one assumes a small leak of gas, T and ³He, from the sample volume during that period. It is enough to identify T decay as a straight line from the two MS measurements shown in Fig. 4a, at 139 days and 285 days, that has the slope of the disintegration constant λ for T. But it is better to show that the intercept point was on the day of the gas collection. A leak during the initial storage period, valve later closed at 139 days, can explain the shift in the timeline intercept. Or possibly doping of the sample volume with DTO might be the explanation for Brian Oliver's intercept date. Tritium is obviously there in the sample volume. If the sample was spiked, it happened before the sample was mailed to Brian Oliver about 30 days after the sample collection. In any case Brian Oliver's data is a good example showing the presence of T in the sample volume Ti 3A (4-2).

The photo Fig. 5 of the Ti 3A target foil shows interesting colorful visual modification of its surface produced by the sonofusion process. Similar observations in Ti 17 are shown in Fig. 6. These colorful standing wave patterns are produced by thin layers of TiO_x deposited during cavitation that is unusual in an apparent reducing environment of D⁺. These standing waves appear to be associated with the Ti target foil's mass and thickness producing an induced MHz resonance frequency via the primary 20 KHz resonance reactor frequency. The Ti surface lattice and D⁺ form stable bonds and the surface is covered with thin layers of mostly TiO_x and TiD_x [1,2]. The jets that implant leave their bulky ionic oxygen atoms combined with the surface Ti of the target foil. The D⁺ and e⁻ are implanted into the Ti lattice and form the transient imploding cluster, the cluster model [3,4,5]. Surface color and erosion patterns are not unique to Ti target foils [6].

The SEM of the surface of the two Ti target foils, Ti 3A and Ti 17, are very informative via SEM photos, Fig. 7 and Fig. 8. The two are almost indistinguishable from each other. The 20 to 50 nm nodule surface of sonofusion Ti target foils are different from those foils that have mobile D⁺ in their lattice [5]. The very mobile D⁺ ejecta from the lattice matrix as found in Pd and Ag target foils [3,5,6]. The SEM of the surface of Ti 3A shows the presence of very small hollow 1 μ m diameter tubes of Ti. They appear as a complex network of black lines on the target foil surface, see Fig. 9. SEM photos discovered these several years after Ti 3A foil removal from the M II reactor. Further SEM magnification shows that these tubes are only a few Ti atoms thick and about a micrometer in diameter, Fig. 10. The Energy Dispersive X-ray Spectroscopy, EDS analysis, shows a degree of transparency and perhaps shadows, Fig. 10. These tubes were thought to be fragile and certainly would not last long in the cavitation environment so their existence would be limited to a time period just before the reactor was turned off. The SEM photos, Figs. 7, 8, and 9, were taken by Jane Wheeler of Evans Lab, Sunnyvale, CA, and six months later Ti 3A was reanalyzed by Lorenza Moro of SRI, Menlo Pk., CA., Fig. 10.



Fig. 5 - surface Ti 3A (20 KHz).



Fig. 6 - surface Ti 17 (46 KHz).



Fig.7 - SEM photo of Ti 3A.



Fig. 8 - SEM photo of Ti 17



Fig. 9. - SEM; tube network

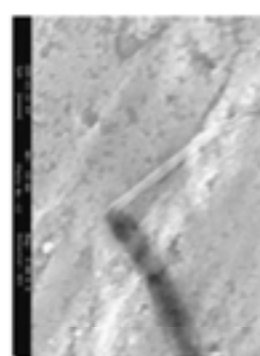


Fig. 10 - SEM of 1 μm

4. Summary

The Ti experiments are worth repeating and the many unanalyzed foils are worth analyzing [6]. T was measured and definitely decaying in the sample volume. The MS analysis showed a 30-day shortfall of the true collection date that can be corrected by assuming a small initial leak from the sample volume before the first MS measurement. Introducing a phantom leak improves the data to the correct time line. The TiO_x and TiD_x surface appearance for the two Ti target foils at different frequencies were the same except that the pattern was larger for the 20 KHz foil. The Ti tubes defy explanation at this point. Collapsing bubbles, their implanting jets, and D^+ clusters produce heat and nuclear products and exist in other systems [5].

Acknowledgements

Tom Passell of EPRI funded Brian Oliver's DOE MS analysis, $\text{T} \rightarrow {}^3\text{He}$ and $2\text{D}^+ \rightarrow {}^4\text{He}$.

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Diurnal Variations in LENR Experiments

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Abstract. Two very different LENR experiments exhibited daily variations in their characteristics or outputs. Comparison of the variations for the experiments forces the conclusion that the measured variations are artifactual. That is, they are not due to the influence of an external diurnal mechanism such as cosmic rays. However, the causes of the observed variations are not understood. Such understanding is important for the conduct of robust LENR experiments to obtain credible data. It is also critical to the reliable operation of eventual LENR power sources.

1. Introduction

Diurnal variations occur over the course of a day, and typically recur every day. Daily variations in light and temperature due to the rotation of the earth are familiar examples. Low Energy Nuclear Reaction (LENR) experiments should not be subject to diurnal variations. However, there have been reports of daily cyclic changes in the conditions and output of LENR experiments. The purpose of this paper is to report and examine such variations in two experiments, one in Hokkaido, Japan, and the other in Texas, U. S.

2. Mizuno Experiment

The first experiment, which exhibited long term diurnal variations, was aimed at the study of transmutation reactions [1]. Some of the equipment for that electrochemical experiment is shown in Fig. 1. The experiment was pressurized to about 7.4 atmospheres and operated at temperatures near 375K. The D/Pd loading ratio was measured for the duration of the experiment (about 800 hours).

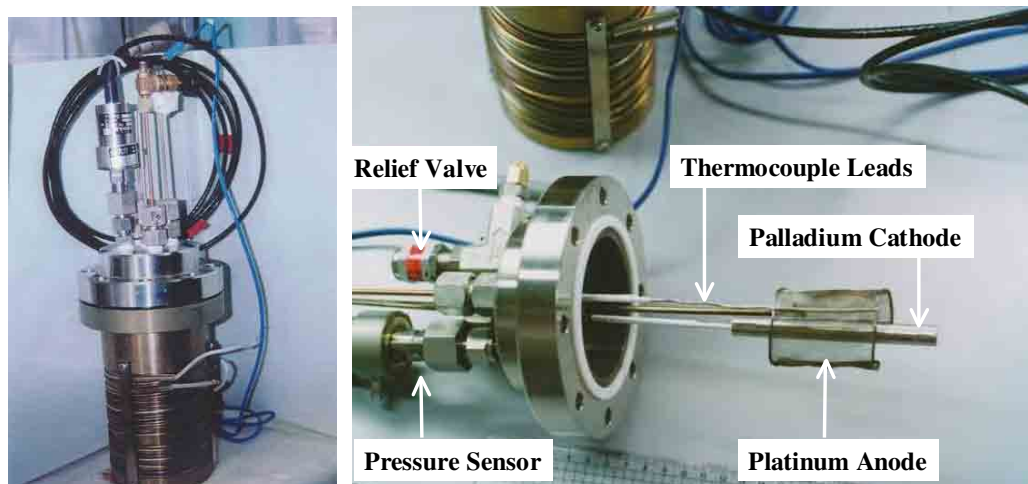


Fig.1 – Exterior and interior of the pressure vessel for a search for transmutation products in Hokkaido.

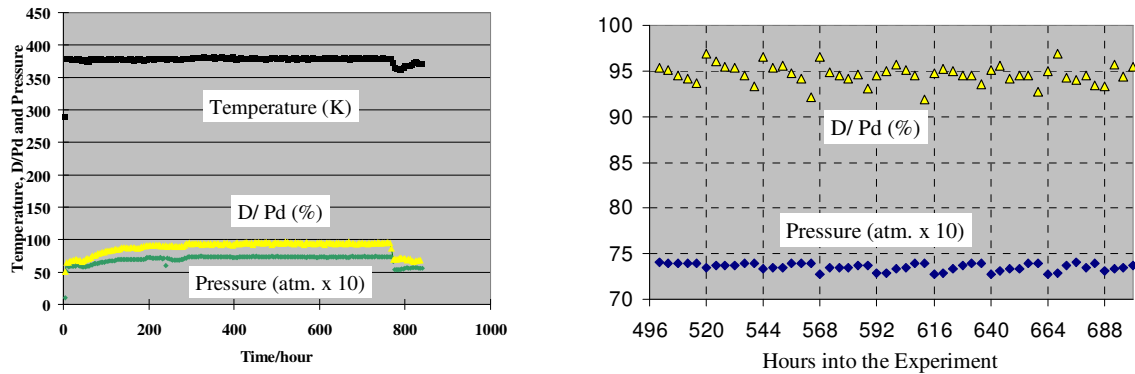


Fig. 2. Time histories of the pressure, loading and temperature for the high-pressure transmutation experiment.

The long-term record of the pressure, loading and temperature for the experiment is given in Figure 2. A blow up of the data from 500 to 700 hours is also in that figure. It can be seen that the pressure (P) and loading (L) vary inversely with each other on a 24 hour cycle. The degree of the two modulations is small in both cases, with $\Delta P/P$ and $\Delta L/L$ both being a few percent. The variations have sawtooth shapes, with the discontinuity occurring at midnight local time. The regularity of the sawtooth shapes evolved during the experiment. Variations in the ambient temperature in the laboratory cannot account for the measured variations because the temperature of the experiment was much greater than the laboratory temperature.

3. Letts-Cravens Experiment

The experiment in Texas was run for a much shorter time than the one in Hokkaido. It involved the use of laser stimulation and the measurement of excess heat. The experiment was controlled remotely via the internet from Cambridge MA during the 10th International Conference on Condensed Matter Nuclear Science [2]. Figure 3 shows the equipment for the experiment.

Figure 4 shows the excess power (mW) for somewhat over 2.5 days of the experiment. It is seen that the signal-to-noise for the excess power measurement is about 10. The power varies with a cycle time of about one day, although the shape of the daily variation is not the same on each of the days. The peaks of maximum output power occur in the range of 1800 to 2000 local time. The most remarkable aspect of the



Fig.3. Overall photograph of the excess power experiment and close-up of the electrochemical cell in Texas.

power data in Figure 3 is the depth of the modulation. The variation the first day is from a low near 50mW to a peak at 450 mW. The corresponding variation the second day is from 200 to 600 mW. The third day exhibits a variation of about five-fold from 150 to 750 mW.

The time history of the laboratory temperature during the experiment in Texas is also in Figure 4. It is seen that the magnitude of the noise decreases noticeably when the excess power is high. However, the temperature variations both during and between episodes of peak excess power is 0.5 C or less. These are small changes compared to the large modulation of the excess power. Nonetheless, the clear changes in the noise of the temperature measurements over the course of this experiment are interesting.

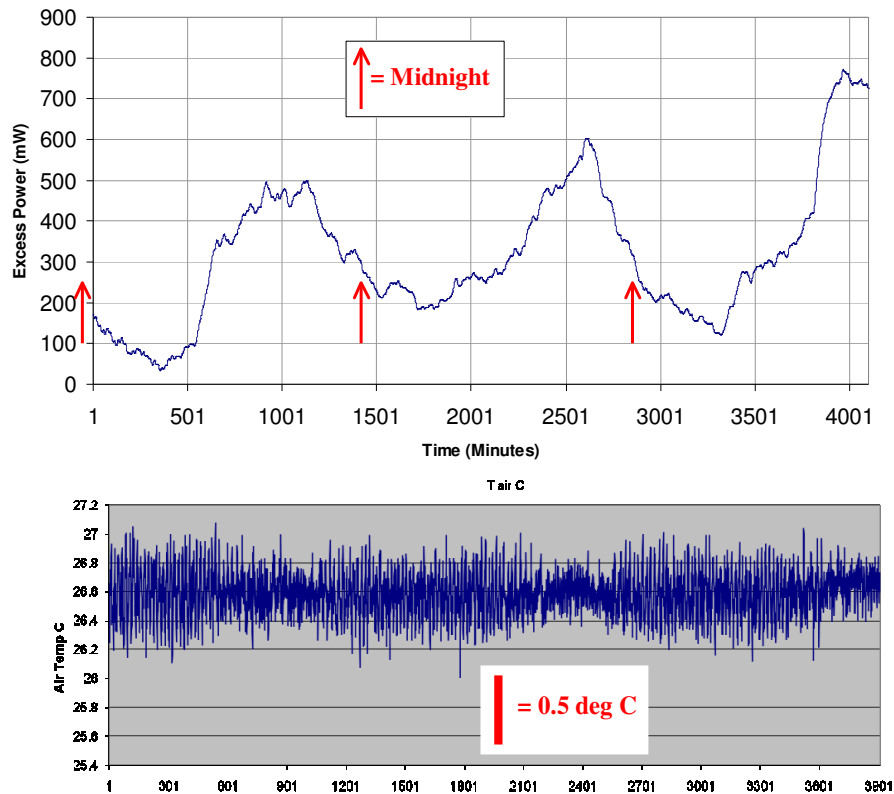


Fig. 4. Time histories of the excess power and the laboratory temperature in the laser-stimulation experiment. The two time traces are aligned vertically to permit comparison of power excess and temperature variations.

4. Discussion and Conclusion

One of the primary motivations for this study was to learn if the observed diurnal variations in LENR experiments could be due to cosmic ray particle bombardment. That was not thought to be likely because of two reasons. First, the fluxes of cosmic rays at sea level are relatively small, save for neutrinos, for which the interaction cross section in experiments, such as the two of concern here, is negligible. Second, if globally-present cosmic rays were involved in LENR experiments, diurnal variations would be more widely observed in the field. However, if a connection between observed variations in LENR experiments and cosmic rays could be made, then LENR experiments might be made to serve as cosmic ray detectors. In that case,

comparing the responses of LENR experiments on the surface of the earth and in deep mines would take on another significance.

What if the case can be made for the fundamental reality of diurnal variations in LENR experiments can be made? Then, there would arise the need for their theoretical and computational explanations. This would further complicate the understanding of LENR.

Contrasting the daily variations in the Hokkaido and Texas experiments is instructive, as shown in Table 1.

Table 1. Comparison of the Characteristics of Two LENR Experiments Exhibiting Diurnal Variations

Factors	Mizuno	Letts-Cravens
Duration of experiment (Days)	35	2.7
Shape of Daily Variation Curve	Sawtooth	Pseudo-Sinusiodal
Peaks (Local Time)	Midnight	1800-2000
Depth of Modulation (% of Average)	About 2	> 50

The major variations in the shapes, local times for peak values and extent of daily swings in Table 1 indicate that the variations are probably not due to some external cause, such as daily variations in cosmic ray neutron or other fluxes [3]. That is, the variations appear to be artifactual. It remains to be seen if an explanation for the observed variations can be found for either experiment.

Understanding and explaining uncontrolled variations in the behavior and output of LENR experiments is important for two reasons. The first is the ability to conduct scientific experiments that yield reproducible, reliable and credible data. Given the large daily variations in the excess power in the Texas experiment, the controllability, and hence the utility of potential engineered commercial LENR power sources, are at stake.

Acknowledgements

Interesting discussions and email exchanges on diurnal variations with Jean-Paul Biberian, Dieter Britz, Xing Zhong Li, Michael C. H. McKubre, Michael E. Melich, Peter Mobberley and Mahadeva Srinivasan are recalled with pleasure.

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Can Water be the Origin of Excess Energy?

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Abstract. This study was initiated due to the concern of some critics of LENR research that small energy changes in many H₂O or D₂O molecules in electrochemical cells can explain observed excess heat. More than three hundred LENR papers from 1989 to 2008 that reported excess energy were acquired and reviewed to extract quantitative results and other information. Excess energies and cell volumes were found in 17 papers. These data were used to compute eV per water molecule values. Most experiments showed excess energy outputs that would lead to ratios below the vibrational energy of water molecules at room temperature (0.04 eV/molecule). However, 65% of the papers, which reported both excess energies and cell volumes, indicated values significantly higher. The highest reported value was 42.6 eV/molecule. Eleven ratios are far beyond what is plausible for water to be the source of anomalous heat. Therefore, it is concluded that some unknown rearrangement of water molecules in many LENR experiments is not the source of excess heat.

1. Introduction

Ever since first publically announced in 1989 by the two chemists, Martin Fleischmann and Stanley Pons, the discovery of Cold Fusion has caused great controversy. Criticism stems partly from the lack of theoretical understanding. And, there are substantial implications of the field, which promises abundant and distributed energy sources with little radiation, in competition with other developing energy sources. One main criticism that faced this field throughout its past 20 years has been the source of reported excess energy, whether or not it can be attributed to nuclear mechanisms, chemical reactions, or molecular rearrangements. Excess energy is defined as the final energy output in excess to the energy applied to an experimental cell.

Several papers have been published in the defense of LENR. Their main objectives were to explain the validity of the observed excess heat to rebut critics and minimize skepticism. One such paper published in 1989 was the “Eight Chemical Explanations of The Fleischmann-Pons Effect” [1]. It highlighted possible factors responsible for the 3W/cm³ observed in the author’s experiments. In another response to critics, it was shown that energy stored in defects in an electrode could not account for observed excess energies.

This study was designed to quantitatively examine the possibility that small energy changes in the many water molecules in electrochemical LENR experiments could account for measured excess heat. Lists of scientific papers, articles, and reviews were thoroughly screened to create a database of reports of excess heat. Cell volumes and excess energy data from these papers were tabulated and graphed. The results counteract claims that attribute excess energy to water molecule rearrangements. A secondary goal of this work was to create a database for additional useful information. Later publications will be based on that information.

2. Water Energies

Water is arguably the most important chemical on earth. As a result, it might be the most studied. And, it is also a very unusual substance. For example, water is most dense at about 4 C above its melting point, unlike most substances that are denser in the solid phase rather than in the liquid phase. Hence, water ice floats. Were that not true, the world would be very different. Despite its unusual and complex properties, there are only two component elements in water, and its structure is simple. The water molecule is polar, with more negative character on the side with the oxygen atom and more positive character on the sides with the two hydrogen atoms. This enables electrostatic hydrogen bonding, as indicated in Fig. 1. The attraction between any two neighboring molecules is very transient due to the constant thermal motions of the water molecules.

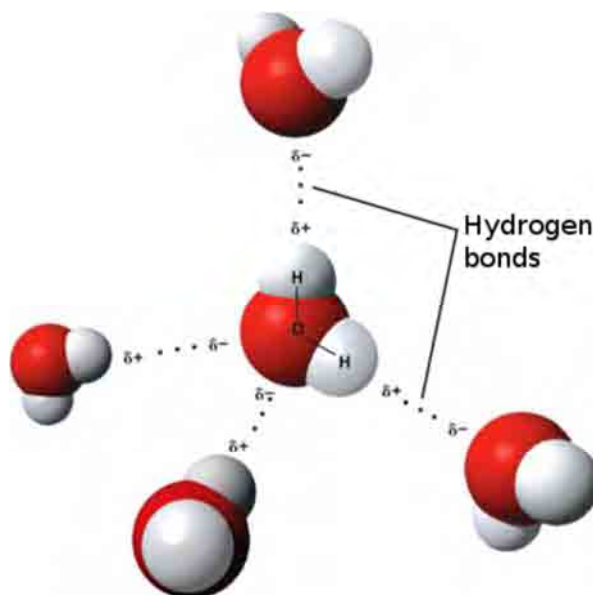


Fig.1 - Schematic of five water molecules, showing the 104.5 degree H-O-H angle and the hydrogen bonding between molecules. [2]

However, despite the chaotic dynamics, there is a net time-averaged attractive force between nearby molecules. It is such hydrogen bonding which is responsible for the relatively high boiling point and large heat of vaporization of water.

Some critics still attribute the perceived excess heat to the recombination of free hydrogen or deuterium with oxygen, as given off by electrolysis, to form liquid water. It is known that, in the presence of a catalytic material, those gases can easily recombine. This recombination gives off the heat of formation of water and can result in the erroneous appearance of excess heat. However, recombination is not the source of excess heat for two reasons. First, a properly conducted experiment will spend energy to electrolyze water and then recapture that energy when electrolysis occurs. And, very high values of measured excess energy cannot be due to recombination of atoms that were in the experiment at its outset.

Besides the heat of formation there are other characteristic energies for water molecules. They include the heat of vaporization, which is the energy to cause a molecule to transition from the liquid to the gas phase. The heat capacity of water is high, and there is an energy associated with raising the temperature of water. And, at a given temperature, there is a thermal vibrational energy associated with each water molecule. Some of the energies of water in table 1 provide a baseline for assessment of the eV/molecule values measured in LENR experiments.

Table 1. Water Molecule Energetics.

Heat of Formation (Recombination)	1.48 eV/molecule
Heat of Vaporization	0.42 eV/molecule
Energy to Heat Water from "room T" to boiling	0.06 eV/molecule
Vibrational Energy (3kT/2) at "room T"	0.04 eV/molecule

Rearrangement of water molecules involves energies from a few percent to almost half of 1 eV. Such energies are very low in comparison to those due to nuclear reactions, which are in the order of mega-electron Volts. The lowest value in Table 1, the vibrational energy of water at room temperature, will be used for comparison with eV/molecule values reported from LENR experiments. It will be seen that many measured

eV/molecule values fall below the vibrational energy. However, some values are well beyond even the molecular heat of formation.

3. Methodology

Several lists of Cold Fusion papers were examined to generate a broad and unbiased database for the study. Those lists included: (a) the Craven-Letts tabulation for ICCF-14, (b) Rothwell's website (www.lenr-canr.org) [3], (c) the Britz compilation of Cold Fusion papers, and (d) a list of papers submitted for the proceedings of ICCF-14 [4]. For our purposes, only papers that reported incidents of temperature increases and generation of excess heat, rather than production of tritium, neutrons or atoms, were included.

In all, 335 papers were examined. The information extracted from them formed an Excel spreadsheet. Experimental parameters, such as cathode material and dimensions, reference electrode, anode characteristics, Pd loading ratio, electrolyte composition and volume, type of water, current density, operating and delta temperatures, operating time, applied voltage and current, power, and excess energy were tabulated. However, our main focus for this study was directed towards information pertaining to excess energies and cell volumes. These factors were either provided explicitly, or else calculated by subtracting the input energy from the total energy output to obtain "excess energy". Grams of heavy water were converted to milliliters, or cubic centimeters, for the "cell volume". Some of the papers included numerous experiments with varying outcomes. In such cases, values were averaged to obtain a single representative value. eV/molecule values were obtained using the conversions:

$$\frac{kJ}{ml D_2O} \times \frac{6.34 \times 10^{21} eV}{1 kJ} \times \frac{1 ml D_2O}{1 g D_2O} \times \frac{18 g D_2O}{1 mol D_2O} \times \frac{1 mol}{6.02 \times 10^{23} molecule}$$

4. Results and discussion

The documented values were used to create four plots. The first plot compares excess energy and water volume information on a logarithmic scale. It has two purposes. One is to provide an overall comparison of the excess energies and cell volumes. The second is to permit assessment of a possible correlation between the two factors. The other three plots are histograms: (a) one that represents the distribution of excess energies, (b) another that presents the distribution of cell volumes, and lastly, (c) one that shows the distribution of eV/molecule values. The first two histograms are used to exhibit the overall trend in reported values for both excess energies and cell volumes. The third histogram is essential to demonstrate the number of papers that reported values higher than the vibrational energy of water molecules at room temperature.

Excess energy and water volume values were available from only 17 papers. They are plotted in Fig. 2. The trend of the data points suggests a rough correlation between both factors, where higher cell volumes seem to result in higher excess energies.

Only 40 out of 335 papers provided quantitative results for the amount of excess energy achieved in LENR experiments. The rest either failed to report any information about the output or reported excess power instead of energy. 60% of the 40 papers, as indicated in Fig. 3, reported results of 200 kJ or below. 200 kJ is enough energy to light a 100W bulb for about half of one hour. Such low values are considered by many as insufficient evidence to properly address critics of LENR. Only 40% of the papers reporting values for excess energy showed results above 200 kJ, with the highest documented value being 200 MJ. Notably, excess energy values up to 900 MJ were reported in experiments involving hydrogen-loaded nickel systems.

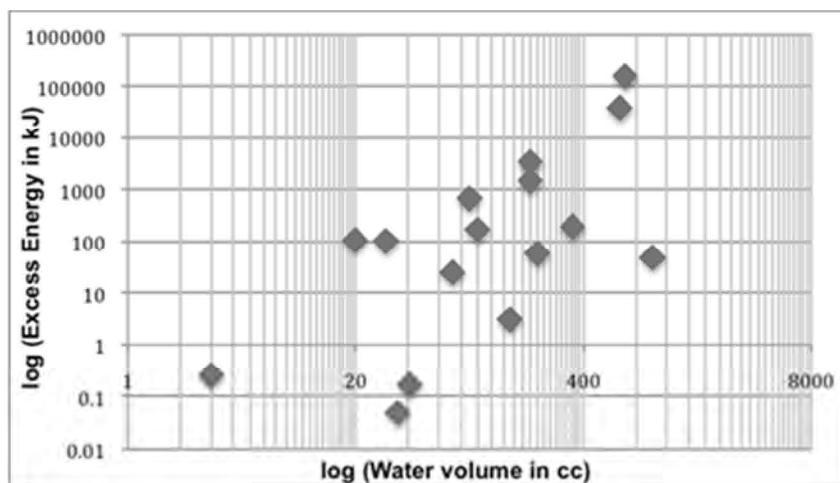


Fig.2 - The plot shows the relationship between excess energy and heavy water volume.

Only 57 out of 335 papers indicated the amount of heavy water or the amount of electrolyte used in the experiments, as can be seen in Fig. 4. Most experiments involved cells with volumes at or below 200 cc, with the highest volume used being 1000 cc in Lautzenhisser's Amoco experiment in 1990 [5].

Lastly, excess energy per water molecule values were calculated from papers that reported both values and a histogram was created, as shown in Fig. 5. Many of the reports had high eV/molecule outputs. In fact, 11 of the papers resulted in energy per molecule values higher than that of the vibrational energy of water at room temperature. Those papers are listed in table 2. The highest value obtained is 42.6 eV/molecule. The fact that some of the papers had very high eV/molecules is enough to conclude that there is some other explanation of excess energy than new molecular rearrangements.

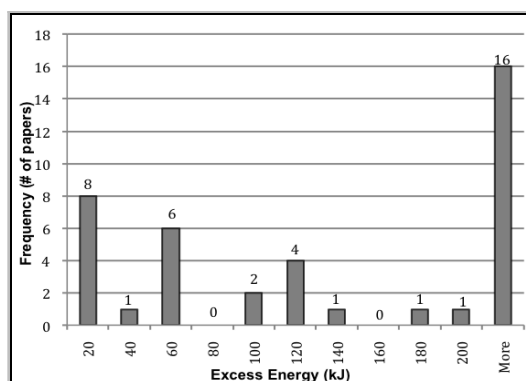


Fig. 3 - Histogram showing the distribution of excess energy values.

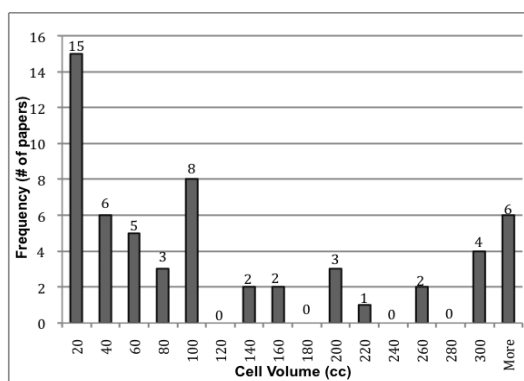


Fig. 4 - Histogram showing the distribution of experimental cell volumes.

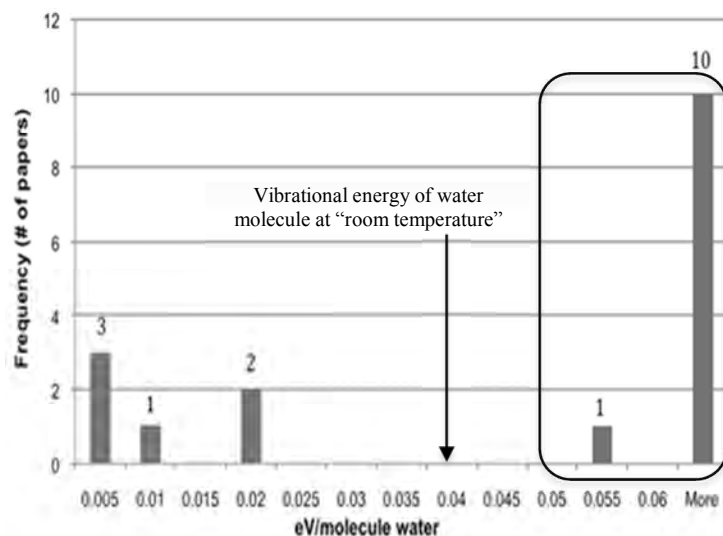


Fig. 5 - Histogram showing the distribution of eV/molecule values based on data provided by LENR papers.

Table 2. LENR articles that showed excess energy per water molecule values above the vibrational energy of water at room temperature.

Author	Reference	Year	eV/molecule
Oriani	6	1990	0.051 *
Lonchamp	7	1996	0.067 **
Takahashi	8	1998	0.106
Ohmori	9	1993	0.328
Storms	10	2006	0.659
Miles	11	1990	1.03
McKubre	12	1992	1.40
Miles	13	2001	1.45
Dardik	14	2008	3.27
Bockris	15	1993	11.2
Takahashi	16	1992	42.6

* highest value amongst 11 experimental runs.

** highest value amongst 6 experimental runs.

5. Conclusion

An extensive study of LENR papers has been performed to tabulate experimental conditions and data on excess energy. The goal was to address the question in the title of this paper. But, some unexpected results emerged during the course of the study. We summarize them, and then return to the question of the possible role of water in the production of excess energy.

Fewer than one out of five of the many papers examined reported the water volumes used in electrochemical experiments. More surprisingly, only one in eight papers gave the integrated excess powers, that is, the total excess energies for the experiments they described. Only 17 papers gave both the electrolyte volumes and the excess energies. After two decades of research on LENR, and thousands of experiments, it is noteworthy that the documentation of the experimental conditions and results is so sparse. There is clearly a need for more conscientious documentation of what was done and found in LENR experiments.

The second unexpected result is seen in Fig. 2, which shows the relationship between excess energy and heavy water volume. That plot is suggestive of a correlation between electrolyte volume and excess energy. Higher excess energy values tend to come from larger cells. However, there may be no basis for such a correlation, if the generation of excess energy occurs on or in the cathode and not in the volume of the electrolyte. Such a correlation might exist if the production of excess energy depended on some elements dissolved in the electrolyte. In that case, the greater the amount of electrolyte, the greater the amount of a reactant and the more excess energy, assuming adequate movement of the reactant elements to the reaction sites on or in the cathode.

Even if there were some reason for a correlation between excess energy and cell volume, the data in Fig. 2 are very scattered. Hence, it is not worth computing a correlation coefficient. However, it might be useful to conduct parametric experiments in which the same concentrations of the solutes in the electrolyte are used in cells of markedly different sizes. If one of the nuclear reactants is in solution at the start of an experiment, then the excess power might scale with electrolyte volume.

The range of cell volumes used in LENR experiments was quite well known. But, this study showed quantitatively that 44 of 57 cases had volumes of 200 cc or less. In fact, 37 of the 57 instances had electrolyte volumes equal to or less than 100 cc.

The experimental papers showed that 24 of the 40 reports of excess energy were equal to or below 200 kJ. Hence, only 16 were greater than 200 kJ. A few of the values of excess energy were in excess of 1 MJ. The more common and relatively small values for excess energy, some gotten during runs of days and weeks, emphasize the need for scaling up power and energy production in LENR experiments. Such scaling would also broaden the range of potential applications of LENR generators.

Returning to the motivating question for this study, we found that the values of eV per water molecule from some experiments are far beyond what is reasonable for water to be the source of observed excess heat. It is thus concluded that some unknown rearrangement of water molecules in an LENR experiment is not the source of anomalous heat production.

The mechanism(s) causing LENR remain mysterious. However, the experimental database evidencing the ability to trigger nuclear reactions using chemical energies is robust. That information has not been studied by most scientists in the physics community. The existence of LENR is still criticized occasionally, usually by people who have not read the available literature. Criticism is absolutely basic to scientific research and communications, as it brings up many useful questions. Nonetheless, it is crucial that scientists who think that LENR is real, even if not fully understood, respond to critics on the basis of experimental data. That motivated this study. It has shown that further experimentation, long-term and detailed data logging, and thorough documentation are required. Better experiments and reporting may render this field more acceptable to the broader scientific community.

Acknowledgements

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Production of Helium and Energy in the “Solid Fusion”

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Abstract: In this paper, a new type “Solid Fusion Reactor” has been developed to test the existence of solid state nuclear fusion (“Solid Fusion”): reproducible experiments have been made at room temperature and without external power input. (Both of the energy and helium generation affected by the reactor structure, gas flow rate, powder weight, and cooling condition were studied.) Deuterium gas loading processes of two types of nano material ($\text{ZrO}_2\text{Pd}_{35}$ and $\text{ZrO}_2\text{Ni}_{30}\text{Pd}_5$) were studied respectively in this paper. The results showed the energy produced in ZrNiPd powder is higher than in ZrPd powder. Helium as an important evidence of solid-state fusion was detected by mass analyzer “QMS”. As results, “Solid Fusion” has been confirmed by the helium existence.

1. Introduction

Though enormous reports [1-3] have been published on the deuterium nuclear fusion reactions, and scientists have hoped that “cold fusion” finally will solve the world’s energy problems. “Cold fusion”, however, has not been generally accepted due to the lack of experimental evidences on the stable and/or continuous generation of large amount of excess heat or nuclear reaction products [4]. It is well known that excess heat and Helium (or Tritium) have been considered the Solid Fusion Reaction’s products in Pd/D system [5].

It was studied that many factors having effects on the reaction heat in solid-state fusion, for instance: the gas flow rate, vessel structure and size, and cooling condition. Helium as an important evidence of solid-state fusion was detected by mass analyzer “QMS” in this paper.

Two kinds of powder were investigated under the same conditions in this paper: one is nano powder $\text{ZrO}_2\text{Pd}_{35}$ (: ZrPd alloy), and the other is $\text{ZrO}_2\text{Ni}_{30}\text{Pd}_5$ (: ZrNiPd alloy).

As shown in Fig.1, X-ray diffraction analysis was carried out for both of the nano powder ZrPd and ZrNiPd . From Fig.1 [A], we can see that almost all of the palladium elements exist as the palladium oxide (PdO) in the original nano powder (ZrPd). Based on these X-ray analysis results, to remove the Oxygen from the original ZrPd powder, a “deoxidization treatment” is very important for the nano powder ZrPd before the general pressurization of the powder with D_2 gas.

The process of “deoxidization treat” is as follows:

- (1) Firstly, the nano powder ZrPd was sealed inside the stainless vessel and then vacuumed at room temperature until the vacuum up to about 5×10^{-5} [torr]. Then the vessel (with the sample powder inside) was baked and vacuumed at $150[^\circ\text{C}]$, kept for 6 hours, then was cooled down to the room temperature. The vacuum degree of vessel was finally about 5×10^{-6} [torr] at room temperature;
- (2) Secondly, D_2 gas was loaded into the high vacuumed vessel with a fixed flow rate $20 [\text{cc}]/[\text{min}]$. The total gas volume was decided by the sample weight (16.5 to $18 [\text{cc}]/[\text{g}]$). As results, this process made the PdO transmute into Pd, and D_2 gas into D_2O ;
- (3) Finally, exhausting the D_2O from the vessel: the reaction vessel was vacuumed at room temperature until the vacuum up to about 5×10^{-5} [torr], then baked and vacuumed at $150 [^\circ\text{C}]$ until the vacuum up to 2×10^{-6} [torr], kept for over 6 hours. Then the vessel was cooled down to room temperature.

Fig.1 [B] shows the X-ray analysis result of powder after “deoxidization treat”. The intensity of PdO got a big fall, but little PdO still exists in the powder. And Fig.1[C] is the X-ray analysis result of powder after fusion reaction (after D_2 gas loading), the intensity of PdO is about the same as the Fig.1 [B]’s. Accordingly, even if much more D_2 gas loaded, the PdO cannot be removed completely. This residual intensity of PdO in Fig. 1 [B] and [C] may be the limit contents of ZrPd powder.

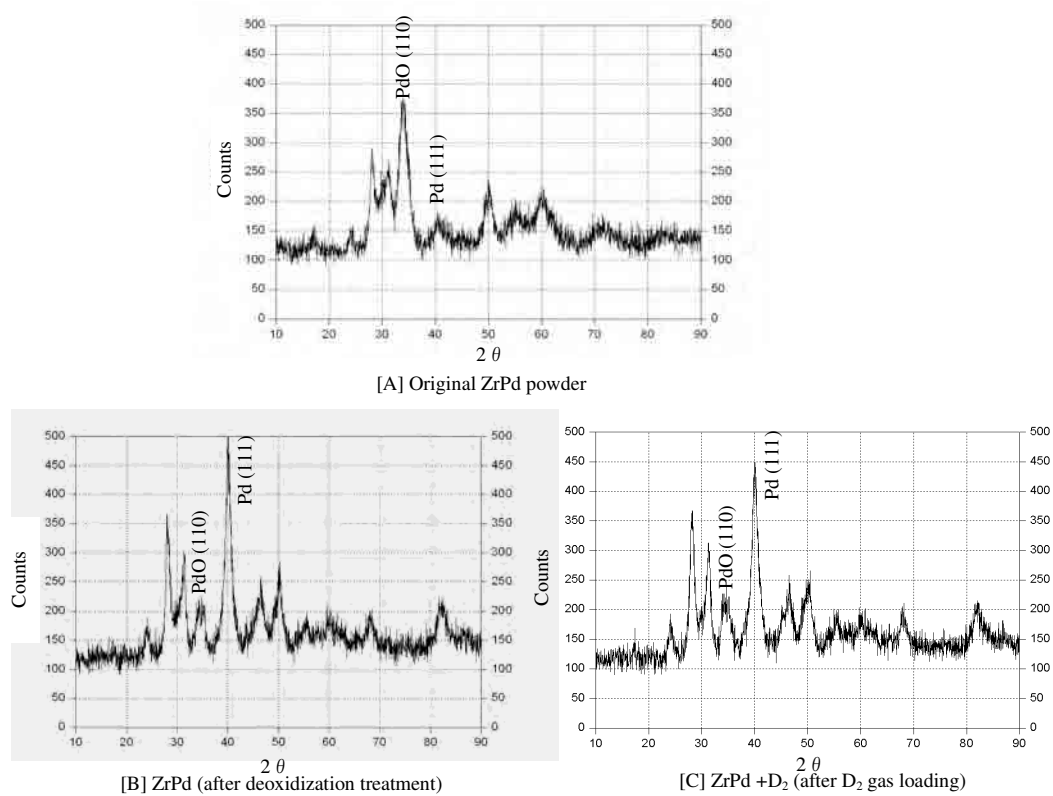


Fig.1 - X-ray diffraction analysis of ZrPd powder

Note: Based on the X-ray analysis results, the process of “deoxidization treat” is unnecessary for ZrNiPd powder. So only process (1) mentioned above is necessary when ZrNiPd powder is adopted.

2. Experiments and results

We used two kinds of material: nano powder (ZrPd) and powder (ZrNiPd) to investigate the process of D₂ gas loading at the same conditions: the stainless vessel; the weight of powder (16 [g]); the final pressure inside the vessel (P_{in}) is 10-16 [atm].

To make the powder's surface contact with D₂ gas as much as possible, we developed a small new plate shape device inside the reactor, as shown in Fig. 2. Powders are put in every plate with equal weight, and then the experiment is carried out according to the process as mentioned above, namely, process (1-3) and process (3) for nano powder (ZrPd) and powder (ZrNiPd) respectively. Within Fig.2, T_{in} is powder temperature, T_s ($T_{surface} = (T_{surface1} + T_{surface2})/2$) is the temperature of vessel surface and T_f (T_{flange}) is the temperature of the vessel flange and lid.

2.1 Experiment 1 (Energy generation):

Firstly, the above mentioned process (1)-(3) for ZrPd powder and process (1) for ZrNiPd powder was carried out; after that, pure D₂ gas was loaded into the closed vessel with a fixed flow rate ($v_G = 20, 50, 70 \text{ cc/min}$, respectively) until the inner pressure (P_{in}) reaches at the range of 10-16[atm].

Fig. 3 [A] and [B] show the survey data of the temperature change with time applying nano powder (ZrPd) and the powder (ZrNiPd) respectively, using the above mentioned reactor vessel, as shown in

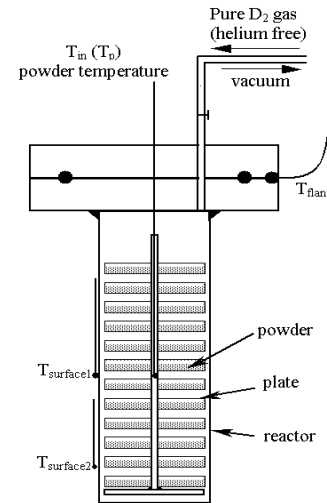


Fig.2 - Fusion reactor

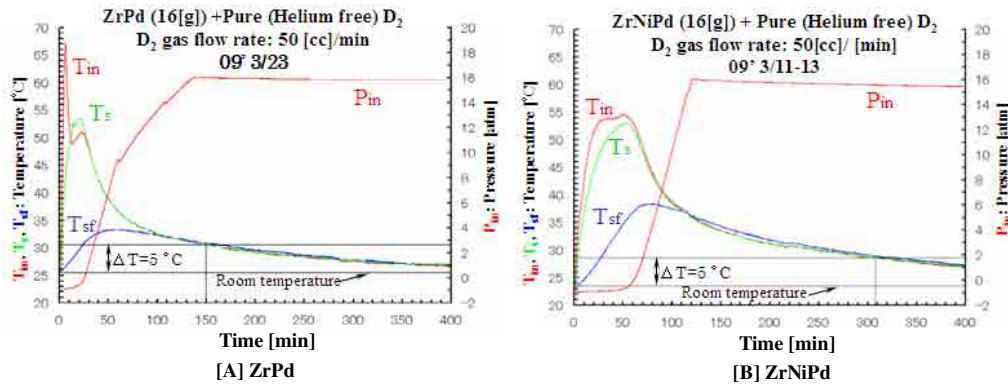


Fig.3 - Distribution of temperature and inner gas pressure

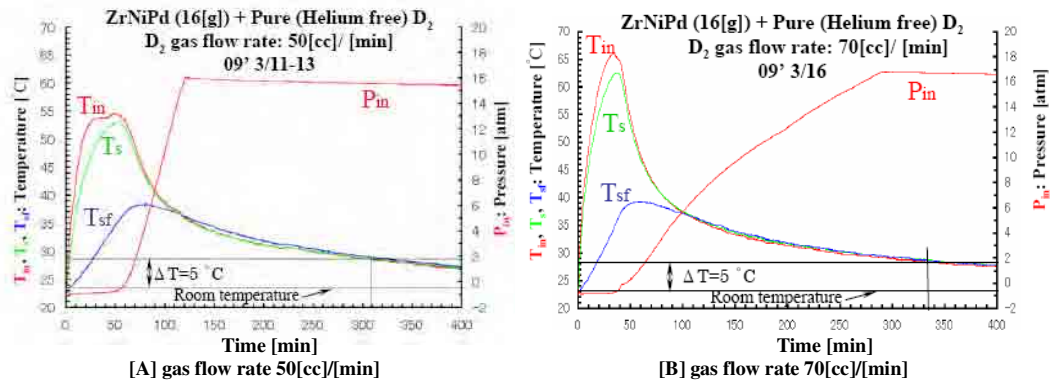


Fig.4 - Distribution of temperature and inner gas pressure

Fig.2. The reactor vessel is cooled in air with shelter during D₂ gas loading. Within Fig.3, T_{in} is powder temperature, T_s ($T_{\text{surface}} = (T_{\text{surface1}} + T_{\text{surface2}})/2$) is the temperature of vessel surface and T_f (T_{flange}) is the temperature of the vessel flange and lid, P_{in} is the pressure inside the reactor vessel.

As for a time interval of 5 [°C] of T_{in}, T_s and T_f above room temperature, Fig.3 [A] (nano powder (ZrPd)) lasts about 150 [min]; Fig.3 [B] lasts about 308 [min]. Namely, the heat that ZrNiPd powder generated is much more than nano powder ZrPd.

Fig. 4[A] and [B] are using the same powder (ZrNiPd (16 [g])), at the same conditions except D₂ gas flow rate. D₂ gas flow rate in Fig. 4[A] and [B] are 50 [cc]/[min] and 70 [cc]/[min] respectively. Comparing the time interval of 5 [°C] above room temperature between [A] and [B], the [B] lasts about 335 [min], it is longer than [A] (about 308 [min]).

Applying this cooling type, we can know the temperature change process of the powder (T_{in}) and the reactor vessel (T_s) during D₂ gas loading. However, the reaction temperature of powder cannot be controlled, so the reaction rate of powder is unable to be kept in a high range. Accordingly, the excess energy cannot be put into practice.

Therefore, to obtain a quantitative excess energy in solid fusion, three cooling type were applied. The sketch of these three cooling type is shown in Fig. 5.

Type-1, the reactor vessel is cooled down in air with shelter; the reaction energy was calculated on the basis of the data of the temperature change of T_{in}, T_s and T_f;

Type-2, the reactor vessel was put in a water bath with a constant water volume at room temperature, and the energy was calculated on the basis of the temperature change of the cooling water. This type makes to get excess energy easily but cannot be controlled for a stable output;

Type-3, the reactor vessel was enclosed by the copper tube, which was welded on the surface of the reactor vessel. During the D₂ gas loading, the reactor was cooled down by the water flowing through the copper tube with the constant water flow rate (40[cc] / [min]); the water was from a water chiller. And then the energy was calculated by the temperature difference between the outlet and inlet of cooling water.

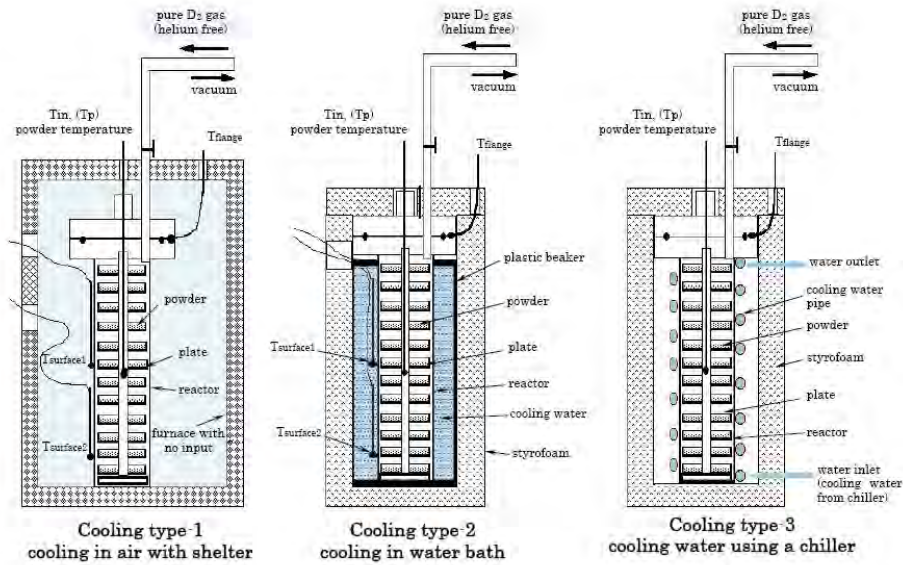


Fig.5 - Three kinds of cooling type during D₂ gas loading

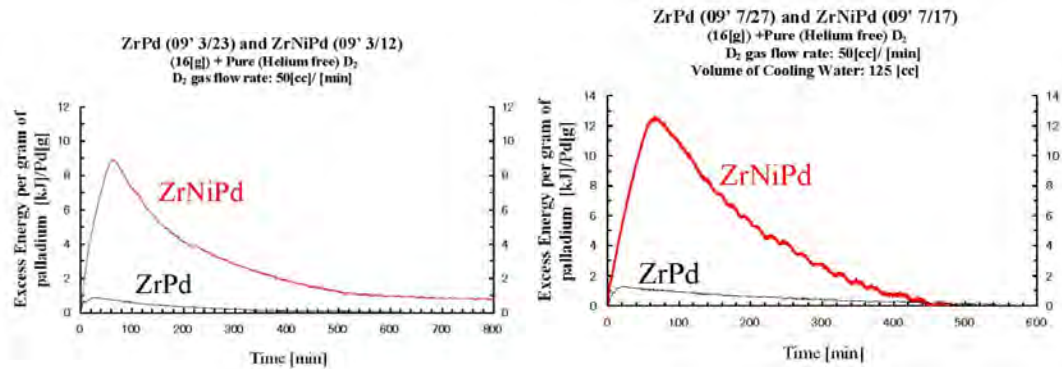


Fig.6 - Excess Energy change with time (cooling type-1)

Fig.7 - Excess Energy change with time (cooling type-2)

Among the three types, the cooling type-3 is the most useful one to get a stable excess power output.

Fig. 6 is one example of using the cooling type-1, which shows the distribution of reaction energy of both the ZrNiPd powder and ZrPd powder. Comparing the excess energy per one-gram palladium between the ZrNiPd powder (red line) and the ZrPd powder (black line), it can be found very clearly that the energy of ZrNiPd powder is larger than that of the ZrPd powder. Also, the same result was obtained by using cooling type-2 as shown in Fig. 7.

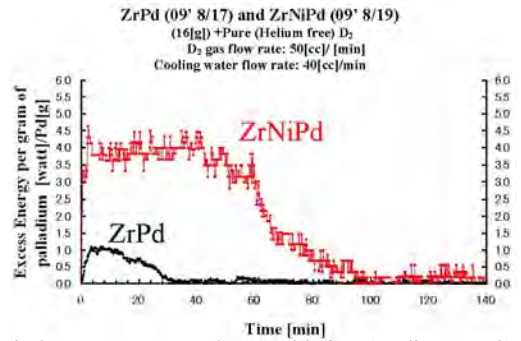


Fig.8 - Excess Energy change with time (cooling type-3)

To obtain the output power change with time precisely, we applied the cooling type-3 for both of ZrNiPd powder and ZrPd powder. The sample weight was 16 [g], cooling water flow rate was 40 [cc] / [min]. Fig. 8 is an example showing the reaction power (per one gram palladium) change with time. In the case of ZrNiPd powder (red line), the generated power is 4 [watt] lasting 60 minutes, then the power dropped gradually with the time last. The total lasting time is about 100 minutes. For the case of ZrPd powder (black line), the generated power is only 1 [watt] lasting only 10 minutes, and the total lasting time is about 32 minutes.

Fig. 9 and Fig. 10 are the comparison of the measuring data among three cooling types. The two

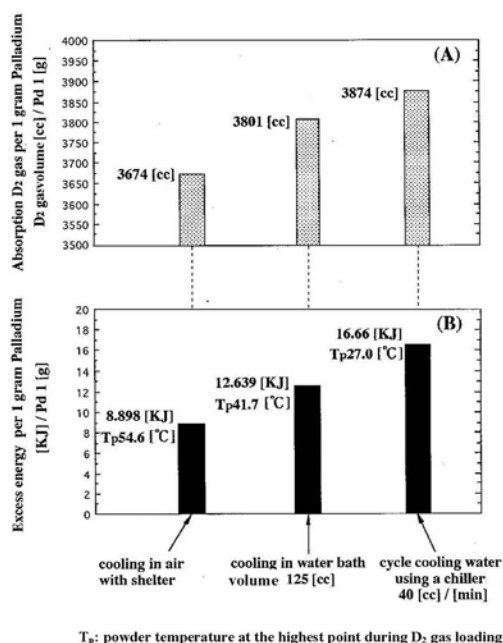


Fig.9 - Absorption volume of D₂ gas and excess energy of the ZrNiPd powder (16[g]) during the pure D₂ gas loading under the same conditions except for the cooling condition.

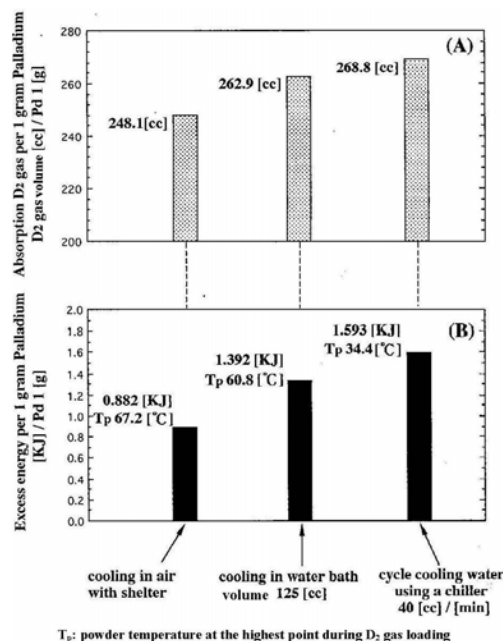


Fig.10 - Absorption volume of D₂ gas and excess energy of the ZrPd₃₅ powder (16[g]) during the pure D₂ gas loading under the same conditions except for the cooling condition.

figures show that the absorption volume of D₂ gas and excess energy changed with the different cooling conditions. Both of the powders, either ZrNiPd or ZrPd, when applying the cooling type-3, the absorption volume of D₂ gas and excess energy are higher while the powder's temperature is lower than other two cooling types during the D₂ gas loading.

Furthermore, the two powder's absorption capacity of D₂ gas and excess energy (per 1 gram palladium) are compared, as shown in Fig 11. Both of the powders, ZrNiPd and ZrPd, are tested with the same conditions and applying two kinds of D₂ gas flow rate. In Fig. 11, we can see, on the case of ZrNiPd powder, the absorption capacity of D₂ gas is fifteen times higher than that of the ZrPd applying the gas flow rate of both 50 [cc]/[min] and 70 [cc]/[min]. Also its excess energy is ten times higher than that of the ZrPd powder.

In the case of the cooling type-1, the reactor was cooled in air with shelter and the powder temperature rose up with the increase of the absorption volume of D₂ gas. The powder temperature cannot be controlled. While using the cooling type-3, the powder temperature can be stably controlled around 25 [°C] as shown in Fig.12.

As we known, the normal palladium absorption capacity of D₂ gas decreases with the rise of temperature. When using the cooling condition of type-1, the powder's temperature is higher than other two, so the absorption capacity of D₂ gas and excess energy is lower than other two types.

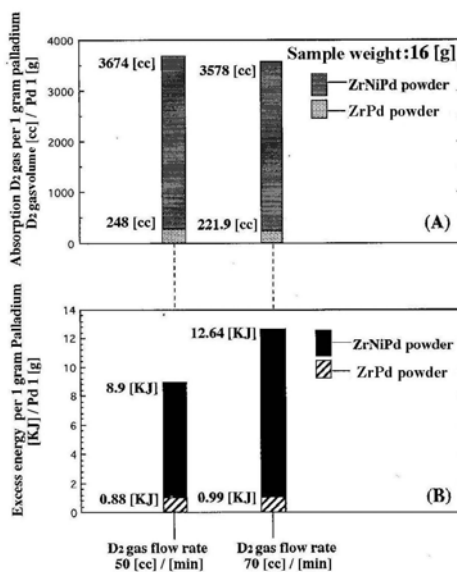


Fig.11 - Comparison of the absorbed D₂ gas volume and excess energy between ZrNiPd powder and ZrPd₃₅ powder under different gas flow rate.

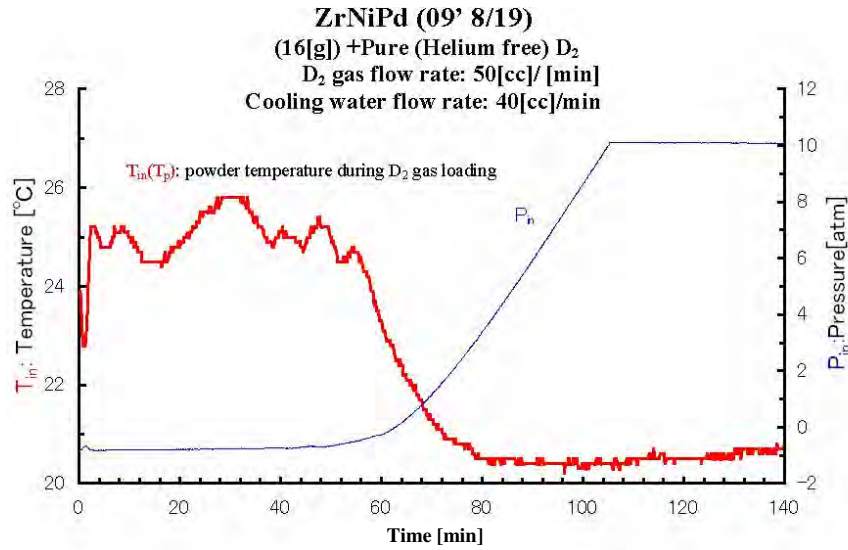


Fig.12 - Powder temperature change with time using the cooling type-3

Therefore, the change of the cooling condition not only decreases the energy losses, but also increases the powder's absorption capacity, which is in favor of increasing the solid fusion reaction rate.

However, it must be confirmed by the fusion reaction products of helium.

2.2 Experiment 2 (Helium generation):

By using quadrupole mass spectrometer -"QMS", the helium can be detected for reacted powders and gas [6]. The helium has been detected many times for reacted powders and gas by using "QMS", as shown in Fig. 13. The "QMS" have two functions: normal resolution and high-resolution test. Both of the gas and powder can be analyzed by the "QMS". The helium can be identified by three kinds of analysis

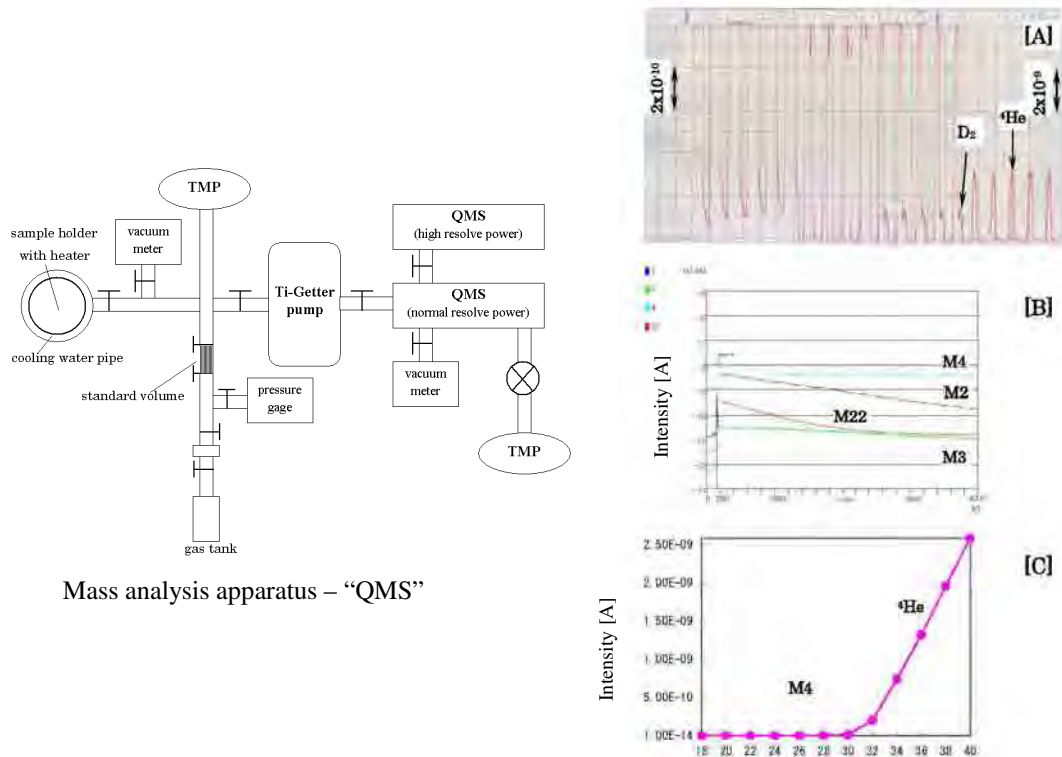


Fig.13 - QMS analysis principle and characteristic

methods. The first one is the normal resolution analysis; the second one is using the high-resolution test to separate the spectrum peak of helium from that of deuteron. During the analysis of gas, both functions of normal and high resolution were applied at the same time. At the right side of Fig. 13, an example of high resolution results is shown (Fig. 13 [A]), the helium (He4) and D_2 were separated clearly; Fig.13 [B] shows the normal resolution analysis result, many mass of element can be detected, because the Ti-getter has the absorption function of hydrogen system gas, but it can not absorb the helium. If the helium exists in the sample gas, the line of mass 4 will finally become parallel after most of D_2 gas absorbed.

The third one, Fig. [C] shows the result of measuring the ionization voltage of the main mass number 4 (helium, deuteron) and number 22 (neon-Ne22) by using ionization mechanism. The ionization voltage of hydrogen system is from 22 [volt] and that of He4 and Ne22 is about 28 ~ 30 [volt]. It can be confirmed whether the He4 or Ne22 exists or not, and the intensity of that element. As we know, the ratio of He4 per Ne22 is near 3 in the case of air gas. According to the measuring results of above mentioned three methods, the existence of helium can be confirmed clearly, and it also can be identified that helium is generated by solid fusion reaction not from air by calculated the element ratio of Helium / Neon 22.

But some people still have a prejudice, doubting it is true or not.

Recently, to make everyone understand clearly at a glance, we performed an interesting experiment: the concentration of helium from the fusion reacted gas. The apparatus's schematic diagram is shown in Fig. 14.

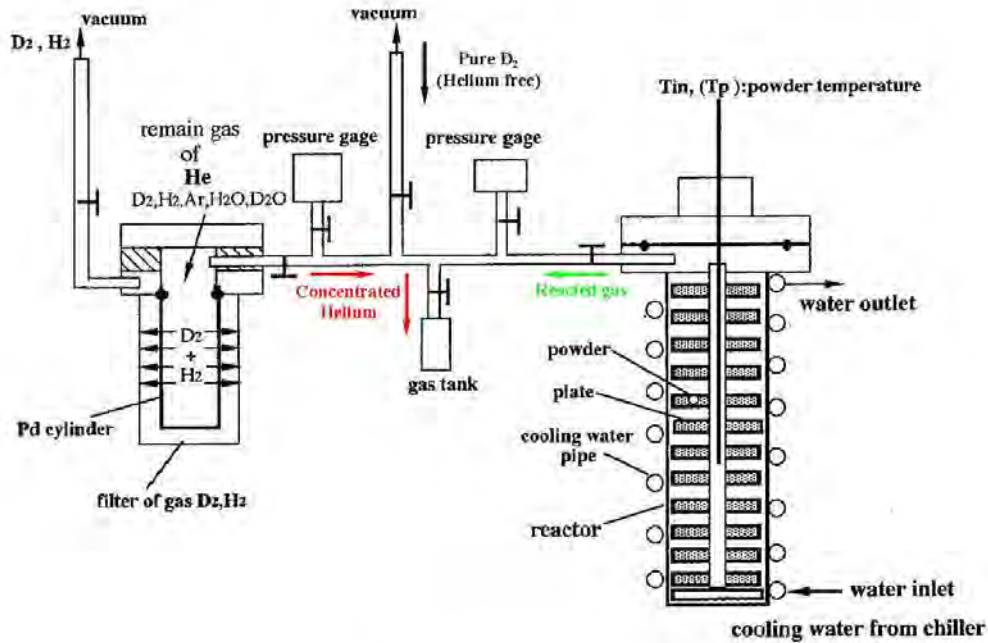


Fig.14 - Concentration apparatus of Helium from reacted gas and powders

By using the palladium filter, the D_2 and H_2 gas were removed from the fusion reacted gas. As results, if helium exists in the reacted gas, it will be concentrated, and we can control the concentration times of the gas easily by controlling the gas pressure.

Fig 15 [A] and [B] shows one example of the mass analysis of the fusion reacted gas of ZrNiPd powder and ZrPd powder (sample weight: 16 [g]). The measuring gas volume is 2.5 [torrcc]; the spectrum peak of Helium and D_2 gas analysis using high resolution mass analysis, the left one shows the reacted gas before concentration, and the right one shows the concentrated gas. You can see helium intensity of the concentrated gas of ZrNiPd is much higher than that of the ZrPd powder.

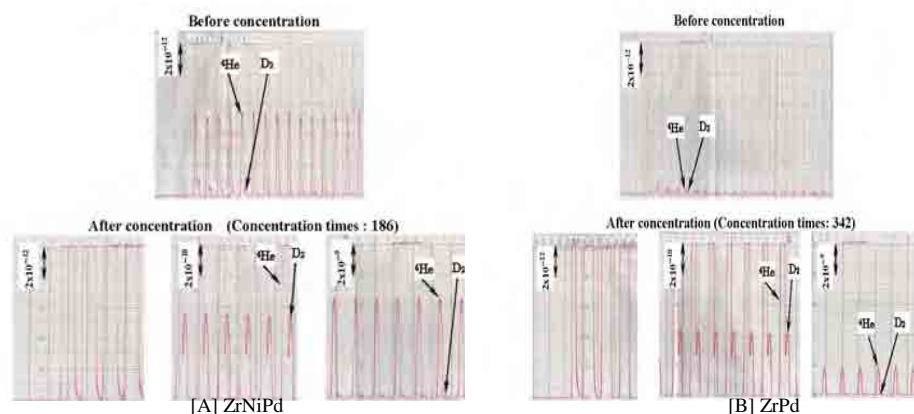


Fig.15 - Spectrum of reaction products by high resolution mass analysis

Helium intensity and the intensity ratio of Helium per Neon22 detected from reacted gas of ZrNiPd powder using "QMS" were shown in Fig.15[C].

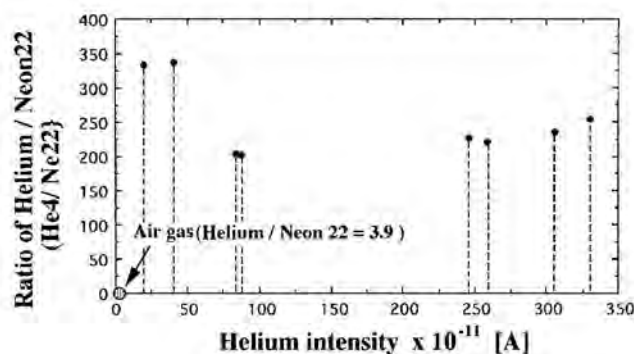


Fig.15[C] - Helium intensity and the intensity ratio of Helium per Neon22 detected from reacted gas of ZrNiPd powder using "QMS"

Fig 16 [A] and [B] is the graph of the mass analysis results of the fusion reacted gas of ZrNiPd powder and ZrPd powder respectively. Sample weight: 16 [g]), the measuring gas volume is 2.5 [torrcc].

Fig. 16 [A] shows the helium intensity relates to the concentration times of the ZrNiPd powder with D₂ gas loading. The helium intensity increases with the increase of the concentration times of the reacted gas. The highest helium intensity is up to 330×10^{-11} [A] after 189 times concentration, which is 654 times of the gas before concentration

And Fig. 16 [B] is the results of ZrPd powder. Like the ZrNiPd powder, the helium intensity also increases with the increase of the concentration times of the reacted gas. The highest helium intensity is 116×10^{-11} [A] after 331 times concentrated.

Comparing Fig.16 [A] and [B], we can see that the highest helium intensity of the concentrated gas of ZrNiPd is much higher than that of the ZrPd powder, even if the concentration time of the former is less than the latter.

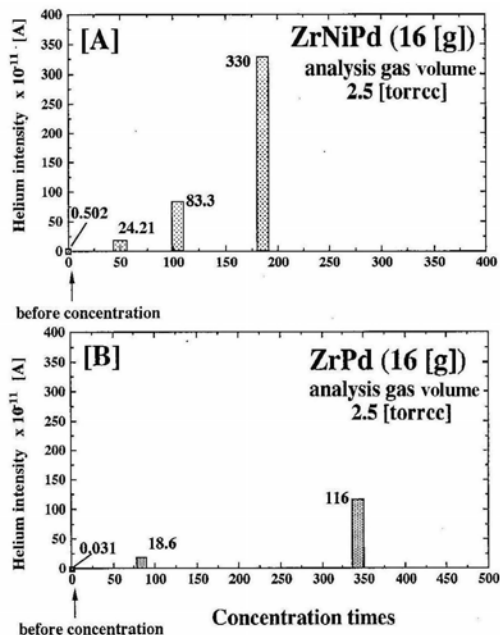


Fig.16 - Helium intensity relation to concentration Times with D₂ loading using cooling type-3

The comparison of the helium intensity of reacted gas with excess energy is shown in Fig. 17. It is the helium intensity per one gram palladium related to the excess energy per one-gram palladium, concentration times is also shown in this figure. We can see ZrNiPd powder generated not only the higher energy but also larger numbers of helium than the ZrPd powder. It indicated the helium intensity increases with the increase of the excess energy.

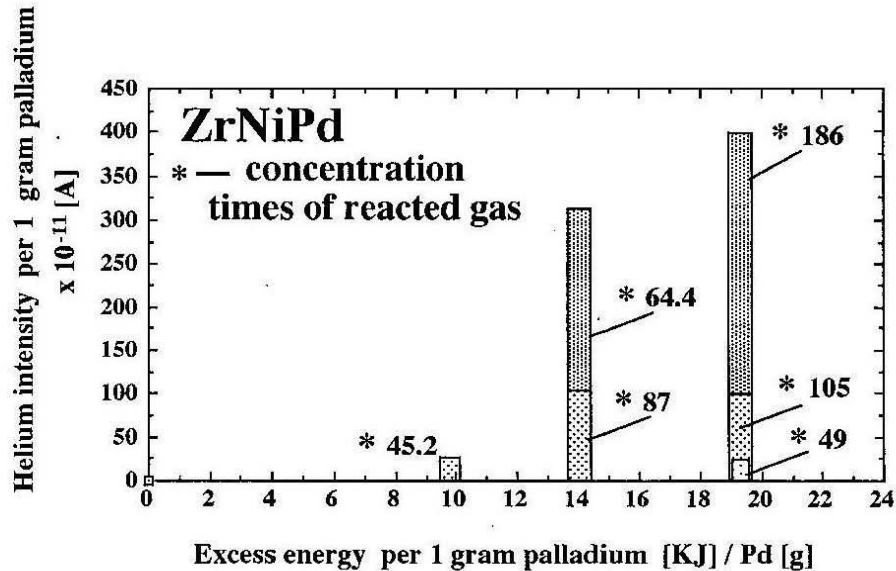


Fig.17 - Comparison of the helium intensity of solid fusion reacted gas with excess energy

3. Conclusions

(1) Both powder of ZrNiPd and ZrPd were used in solid fusion which generated the excess energy and the helium as products of fusion reaction, and the helium were measured many times by using mass analysis apparatus "QMS". As results, as for either excess energy or helium, the ZrNiPd powder is always about ten times higher than the ZrPd powder;

(2) Using the weight 16 [g] of the ZrNiPd powder, the excess power 4 [watt] continued stably for about one hour, and only consumed the palladium less than one gram, its cost is lower than the ZrPd powder and the experiment operation is easy with good reappearance, it is very useful of practical use, so we choose the ZrNiPd powder as a good material for the solid fusion at now;

(3) The concentration of helium was very successful; these results hint that the reacted gas of "solid nuclear fusion" will be a helium source as a helium production. However the powder is made in the ambient atmosphere, accordingly the original powder contains a little other composition like as air gas. Even if after the powder was baked at 150 [°C] for 16 ~20 hours to remove these gases before D₂ gas loading;

Though a trace of the gases still remain in the powder and these remained gases have a higher mass number than mass four, it maybe removed by a centrifugal separator. Of course it's not so easy, and these problems will be solved by a factory, but not by us in laboratory.

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Towards a High Temperature CMNS Reactor: Nano-Coated Pd Wires with D₂ at High Pressures.

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Abstract. There were improved measurements on our reactor presented at ICCF14 (2008): long-thin Pd wires with surfaces nano-coated by multi-layers of several elements, D₂ at P<10bar; wires temp. <500°C; SS reactor wall temperature <100°C; longitudinal current density up to 45 kA/cm² (voltage drop up to 70V); transversal electric field up to 700V/cm. Previous ICCF14 results *confirmed*: anomalous excess power, stable over time and power cycling, up to 400 W/g of Pd. Made a new experiment with D₂-Ar mixture: demonstrated the role of high temperatures (into “nano” Pd-D) to enhance production of anomalous thermal effects. The combined effects of high concentration *and* mobility of D inside Pd seem the key points to get them: models based on **High Temperature** BEC Nuclear Fusion (Kim, Premuda) fits several of our experimental results. Experiments on the planned (new) High Pressure (60 bar) High Temperature (>600 °C) reactor wall are still in progress: experienced *heavy problems* coming out because degassing of impurities (specially S, P) from SS (304, 316) used in the reactor wall. The scavenger effect of H₂ (and D₂) on SS and other materials makes the impurities problem quite difficult to be overcome: designed and build a new, multiple layer wall (SS/Cu 3N), reactor that is now under the stage of final test.

1. Introduction

In the framework of experiments using Pd-based nano-materials and D₂ pressurised gas loading, we developed since 2004 an *hybrid* procedure that, in principle, takes advantage of several reproducible effects up to now introduced both from other Researchers and ourselves: Pd nano-particles, multi-layers, enhanced D diffusion (and D/Pd ratio) by flowing large current on thin Pd wires (with even transversal electric field up to 700V/cm). In short: high temperatures and D forced mobility through nano-Pd.

We recall that the Researcher that, in the field of Condensed Matter Nuclear Science, at first used concentrated Pd nano-particles to increase the D/Pd ratio was Prof. Yoshiaki Arata (Osaka University-Japan) since 1993 [1]; the first that developed multiple nano-layers of Pd-CaO was Dr. Yasuhiro Iwamura (Mitsubishi Heavy Industries, Yokohama-Japan) since 1999 [2]. Both used D₂ gas loading.

Our group applied (since 1995) the so-called *Preparata Effect* [3], to improve the D/Pd ratio on long and thin Pd wires by large voltage drop along the wire itself in electrolytic environments [4], i.e. with

maximum temperature $\ll 100^\circ\text{C}$ (cell not pressurised). In the experiment discussed in [4], was observed also the beneficial effect by coating thin layers of Ni, Li salts (the electrolyte), Pd to the main Pd wire due to side effects of both anodic corrosion of Ni (used as anode) and partial dissolution (and subsequent deposition) of Pd cathode itself due the specific pulsed operation ($T_w = \text{few } \mu\text{s}$) of the kind of electrolysis regime we developed (there was always present a little anodic component of the high power pulse, with voltage up to 200V and rise/fall time of less 100ns, due to inductive reasons). The main drawback of such procedure was that the kind of deposit and thickness was out of any control because both spontaneous and due to side effects (voltage undershoot) of pulses. Starting from 1999 we published several papers [5, 6] where was reported the beneficial effects of addition of soluble salts of alkaline earth elements (Ca, Sr, Ba), at very low concentration (10^{-4}M), in order to improve the D/Pd; moreover, the effect was magnified by several cathodic-anodic regimes: we observed (and published in 2003), by SEM, that Pd surface was similar to *fractals*. Later (2004) the effect to generate fractals was kept under better control by both deposition of proper elements (and subsequent heat treatments) before the use the Pd wire and using gaseous environments ($P = 6\text{bar}$) at wire temperatures of the order of $200\text{--}300^\circ\text{C}$. Since 2007 were made noticeable changing both to the procedure of preparation of the Pd wire and experimental set-up (Fig. 1, Fig. 2) in order to can operate up to about 500°C [7] and measure the Pd wire temperature/power emitted: by 2 similar wires (in Pt) one used as calibrator (Pt_cal) and the other as monitor (Pt_mon). For a deeper understanding of our paper, because of length constraints of the Proceedings, we suggest reading: the ICCF14 paper [7], the ICCF15 oral presentation at: http://iccf15.frascati.enea.it/ICCF15-PRESENTATIONS/S4_O3_Celani.pdf

2. Descriptions

We have made verifications, among others by instrumental improvements, of measurements previously presented at ICCF14 (2008, Washington D.C.-USA) on anomalous excess heat using thin ($\Phi = 50\mu\text{m}$) and long ($l = 65\text{cm}$) Pd wires with surface covered by *several multi-layers of nano-materials* Pd included (nominally: $\Phi = 6\text{--}9\text{nm}$, $S = 300\text{m}^2/\text{g}$; layers thickness $< 1\mu\text{m}$). The excess heat was at macroscopic levels (up to 5W at the highest wire temperature operated of 500°C); the power density was 400W/g of bulk Pd or even larger (up to $5000\text{--}15000\text{ W/g}$) if it is supposed that the main excess heat is generated between the several nano-layers. The current flowing inside the bulk Pd wire was up to 900mA, equivalent to a DC current density of 45 kA/cm^2 . The contribution of nano-layers to the total electric conduction is just *supposed* to be negligible in respect to one of Pd bulk.

* We decided to modify further our previous preparation procedures (very shortly described also at ICCF14, [7]) of nano-coating proper (several) materials onto the Pd wire surface in order to make the nano-coated wire more “resistant” to aging effects due to several, *partial*, loading-unloading cycles.

* In addition, the material of the braid was changed from glassy fibres to pure quartz (in order to can increase wire’s temperature, from about 520°C to 850°C): such changing, in principle, improves the thermal coupling between braids (thermal conductivity of pure SiO_2 is higher than mixed oxides of Si-Na-B glasses) but, at the same time, the overall thermal losses from the hot wires to the cold ($30\text{--}60^\circ\text{C}$) internal wall of the reactor increase (wire temperatures are lower at the same electrical input power).

The main instrumental improvements were: a) addition of another long Pt thermometer surrounding all the previous 3-wires braid (the length of such Pt thermometer was 190 cm, i.e. about 3 times longer in respect to the (Pd-Pt-Pt) wires inserted into the braid); b) addition of others 2 thermocouples inside the pressurized SS chamber; c) external cooling (flow rate of 3–4 cc/s) water’s bath (volume 15 l) temperature made more homogeneous by bubbling air inside it from the bottom. All the data acquired, after correction by calibrations using ^4He , were consistent each-others.

According to our measurement procedures, we made experiments in ^4He (calibrations, Fig. 3) and subsequently in D_2 (Fig. 4) gas atmospheres (both at 6.5 bar). Some crosscheck tests were performed also under vacuum conditions (P about 10^{-5}bar), pure Ar ($1\text{--}5.5\text{bar}$), dry air ($1\text{--}7\text{bar}$).

We made new experiments also with a mixture of $\text{D}_2\text{--Ar}$ ($P = 4.62\text{--}1.68\text{bar}$; Fig. 5). The reason was to study if the effect of larger temperature of Pd wire, at same input power, could compensate for lower pressure of D_2 ($6.5 \rightarrow 4.6\text{ bar}$) or even increase anomalous heat production. Thermal conductivity of Ar is over 7 times lower in respect to D_2 ($T = 35\text{--}90^\circ\text{C}$): in the case of mixture $\text{D}_2\text{--Ar}$ [8], adding 24% of Ar to pure D_2 , the thermal conductivity is reduced (at 95°C) of 56% (from 151 to $96\text{mW}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$).

The answer was that the increase of temperature improved, in a large way, the anomalous heat production and overcame the deleterious effect of D_2 partial pressure reduction. Such important result pushed us to increase the efforts to overcome the technological problems of high temperatures: we get strong indications that, at least in our experimental conditions, the Pd- D_2 system has a “*positive feedback*”

behaviour from the point of view of anomalous heat generation with the increasing of Pd wire temperature. Moreover, after some temperature threshold value has been overcome (about 200°C in our experimental conditions), the energy gain slope looks *larger* than linear versus temperature increase.

3. Key characteristics of nano-coated Pd wires

The loading time to get a 0.8 D/Pd ratio (of the *bulk Pd*) at RT, using pressure of Hydrogen or Deuterium gas of 6.5bar, was of the order of 10-20 second. The gas addition time, from vacuum condition, was 4-5 s. The deloading time, using vacuum and high temperatures, is quite long and depends on the “quality” of nanomaterials deposited on the Pd surface: as a general behaviour, as short was the loading time as long, and difficult, will be the deloading procedure. Several times it was necessary to reach, under vacuum, by Joule heating, temperature as high as 350-400°C for time as long as 1-2 hours, to get an almost “full” deloading. Anyway, we had indications that even such “heavy” procedures did not assure always a fully 100% Deuterium (or Hydrogen) out-gassing from Pd.

The whole effect was observed since 2002 even in electrolytic experiments: we named it the *DIODE EFFECT*. In other words, the good wires adsorb very easily the H₂ or D₂ and such gases, once absorbed, are very difficult to be desorbed.

In addition, we have some indications that the de-loading by direct heating of Pd wire (by Joule effect, and as a consequence some large voltage drop along the long Pd wire) is more difficult than of the deloading in indirect heating conditions (by the Pt_{cal} wire, near the Pd, used as heater, [6]). An innovatively speculative interpretation of such experimental behaviour is that the voltage drop along the Pd wire is operating against the D₂ deloading (possible experimental proof, of *Preparata Effect*).

4. Figure description.

The description of five figures are shortly reported as following:

Fig. 1. Photo of the three wires, each of $\Phi=50\mu\text{m}$ and $l=65\text{cm}$, before insertion in the SS reactor. Each wire (Pd, Pt, Pt) is inserted inside a quartz flexible sheath: they are closely braided each other. The braid is surrounded by several sheets of thermal insulating material (Superwool 607). It is high temperature annealed in air, before the use, to burn the several impregnating oils. Later it is vacuum degassed at 900°C. Similar treatments, at lower temperatures (700°C), are performed to the quartz sheaths.

Fig. 2. Photo of the whole experimental set-up with the SS pressurised reactor surrounded by water tank. The temperature of the water is kept stable by large cooling.

Fig. 3. Diagram of calibrations by ⁴He (at 6.5bar). The wire temperature of Pd is lower (e.g. about 30°C at a Pt temperature of about 480°C) because the increased power dissipation ability of Pd surface due to the nanomaterials coated. Moreover, the apparent detected power is lower (over 1W at an input power of 75W) because nanomaterial effect. The temperature detected by the third Pt wire (Pt_{mon.}), used as monitor, is about 40% of the temperature emitted by the Pd or Pt_{calibration} wires.

Fig. 4. Typical experiment with pure D₂ gas at a pressure of 6.5bar at RT. There are shown the behaviours of R/R₀ of Pd, versus the power applied, both for the power applied to Pd (orange line, direct heating of Pd) and to the Pt_{cal} wire (blue colour). It is noticeable the larger maximum value of R/R₀ (e.g. 2.3) of Pd, with direct heating, in respect to the maximum value with indirect heating (e.g. 2.18). We stress that, in all of our experiments, the maximum value of R/R₀ in direct heating condition is *always* larger in respect to the indirect one. Such behaviour, taking into consideration that the R/R₀ is directly related to D/Pd ratio, can suggest that the large voltage drop along the Pd wire (the so called “*Preparata Effect*”) due the current flowing inside the wire and/or the (new) transversal electric field toward the Pt wires (almost at zero potential) can be the reasons of such completely unexpected (and quite interesting) behaviour. Moreover, the energy gain increases at larger temperatures of Pd wires are due to both the combined effect of transition from β to α phase (larger diffusion coefficient, from $1.8 \cdot 10^{-3}$ to about $4 \cdot 10^{-3} \text{ cm}^2/\text{s}$) and larger temperatures itself (the diffusion speed increase largely increasing the temperature). Such combined effects overcome the reduction of D/Pd ratio (from about 0.8 to about 0.1) that, according to several Authors, will affect negatively the anomalous heat production in D/Pd systems.

Fig. 5. The experiment is like that described in Fig. 4 but with a gas mixture (D₂+Ar) optimised to increase, at the same input power, the wires temperatures. Because of larger temperatures, in spite of reduction of D₂ pressure (from 6.5 to down 4.64 bar), the energy gain increased of about 50% in comparison with pure D₂ experiments. Such behaviour, together with other observation in other our

experiments, suggested us that the *anomalous energy gain*, once overcome the threshold value (about 200°C in such experiments) has a *behaviour larger than linear increasing in Pd wire temperature*.

Fig. 6. Because of the evidence about the relative maximum of R/R_o may be important both for the understanding of the phenomenon of anomalous heat emission (in our experimental conditions) and even for basic studies (like *High Temperature Bose-Einstein Condensate*, see later), *after the Conference*, we assembled a new experimental set-up devoted to study deeper it and rule out the possibility of experimental artefacts. In short, the braid has been wrapped around a small diameter (6/4 mm) Cu tube with a thermocouple inside (called T_{c_inA}): we build a sort of furnace heated externally by the Pd or Pt_{cal} wires. In Fig. 6, apart the temperature measured inside the tube by the insulated thermocouple, it is shown (at high data acquisition rate of 1s) the behaviour of R/R_o of Pd when the power (i.e. under electromigration regime) is applied to Pd itself ($R/R_{o_max}=2.33$) or to the Pt_{cal} ($R/R_o=2.28$).

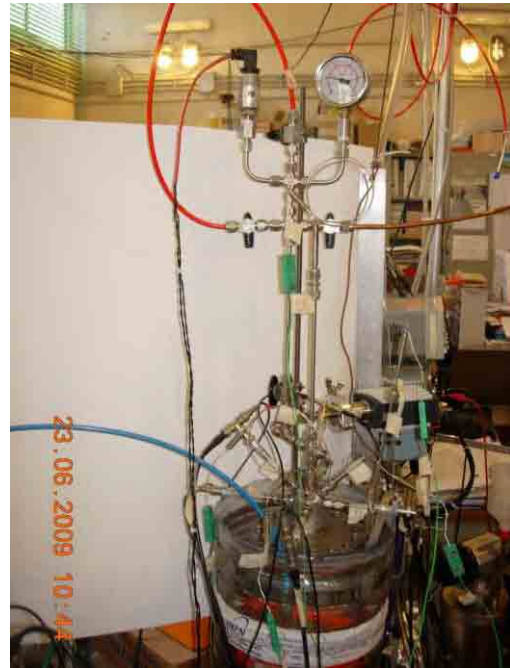


Fig. 1. - Photo of the 3 wires with thermal insulation. Fig. 2. - Photo of the experimental setup.

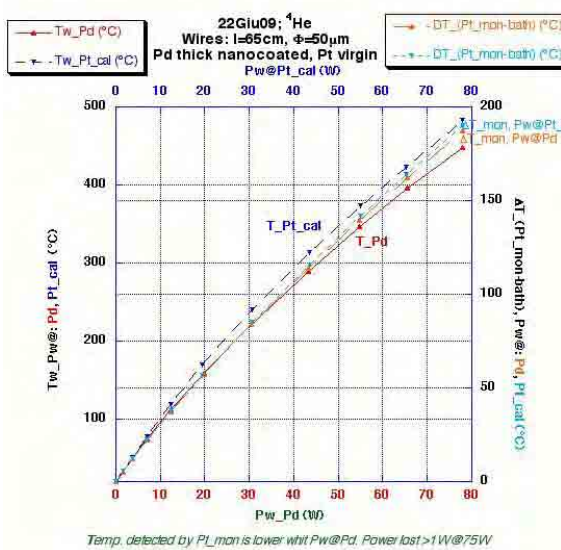


Fig. 3. - Calibration by ^4He .

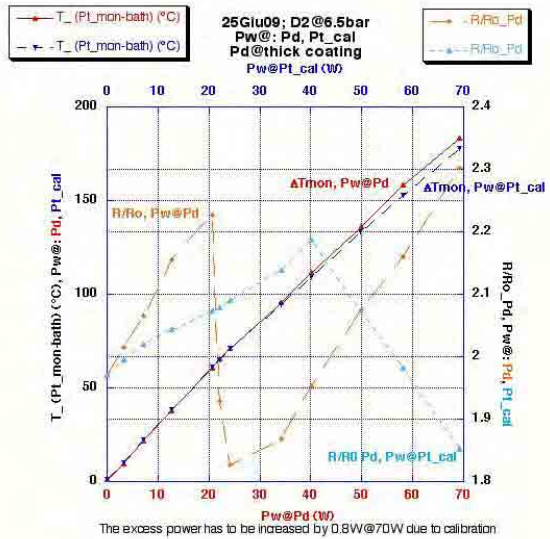


Fig. 4. - Experiment with D_2 pure at 6.5 bar.

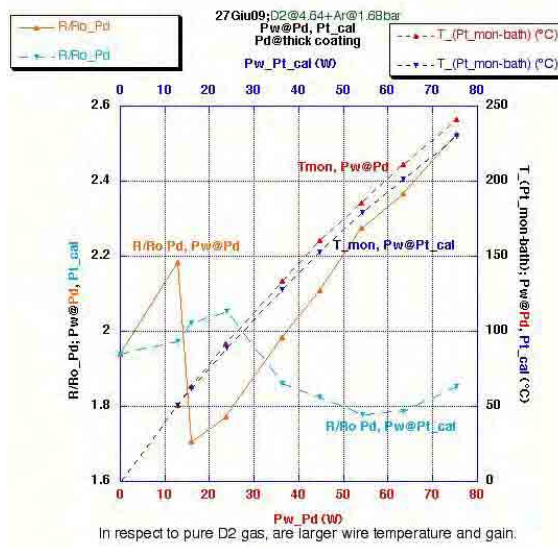


Fig. 5. - Experiment with D₂-Ar mixture.

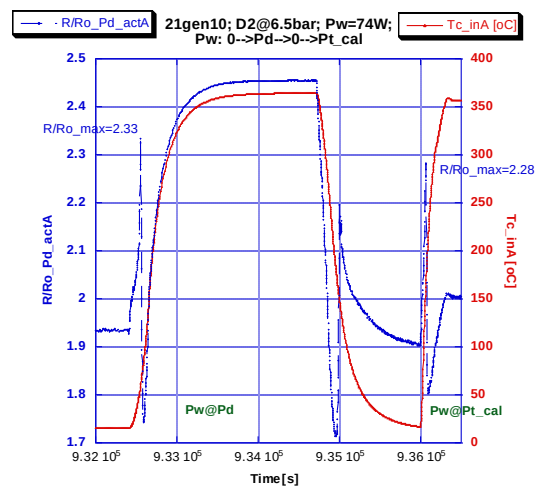


Fig.6. - R/Ro versus kind of power applied.

5. Conclusions

According to the experimental results we can argue that:

- 1) The data presented at ICCF14 were reconfirmed/reinforced (experiment with D₂+Ar mixture);
- 2) There are indications that increasing the temperature (e.g. the experiment with pure D₂ against the mixing D₂+Ar: at 70W of input power the Pt calibration temperature was 460°C in pure D₂ and 560°C in Ar+D₂) and (probably) the pressure on nanocoated Pd wires can be possible to increase the gain. We hope that our improved (multi-layer: SS&Cu 3N) high temperature and pressure reactor (in construction) will allow to overcome the problem of “poisons” coming out from the reactor wall (at least, we identified the S, at 300-700 ppm concentration, that is always present in the typical SS AISI 304 and 316 used for pressurized vessel). The general problem of S was introduced in same details, in the CMNS experiments, by Tatsumi Hioki (and Collaborators) from Toyota Company [9] since 2007 during ICCF13 (Sochi, Russia).
- 3) The new specific nanocoating of Pd wires improved their overall stability against “aging” effects due to loading-unloading cycles (the length of wire is weakly affected by such effect).
- 4) The well known, deleterious, effect of decreasing the amount of excess heat production after the “first” cycle seems not to be present in our experimental materials, set-up and operating conditions. *We can imagine that the continuous flowing of “fresh” Deuterium inside and through the Pd surface “clean up” the ashes of CMNS reactions.*
- 5) Because there are several indications that the system, in our experimental operating conditions, can have behaviour of “positive feedback” versus the temperature, some efforts have to be done to find a procedure to keep the “reactor” under **full control**, specially at temperatures of 700-850°C where the theoretic Carnot efficiency is quite high (of the order of 70%). The Carnot efficiency is the quality factor for practical applications: conversion of heat to “noble” energy.
- 6) Y. E. Kim (Purdue Univ., USA) suggested that the experimental, fully reproducible, evidence of a R/Ro values of Pd larger with direct heating (i.e. power applied, or better to say current-voltage, to Pd wire) in respect to indirect one (e.g. Fig. 4, 5, 6), can be explained as a proof of *Bose-Einstein Condensation* in Pd-D system [10]. F. Premuda (Bologna Univ., Italy) introduced since 1993 the BEC as possible explanation of anomalies in D-Pd systems [11]. Our opinion is that such experimental evidence (if reproduced also in other Laboratories) is the result of several combined conditions: a) voltage drop (and/or large current flowing: e⁻) along the long and thin Pd wire; b) large temperatures that reinforce the D flowing; c) effect of nanomaterials at the surface of the Pd wire (we experienced D/Pd ratio in nanomaterials even >1).
- 7) More work is needed both to increase the anomalous heat generation and identify the nuclear channels of the reaction (e.g. ⁴He, transmutations, isotope changing,...).

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* The welding group (Mr. Urbano **Martini**, Aldo **Olivieri** and Alessandro **Cassarà**), at INFN-LNF, made very patient and accurate work during the soldering of SS vessel: operations both in vacuum and pressure.

* We can't forget the continuous support/advice of the INFN-LNF Director Prof. Mario **Calvetti**.

* As quoted in the introduction, our work was also “inspired” by the experiments with nano-Pd (up to the recent Pd₃₅Zr₆₅ and Zr₆₅-Ni₃₀-Pd₅) absorbing Deuterium, as pioneered by Academician Yoshiaki **Arata** (Osaka University, Japan). Replication experiments (with Pd₃₅Zr₆₅ produced by Santoku Company at Kobe tanks to joint collaboration University-Industry), performed by Akito **Takahashi**-Akira **Kitamura** group (respectively at Technova Inc., Tokyo and Kobe University, Japan), reinforced both the Y. Arata results and our decision to pursue the nano-material “route” [12]. The pioneering work on multi-layer Pd-CaO, performed by Yasuhiro **Iwamura** group (at MHI, Yokohama, Japan), give some hints to develop our simplified “Atomic Layer Deposition” process made by chemical-thermal-mechanical procedures. Obviously, the system operated in tunneling regimes because of small dimensionality and the expertise/comments of Nobel Laureate Brian **Josephson** were important for us. The experiments performed independently by Prof. Li Xing Zhong (Tsinghua University, China; from 2002) and Jan Paul **Biberian** (Marseille University, France; from 2006) using Pd tubes (with even surface oxidized) reconfirmed the importance of surfaces/nanomaterials to promote anomalous thermal effects, although not stable versus time (surface damaged by the reaction itself). In deep discussions with the previous Scientist helped us to avoid mistakes and optimize our operations: we are deeply indebted with them.

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Hydrogen/Deuterium Absorption Property of Pd Fine Particle Systems and Heat Evolution Associated with Hydrogen/Deuterium Loading

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Abstract. Hydrogen absorption capacity and heat evolution upon loading with hydrogen/deuterium gas were measured for Pd-ZrO₂ nanocomposite obtained from Santoku Corporation. In order to examine the influence of oxidized Pd on both hydrogen absorption capacity and heat evolution, the measurements were performed three times repeatedly. Prior to each measurement, the samples were heat treated in vacuum at 523K for more than 2 hours. The first time measurement gave an apparent H/Pd ratio of 2.6 and a heat evolution of 2.6eV/Pd. During the first time measurement, the oxidized Pd was reduced to metallic Pd. It was found that the H/Pd ratio at 1MPa was slightly smaller than that of Pd bulk. It was also noted that Pd nanoparticles grow significantly during the cycles of absorption and desorption of hydrogen. When the sample was loaded with deuterium, intermittent heat evolutions as small as at most 0.1W were observed in the second stage where heat evolutions arising from chemical reactions were hardly expected.

1. Introduction

A very simple solid nuclear fusion reactor has recently been proposed by Arata and Zhang [1]. They have used a material of nano-sized (~5nm) Pd particles dispersed in ZrO₂ matrix. By simply pressurizing the material with deuterium gas, they have observed a long lasting difference in the temperature between the center of the sample powder and the outside surface of the sample vessel. When the sample was loaded with hydrogen gas, no such temperature difference was observed. Furthermore, by using a quadrupole mass spectrometer, they have observed a significant increase of ⁴He for the gas sampled from the powder pressurized with deuterium gas. From these facts, they have claimed a heat evolution arising from a deuteron-deuteron nuclear fusion reaction yielding ⁴He as ash.

Kitamura et al. [2] have constructed a flow calorimeter and measured quantitatively the heat evolution associated with loading of hydrogen or deuterium gas for Pd-ZrO₂ nanocomposite with Pd particle size of ~10nm. The material was obtained from Santoku Corporation and was different from those used by Arata and Zhang. Kitamura et al. have clearly observed a difference in the heat evolution between the loadings with deuterium and hydrogen in the second phase where heat evolution due to chemical reactions is not expected [2]. What seems to be important in the Arata and Zhang's experiment is that they have attained a very high value of hydrogen absorption capacity per Pd atom, i.e. D/Pd or H/Pd ratio, by using nano-sized Pd material. It has been known that attaining a D/Pd ratio larger than 0.88 is favorable to observe an excess heat in the electrochemical loading of Pd with deuterium [3]. Actually, a high value of hydrogen absorption capacity has been reported for nanoscale Pd particles embedded in ZrO₂ matrix prepared from Zr-Pd amorphous alloys [4]. Kitamura et al. [2] also reported a D/Pd or H/Pd ratio of 1.1 for the Santoku's Pd-ZrO₂ composite material, which far exceeds the reported value [5] of 0.74 for Pd bulk.

We have started to investigate the relationships between Pd particle size, hydrogen/deuterium absorption capacity and heat evolution upon loading with hydrogen/deuterium gas for nanoPd materials.

The results for Pd nanopowder and Pd- γ Al₂O₃ composite have been reported elsewhere [6]. In this paper, a similar study has been extended to Pd-ZrO₂ composite obtained from Santoku Corporation.

2. Experimental

2.1 Materials

The material used in this study was a composite of nanoPd and ZrO₂ (Pd-ZrO₂) synthesized by Santoku Corporation. The X ray diffraction pattern for the as-received sample showed that it consisted from PdO and ZrO₂. The contained amount of PdO was 35.4wt%. The crystal phases of the ZrO₂ component were monoclinic and tetragonal. The contained amount of each phase was roughly equal. The specific area was 38m²/g. As a reference for Pd bulk, Pd foils (99.95%, The Nilaco Corporation) with dimensions of 8mm×30mm×0.025mm were used.

2.2 Hydrogen storage capacity

A pressure-composition (PC) isotherm apparatus (Suzuki Shokan Co. Ltd) was used to measure hydrogen absorption capacity as a function of pressure up to about 1MPa at room temperature (300K). The purity of hydrogen and deuterium was 99.99999% and 99.995%, respectively.

2.3 Calorimetry

The heat evolution associated with loading of hydrogen isotope gas was measured with a flow calorimeter. The difference in the temperature between the inlet and outlet of the cooling water was measured with thermocouples of alumel-chromel. The flow rate of water was measured by using a Coriolis-force type flow meter. The temperature difference and the flow rate of water were registered every 30 seconds and used to calculate the heat power. An electric heater was mounted at the center of the sample vessel and used to determine the recovery rate of heat, i.e. the ratio of the calculated heat power with the measured temperature difference and the flow rate of water to the heat power supplied by the electric heater. A value of 0.55 was used as the recovery rate, which was almost independent on the species of the used gas (H₂, D₂, He), the gas pressure in the range 0 ~1 MPa, and the electric heater power in the range of 1~5W. In order to suppress the fluctuation and the drift of the measured output power, the calorimeter system was thermally insulated from the ambient atmosphere by using a thermal insulation material. The accuracy of the calorimeter was ± 50 mW. The gases were supplied into the sample vessel through a needle valve and a mass flow controller. The flow rate of gas was about 20ml/min.

3. Results and discussion

3.1 Hydrogen absorption capacity

The as-received Pd-ZrO₂ composite sample of about 10g was mounted in the sample vessel of the PC isotherm apparatus. First, in order to remove absorbed gases or molecules, the sample was evacuated for a day, heated up to 523K in vacuum and maintained at the temperature for about 2 hours, followed by natural cooling to room temperature. After these pre-treatments, hydrogen gas was supplied to the sample until the pressure of the sample vessel reaches a given value. At around the given pressure, about 30minutes were needed to achieve an equilibrium pressure. Thus, the hydrogen pressure was increased step by step up to 1MPa. After the course of this first time measurement, the sample was again evacuated for a day, heated up to 523K and maintained at the temperature for about 2 hours, followed by natural cooling to room temperature. Then, the second time measurement was performed following the same procedure as those of the first time.

In Fig.1, the relationship between pressure and composition (H/Pd) are shown for three times successive measurements. It is seen that in the first time measurement, H/Pd ratio at 1MPa reaches a value of 2.6, while this value decreases greatly to a value of 0.70 in the second and third measurements. This difference is attributed to the fact that the Pd particles are initially oxidized and reduce to metallic Pd during the first time measurement. Then, in the first time measurement both of the following chemical reactions occur :



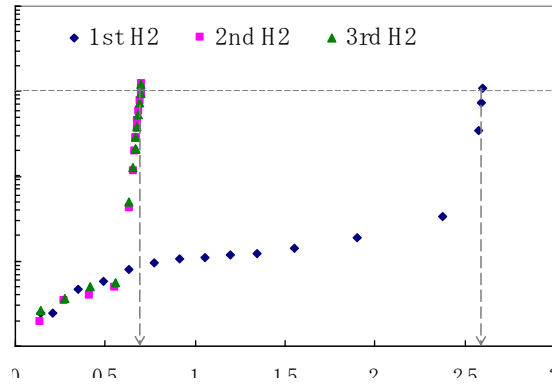


Fig.1 - Pressure- composition isotherms for Pd-ZrO₂ composite. The results of three times repeated measurements are shown.



The water formation reaction (1) gives an apparent H/Pd ratio of 2.0, and the hydride formation reaction (2) gives a true value of hydrogen absorption capacity x . The value of x is obtained from the experiment in the second or the third time measurement and x is 0.70 as seen in Fig.1. Therefore, when the Pd particles are nearly 100% oxidized, an apparent H/Pd ratio of ~ 2.7 is obtained. The observed value of 2.6 indicates that 95% of Pd in the as- received sample is in the chemical state of PdO.

The PC isotherms were also measured for Pd foil samples of about 3g. The measurements were repeated two times. For this sample, no difference in the H/Pd ratio at 1MPa was seen between the two measurements, indicating that the foil sample was nearly 100% metallic. The H/Pd ratio for this sample was 0.74. This value agrees with the literature value [5] for Pd bulk. Therefore, the H/Pd value of 0.70 for the Pd-ZrO₂ composite sample is slightly smaller than the value of Pd bulk. This is contrary to the expectation that the hydrogen absorption capacity for nano-sized Pd particles is increased compared to that for Pd bulk. Similar results have been observed for Pd nanopowder and Pd- γ Al₂O₃ composite, as reported elsewhere [6].

3. 2 STEM observation

In order to examine the size and distribution of the Pd particles, scanning transmission electron microscope (STEM) observations with an electron beam focused to less than 1nm were performed for the samples as-received and after the three times PC isotherm measurements. From Fig.2 (a), it is seen that the size of the Pd particles (white spot) for the as-received state is roughly about 10nm. Fig.2 (b) and (c) show the lateral distribution of characteristic Zr(L) and Pd(L) X-ray intensity, respectively. It is seen from Fig.2 (b), (c) or from Fig.3 (b), (c) that the Pd particles do not distribute uniformly in the ZrO₂ matrix. From Fig.3(a), it is seen that the size of the Pd particles after the PC measurement is 15-20nm, which is significantly larger the initial value. This fact indicates that Pd particles grow during the hydrogen absorption and desorption cycles. Similar growth of Pd nanoparticles during the cycles of absorption and desorption of hydrogen has also been reported for nanoPd powder and Pd- γ Al₂O₃ composite [6]. It should be mentioned that the measured H/Pd ratio, i.e. 0.70, is for Pd particles with a size significantly larger than the initial value determined for the as-synthesized sample.

3.3 Heat evolution upon loading with hydrogen isotope gases

The as-received Pd-ZrO₂ composite sample of 51.4g (Pd :15.6g) was mounted in the sample vessel of the calorimeter. The sample was first evacuated for two days and heated up to 523K in vacuum and maintained at the temperature for about 2 hours, followed by natural cooling to room temperature. Then, deuterium gas was supplied to the sample at a flow rate of 20ml/min with a mass flow controller up to 0.4MPa. From 0.4MPa to 1.0MPa, the flow rate was controlled manually with a needle valve, and the

flow rate was in the range 20–40ml/min. When the pressure reached the value of 1MPa the gas supply was stopped and the sample was maintained under the fixed pressure of 1MPa. Here, we define the first stage as the period where the pressure was raised from 0 to 1 MPa, the second stage as the period where the sample was maintained under the constant pressure of 1MPa. As in the case of hydrogen absorption capacity measurements, the measurement of heat generation upon loading of deuterium /hydrogen gas was repeated three times. Prior to each measurement, the sample was heat treated in the same way as the first time measurement. In Fig.4 (a), (b) and (c), the heat power as a function of time is shown for the first time loading with D₂, the second time loading with D₂ and the third time loading with H₂, respectively. The variation of pressure with time is also shown in Fig.4. It is clearly seen that the heat evolution in the first stage is remarkable in the first time measurement while it decreases greatly in the second or third time measurement. This behavior is quite similar to that of hydrogen absorption capacity, suggesting that the heat evolution in the first stage is related with the chemical reactions (1) and (2). In fig.5, the variation of the heat evolution in the first stage with the order of measurement cycle is shown. The experimental values are compared to the estimated ones. The estimation was made assuming that in the first time measurement, both of the reactions (1) and (2) contribute to the heat evolution while only the reaction (2) in the second and third time measurements. The values of $\Delta H(\text{water})=-178\text{kJ/molPd}$ [7] and $\Delta H(\text{hydride})=-40\text{kJ/molH}_2$ [8] were used. It was further assumed that $\Delta H(\text{hydride}) = \Delta H(\text{deuteride})$ and the ratio of the oxidized Pd to the total Pd before the first time measurement was 95%. It is seen in Fig.5 that the heat generated in the first stage is largely explained by the chemical reactions (1) and (2). Therefore, in the first stage it is difficult to identify the heat evolution from nuclear origin, if any. However, in the second stage, any chemical reactions are hardly expected to occur. In Fig.6, the same figure as Fig.5 is shown with the vertical axis magnified by ten times. It is noted that in the second stage a small heat evolution is observed intermittently for the first and second time loadings with D₂ while no such heat evolution is observed in the third loading with H₂. Similar behavior of heat evolution in the second stage has also been reported for nanoPd power and Pd- γ Al₂O₃ composite [6]. The heat evolution of the second stage observed in the present study seems to be considerably smaller compared to that reported by Kitamura et al. [2]. It is required to enhance the heat power in the second stage in order to clarify the origin of the observed anomalous heat evolution.

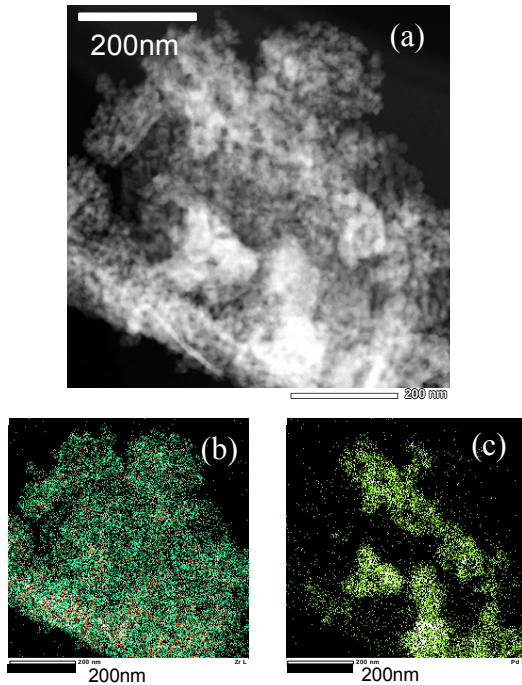


Fig.2 - (a)STEM image of the as-received sample, (b) Zr(L) image, (c) Pd(L)image

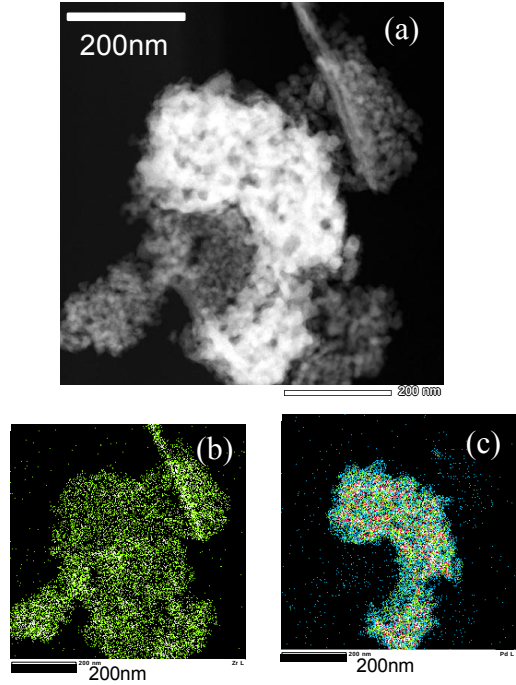


Fig.3 - (a)STEM image after measurements of H/Pd, (b) Zr(L) image, (c) Pd(L) image

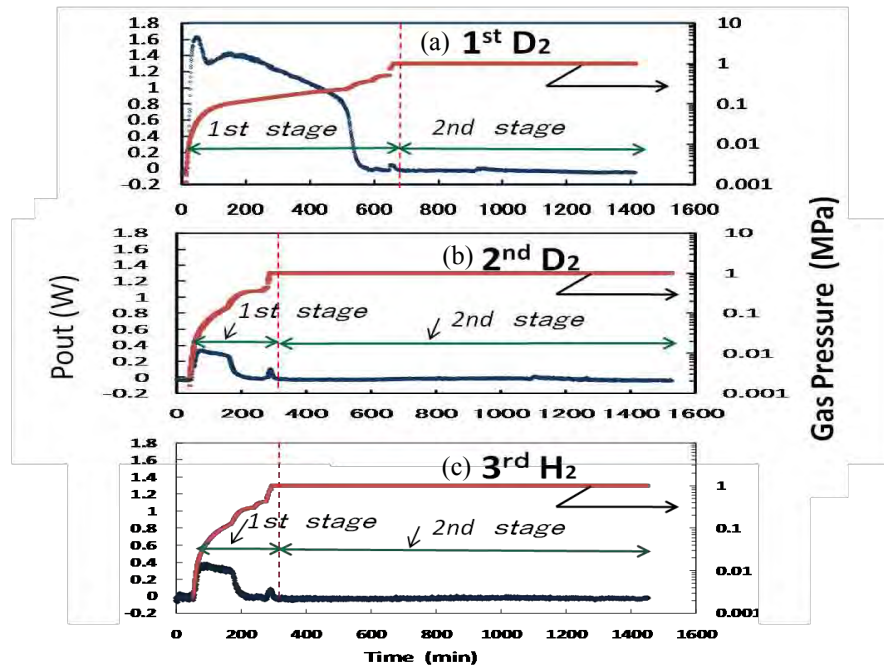


Fig.4 - Heat power and gas pressure as a function of time for Pd-ZrO₂; (a) the first cycle loading with D₂, (b) the second cycle loading with D₂, (c) the third cycle loading with H₂.

4. Summary

Hydrogen absorption capacity and heat evolution with loading of hydrogen isotope gases were measured for composite samples of Pd-ZrO₂ obtained from Sankoku Corporation. The followings were found.

- (1) The chemical state of Pd in the as received powder was 95% PdO. As a result, the first time loading with hydrogen gave an apparent hydrogen absorption capacity at 1MPa as large as H/Pd = 2.6 and heat evolution in the first stage as large as 2.6eV/Pd. These values are largely understood by taking into account the two chemical reactions; the water formation reaction and the hydride formation reaction. The PdO was reduced to metallic Pd during the first time measurement.
- (2) In the second or third time measurement of hydrogen absorption capacity, a true value of H/Pd = 0.70 was obtained. This value is slightly smaller than the value of Pd bulk.

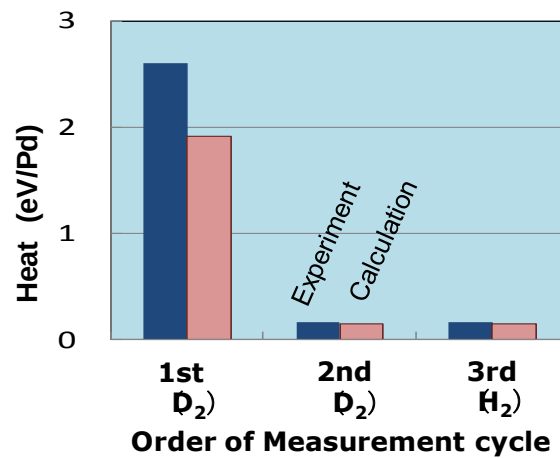


Fig.5 - The variation of the heat generated in the first stage with the order of measurement cycle. The experimental values are compared to the calculated ones.

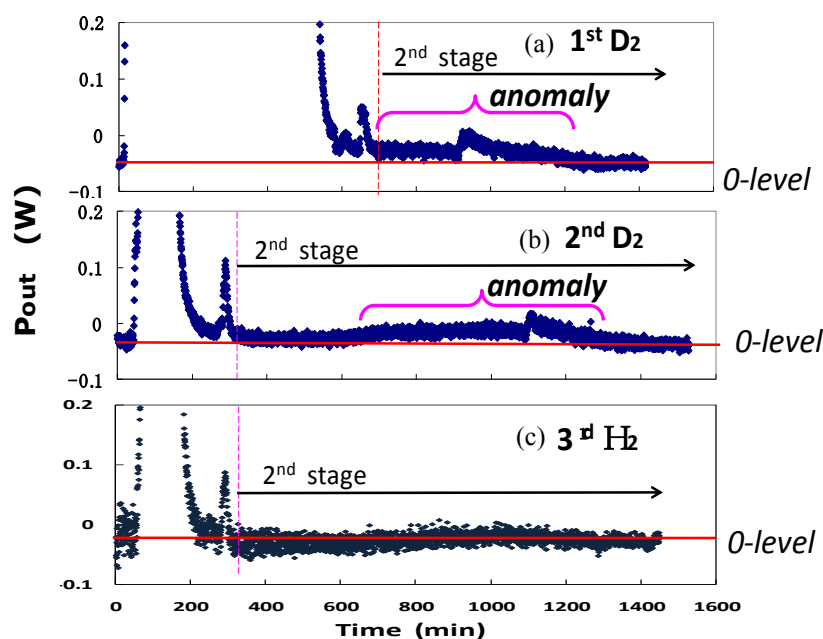


Fig.6 - Heat evolution in the second stage. The vertical axis of Fig.3 is magnified by ~ 10 times.
 (a) the first cycle loading with D₂, (b) the second cycle loading with D₂, (c) the third cycle loading with H₂.

(3) The size of the Pd particles was found to be increased significantly during the repeated measurements of hydrogen absorption capacity.

(4) When the sample was loaded with D₂ gas, a very small heat power was observed intermittently in the second stage where chemical reactions are hardly expected to occur.

Acknowledgement

We greatly thank N. Suzuki for the STEM observations.

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Anomalous Heat Generation in Charging of Pd Powders with High Density Hydrogen Isotopes, (I) Results of absorption experiments using Pd powders

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Abstract. A twin system for hydrogen-isotope absorption experiments has been constructed to replicate the phenomenon of heat and ⁴He generation by D₂ gas absorption in nano-sized Pd powders reported by Arata and Zhang, and to investigate the underlying physics. For Pd-Zr oxide nano-powders, anomalously large energies of hydrogen isotope absorption, 2.4 ± 0.2 eV/D-atom and 1.8 ± 0.4 eV/H-atom, as well as large loading ratio of D/Pd = 1.1 ± 0.0 and H/Pd = 1.1 ± 0.3 , respectively, were observed in the phase of deuteride/hydride formation. The sample charged with D₂ also showed significantly positive output energy in the second phase after the deuteride formation. For comparison, results for 0.1- $\mu\text{m}\phi$ Pd powder samples and Pd-black samples are also shown..

1. Introduction

Arata and Zhang recently reported that highly pure D₂ gas charging of Pd nano-powders in the form of Pd/ZrO₂ nano-composite induced significantly higher temperatures inside the reactor vessel than on the outside wall for more than 50 hours, while runs with H₂ gas showed almost no temperature difference.¹⁾ To verify that the excess heat originated in a nuclear process, a QMAS was employed to show the existence of ⁴He as nuclear ash in the vessel and in the powder after the charging. The charging system is a sophisticated and simplified version of the previous-generation DS reactor²⁾. Replication experiments using systems similar to the DS reactor with Pd-black seem to be successful^{3,4)}. It is extremely important to confirm the phenomenon of heat and ⁴He generation with fully quantitative confidence.

In the present work we constructed an experimental system to replicate the phenomenon and to investigate the underlying physics. Two lots of oxide samples of mixture of Pd (34.6 %) and Zr (65.4 %) were fabricated by Santoku Corporation, Kobe, Japan. The first sample had an average particle size of 7.7 μm , a specific surface area of 37.1 m²/g, and had an average Pd grain size of 10.7 nm, while the second sample had 8.5 nm Pd grain size. If we assume perfect oxidation of the metal elements, 10 g of the sample contains 3.0 g of Pd.

2. Experimental system

The D₂/H₂ absorption system is composed of two identical chambers (an A₁-A₂ twin system): one for a D₂ gas foreground run, and the other for H₂ gas background run. As shown in Fig.1 and Fig.2 each part has an inner reaction chamber containing Pd powder and an outer chamber that is evacuated to provide thermal insulation for calorimetry. A sheath heater and a cooling water pipe (copper) are wound on the outer surface of the reaction chamber for baking the sample powder and for flow calorimetry to estimate the heat production rate, respectively. A pair of thermocouples is provided for the flow calorimetry by measuring the temperature difference between the inlet and the outlet of the cooling water.

The D_2 gas is nominally 99.5 % pure and the H_2 is 99.998 % pure. Flow rate control of D_2/H_2 gas purified through a liquid-nitrogen cold trap is made either with a Pd membrane filter or a 'SuperNEEDLE' valve. The gas flow rate is controllable between 1 and 1000 sccm at 1Mpa by the latter. All parameters measured are stored in a PC with an acquisition period of 1 min.

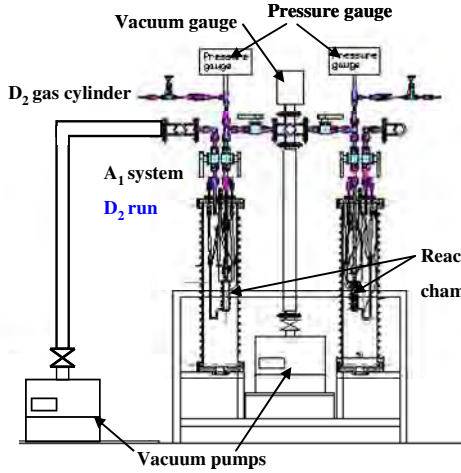


Fig. 1. - Reduced view of the A_1 - A_2 twin system

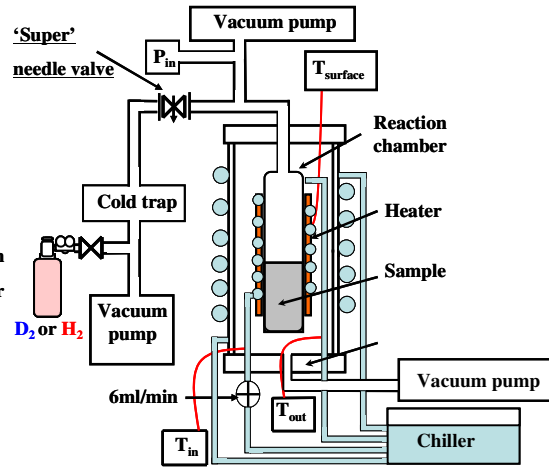


Fig. 2. - Functional view of A_1

3. Preliminary experiments

As a calibration of the flow calorimeter, we measured the heat recovery rate under a variety of conditions; with input power of 1, 3, 6 and 10 W, and D_2 gas pressure of 0, 0.1, 0.3 and 1.0 MPa in the reaction chamber. The coolant flow rate was 6 ml/min in all cases. The heat recovery rate was found to be almost independent of the pressure and the input power, and the averaged value is $(63.1 \pm 5.8) \%$. Temperature response to a stepwise variation of the input power was found to be expressed as a simple exponential function with a time constant of 5.2 min.

We examined temperature uncertainty and drift, with no sample powder put in the A_1 chamber filled with H_2 gas at a pressure of 1MPa. The inlet-outlet temperature difference and the output power deduced from it showed short-term fluctuation as shown in Fig.3. If we regard an experimental error in the present system as the standard deviation of the longitudinal data, the error or the uncertainty for the output power and the integrated output energy measured for the A_1 - A_2 system is evaluated to be 0.014 W and 0.83 kJ for 1000-min acquisition. In the prototype system A_0 , which had the larger time constant and smaller sensitivity of heat measurement, and was used in the 1st stage experiments with the 0.1- $\mu\text{m}\phi$ Pd powder and the Pd-black⁵⁾, a temperature drift observed sometimes resulted in the larger error of 4.0 kJ for 1000-min run.

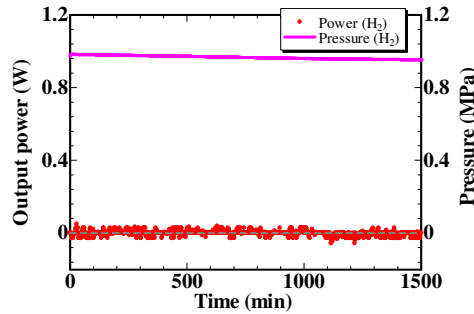


Fig.3. - Blank run with no sample powder.

4. Samples

We used three kinds of samples—PP (Pd powder with particle diameter of 0.1 μm and a purity of 99.5 %), PB (Pd-black with a particle size of “300 mesh”) and PZ (purity of 99.9 %, and mixed oxides of Pd·Zr). Figure 4 shows TEM images of the second lot PZ sample taken by courtesy of Prof. R. Duncan *et al.*, the Nuclear Science and Engineering Institute and Particulate Systems Research Center at the University of Missouri-Columbia.

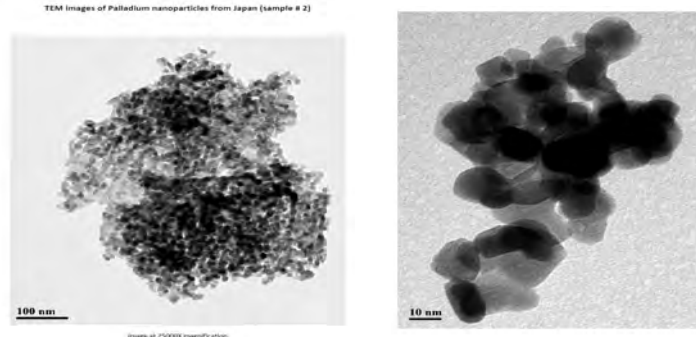


Fig.4. - TEM images of the PZ sample (the second lot).

In the following, the run number is designated by “G-PN#M”, with G, P, N and M being the gas species, the powder species, powder ID, and the number of repeated use, respectively. For example, “D-PB2#3” represents the third absorption run with D_2 using a Pd-black sample “2” following evacuation and baking after two cycles of evacuation-baking-absorption.

5. Results

5.1 Results by $\phi 0.1\mu\text{m}$ -Pd powder

First, we describe absorption runs using the A_0 system for five gram of 0.1- $\mu\text{m}\phi$ Pd powder. The reaction chamber filled with the powder was evacuated and heated for baking at 430 K. Then highly pure D_2 or H_2 gas was introduced into the reaction chamber through the Pd membrane filter. The results for the case of D_2 and H_2 absorption are compared in Fig.5. After the gas was introduced, pressure did not begin to rise for a while. During this phase (the first phase) the Pd powder absorbed almost all of the D_2 (H_2) gas atoms as they flowed in, and heat was released as a result of adsorption and formation of deuterides (hydrides). After about 30 minutes, the powder almost stopped absorbing gas; the gas pressure began to rise, and the heat release from deuteride (hydride) formation subsided. This is the beginning of the 2nd phase, and the gas flow rate in the 1st phase is evaluated from the rate of the pressure increase. From the flow rate multiplied by the duration of the 1st phase, loading was estimated to reach $\text{PdD}_{0.43}$ ($\text{PdH}_{0.44}$).

The output powers are integrated over the 1st phase to give the output energies of 0.10 kJ/g-Pd(D) and 0.08 kJ/g-Pd(H), which are divided by the loading ratio of 0.43 and 0.44 to give the heat of solution ΔH_s .

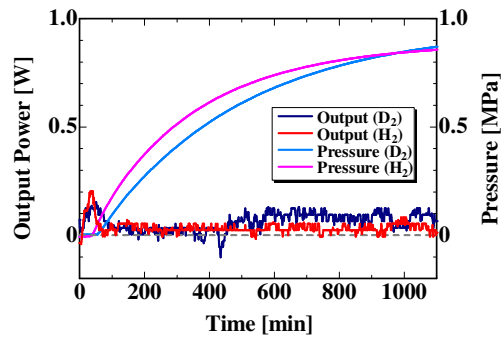


Fig. 5 - Evolution of heat and pressure in the vessel after introduction of D_2 gas (blue/light blue) or H_2 gas (red/pink) to 0.1- $\mu\text{m}\phi$ Pd powder (D-PP1#1 and H-PP2#1). Power is slightly higher for D than H after 500 min.

of 0.24 eV/atom-D and 0.20 eV/atom-H, respectively. The values appear to be somewhat larger than those found in literatures⁶⁻¹⁰. However, they are consistent with each other, when we take into account that the differential heat of solution is a decreasing function of the loading ratio; $\Delta H_s = 0.15, 0.12, 0.070$, and 0.061 eV/H for H/Pd ratio of 0.5, 0.55, 0.6 and 0.65^{9,10}. The difference between D and H, the isotope effect, is rather large, but is not considered to be anomalous, since we find $\Delta H_s(D)/\Delta H_s(H) = 1.25$ in ref. [9]. On the other hand, the output energies in the 2nd phase, *i.e.*, the output powers integrated over the 2nd phase with duration of 1,400 min, are smaller than the experimental error mentioned above, and “excess heat” is not meaningful in this case. The results are summarized in Table I, which includes those for the Pd-black and the Pd-Zr mixed oxide samples.

5.2 Results by Pd-black

The second kind of the sample tested is commercially available 300-mesh Pd-black whose surface has a kind of nano-scale fractal structure finer than the $0.1\text{-}\mu\text{m}\phi$ Pd powder. The performance of Pd-black absorption of D₂ using the A₀ system is compared with that of H₂ in Fig. 6. It is very interesting to note that: (1) much higher loading to PdD_{0.88} or PdH_{0.79} is realized, and (2) the output energies in the 1st phase, $E_{1st} = (0.67 \pm 0.12)$ eV/atom-D and (0.62 ± 0.11) eV/atom-H, are 2 - 3 times larger than those for the $0.1\text{-}\mu\text{m}\phi$ Pd powder and those found in the literatures⁶⁻¹⁰. On the other hand, the output energy of 8.3 ± 4.5 kJ (2.6 ± 1.4 kJ/g-Pd) in the 2nd phase of D₂ absorption appears to be larger than that in the case of H₂. The difference is only marginal compared with the above-mentioned error due to the temperature drift of 5.5 kJ in the present case.

Using the improved twin system A₁-A₂, we compared the performance of the Pd-black sample PB3 with a prolonged duration of the 2nd phase of 4,500 min, which was subjected to repeated use with the sample baking before absorption made at 440 K for 3 h (#2), or at 570 K for 1 h (#3). The results are shown in the 6th row through the 8th in Table I.

First we notice that the first run (D-PB3#1) has essentially the same D/Pd ratio and the energy output E_{1st} as those with the A₀ system. Second the repeated use retains almost the same or even higher energy output E_{1st} in spite of the significantly smaller D(H)/Pd ratio. This interesting fact could be related to some structural change of the sample.

As for the 2nd phase, we have little to discuss, when we take into account that they are comparable to the error of 4.0 kJ/1000-min mentioned above for the A₀ system.

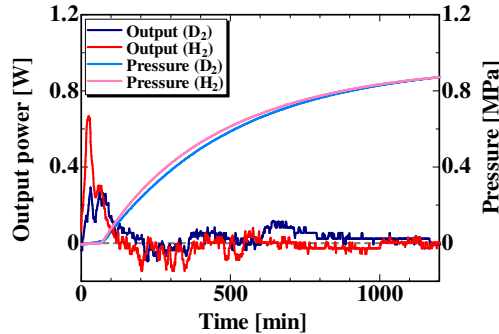


Fig.6. - Evolution of heat and pressure in the vessel after introduction of D₂ gas (blue/light blue) or H₂ gas (red/pink) to 300-mesh Pd-black (D-PB1#1 and H-PB2#1). Power is slightly higher for D than H in the 2nd phase.

5.3 Results by Pd-Zr oxide compounds

Now we describe the performance of the mixed oxides of Pd-Zr that are thought to have even finer mesoscopic structure. The results of 8 runs using virgin PZ samples are summarized in the last 8 rows in Table I. Those of runs with repeated use of the PZ sample will be discussed in the next paper¹² together with the above-mentioned PB samples. Using the A₁-A₂ twin system, the runs H-PZ(2n)#1 were performed simultaneously with D-PZ(2n-1)#1, where $n = 1, 2, 3$, and 5. The A₁ subsystem was used for D-PZ1#1, D-PZ3#1, H-PZ6#1, and D-PZ9#1. In all runs, the PZ sample used was 10 g, and the baking

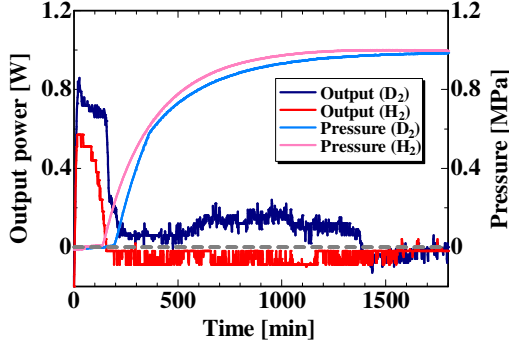


Fig. 7 - Evolution of heat and pressure in the vessel after introduction of D₂ gas (blue/light blue) or H₂ gas (red/pink) to Pd-Zr oxide compounds (D-PZ1#1 and H-PZ2#1). Heat-power level by D is larger than that by H in the 1st phase and also in the 2nd phase.

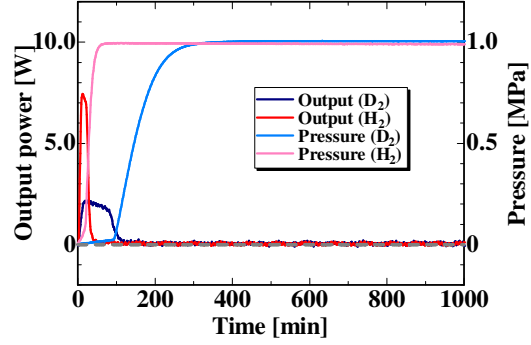


Fig. 8 - Evolution of heat and pressure in the vessel after introduction of D₂ gas (blue/light blue) or H₂ gas (red/pink) to Pd-Zr oxide compounds (D-PZ9#1 and H-PZ10#1).

temperature was 570 K for 3 h. The output energy in the 2nd phase is the power integrated over 1,600 min. In PZ1~6, we use the 10.7-nm sample, while in PZ9 and 10, we use the 8.5-nm sample. Examples of the evolution of the output power and the pressure for runs D-PZ1#1 and H-PZ2#1 are shown in Fig. 7. And D-PZ9#1 and H-PZ10#1 are shown in Fig. 8.

Table I. Comparison of absorption runs for the 0.1- $\mu\text{m}\phi$ Pd powder (PP), the 300-mesh Pd-black (PB), and the Pd-Zr nano-composite (PZ).

run	weight	flow rate	Output energy[kJ]		Specific output energy[kJ/g]		D/Pd or H/Pd	E per D/H atom
	[g]	[sccm]	1st phase	2nd phase	1st phase	2nd phase		
D-PP1#1	5	3.5	0.5 $\pm$ 0.4	2.5 $\pm$ 4.1	0.10 $\pm$ 0.07	0.52 $\pm$ 0.83	0.46	0.24
D-PP1#2	5	4.3	0.5 $\pm$ 0.2	4.0 $\pm$ 4.4	0.10 $\pm$ 0.05	0.79 $\pm$ 0.88	0.43	0.26
H-PP2#1	5	6.8	0.4 $\pm$ 0.2	2.6 $\pm$ 3.9	0.08 $\pm$ 0.003	0.53 $\pm$ 0.8	0.45	0.20
D-PB1#1	3.2	3.5	1.7 $\pm$ 0.3	8.3 $\pm$ 4.5	0.54 $\pm$ 0.1	2.6 $\pm$ 1.4	0.85	0.69
H-PB2#1	3.6	5.6	1.6 $\pm$ 0.3	-2.2 $\pm$ 4.6	0.45 $\pm$ 0.08	-0.62 $\pm$ 1.3	0.78	0.63
D-PB3#1	20	2.9	9.3 $\pm$ 1.1	1.1 $\pm$ 0.5	0.47 $\pm$ 0.06	0.06 $\pm$ 0.02	0.78	0.66
D-PB3#2	20	0.8	3.3 $\pm$ 0.5	3.4 $\pm$ 2.6	0.17 $\pm$ 0.03	0.17 $\pm$ 0.13	0.23	0.79
H-PB4#2	20	1.9	3.2 $\pm$ 0.2	14 $\pm$ 4.6	0.16 $\pm$ 0.01	0.68 $\pm$ 0.23	0.22	0.80
H-PB4#3	20	1.5	16 $\pm$ 2.4	-4.8 $\pm$ 8.1	0.79 $\pm$ 0.01	-0.24 $\pm$ 0.40	0.20	4.42
D-PB3#3	20	1.1	14 $\pm$ 1.7	-2.2 $\pm$ 1.1	0.68 $\pm$ 0.01	-1.1 $\pm$ 0.54	0.22	3.51
D-PB3#4	20	1.1	3.1 $\pm$ 0.4	0.3 $\pm$ 4.7	0.16 $\pm$ 0.02	0.02 $\pm$ 0.23	0.24	0.71
D-PZ1#1	10	1.76	7.0 $\pm$ 0.2	6.8 $\pm$ 1.3	1.3 $\pm$ 0.04	1.9 $\pm$ 0.31	1.08	2.39
H-PZ2#1	10	2.29	3.6 $\pm$ 0.1	-5.1 $\pm$ 1.4	1.0 $\pm$ 0.03	-1.5 $\pm$ 0.32	1.00	1.33
D-PZ3#1	10	1.85	6.4 $\pm$ 0.2	5.5 $\pm$ 0.8	2.13 $\pm$ 0.0	1.2 $\pm$ 0.2	1.07	2.20
H-PZ4#1	10	2.93	5.1 $\pm$ 0.1	1.1 $\pm$ 0.9	1.70 $\pm$ 0.0	-1.3 $\pm$ 0.2	0.86	2.18
D-PZ3#2	10	1.66	0.17 $\pm$ 0.03	9.89 $\pm$ 1.48	0.03 $\pm$ 0.07	2.3 $\pm$ 0.35	0.29	0.13
H-PZ4#2	10	2.79	0.58 $\pm$ 0.05	1.68 $\pm$ 1.46	0.17 $\pm$ 0.01	0.39 $\pm$ 0.34	0.31	0.59
D-PZ3#3	10	1.69	0.29 $\pm$ 0.04	-3.47 $\pm$ 0.34	0.07 $\pm$ 0.09	-0.81 $\pm$ 0.35	0.25	0.29
H-PZ4#3	10	2.99	0.37 $\pm$ 0.02	0.75 $\pm$ 0.35	0.01 $\pm$ 0.01	0.17 $\pm$ 0.34	0.26	0.42
D-PZ5#1	10	2.02	7.14 $\pm$ 0.15	1.26 $\pm$ 1.36	2.37 $\pm$ 0.04	0.29 $\pm$ 0.32	1.04	2.51
H-PZ6#1	10	6.23	7.07 $\pm$ 0.07	-0.23 $\pm$ 1.44	2.33 $\pm$ 0.02	-0.05 $\pm$ 0.33	1.41	1.82
D-PZ5#3	10	9.93	0.54 $\pm$ 0.03	0.23 $\pm$ 1.51	0.18 $\pm$ 0.01	0.08 $\pm$ 0.50	0.25	0.74
H-PZ6#3	10	10.69	0.92 $\pm$ 0.03	4.18 $\pm$ 1.51	0.31 $\pm$ 0.01	1.39 $\pm$ 0.50	0.30	1.10
D-PZ9#1	14	6.42	10.23 $\pm$ 0.10	3.81 $\pm$ 1.51	2.44 $\pm$ 0.02	0.91 $\pm$ 0.36	1.41	1.87
H-PZ10#1	14	22.55	9.56 $\pm$ 0.03	3.82 $\pm$ 1.51	2.28 $\pm$ 0.01	0.91 $\pm$ 0.36	1.02	2.46

We notice the following five facts in the 1st phase: (1) very large output energies that are more than 3 times greater than those for the Pd-black samples, (2) very large D/Pd (H/PD) ratios of 1.1 ± 0.0 (1.1 ± 0.3) that are even higher than those for the PB samples, (3) surprisingly large $E_{1st} = (2.4 \pm 0.2)$ eV (D) and (1.8 ± 0.4) eV (H) on the average, and (4) larger isotope effect in E_{1st} compared with those for 0.1- $\mu\text{m}\phi$ powder and Pd-black; the difference just exceeds the error range determined from standard deviations, (5) the output energy increases with increasing flow rate.

For the 1st phase heat data of D-PZ9#1 and H-PZ10#1, we observed that power levels increased almost proportionally to the increase of flow rates. In the 2nd phase, D-PZ9#1 has no positive net output heat. The sample size and the flow rates are thought to be causally related to this phenomenon. In the PZ9 and 10, the flow rates might have been set too large to get the positive net output heat, because the faster formation of the saturated pressure condition might affect the dynamic condition. We need further study by changing the flow rate to this respect.

In two runs using H₂, we have negative integrated values for the specific output energies in the rather stable 2nd phases. This should be considered to be due to a slight shift in the zero point of the thermocouple signal.

Finally, it should be mentioned that we observed nothing other than steady background in the neutron counter and the scintillation probe located just outside the outer chambers.

Further discussions and conclusions on the results and a possible underlying physics are given in the succeeding paper¹²⁾ in this Proceedings.

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Yes, Virginia there is Heat, but It is Likely of Chemical Origin

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Abstract. Gas loading of palladium particles <2 nm in size produces anomalous amounts of heat in a reproducible manner. This heat is produced in the presence of deuterium but not in the presence of hydrogen. Control experiments have ruled out the excess heat was due to impurities in the deuterium that were absent in the hydrogen. Because the system is simple and mostly reversible, all extra heat must be of chemical or some other origin. Neither radiation nor nuclear “ash” was found to correlate with the anomalous heat. In some matrices, the likely source of the anomalous heat is D-H exchange with the water present in the matrix, where an approximate third increase of the expected energy from calculations can account for most of the excess heat. In other matrices, no simple explanation of the excess heat can be made.

1. Introduction

Palladium electrochemically loaded with sufficient amounts of deuterium has been reported to produce anomalous amounts of heat that may be nuclear in origin.¹ The complete requirements for heat production have not been determined. However, one criterion for having a high likelihood of producing heat appears to be that the D-Pd ratio must be above 0.9.² Electrochemical loading of palladium can reach these high levels, which correspond to 10⁵ to 10⁶ atmospheres³ of deuterium overpressure in bulk palladium – a challenge for simple gas pressurization. Pressure alone appears to be insufficient, because Isaac, *et al.* had pressurized palladium with deuterium in a diamond anvil cell and saw no radiation emitted.⁴ Although a temperature change was observed, it was attributed to instrumental drifts.

Most of these claims of excess heat have been dismissed as experimental error rather than nuclear chemistry because almost any conventional nuclear event, such as D-D fusion, should produce some form of radiation (X-rays, neutron, gamma rays) or transmuted atoms (nuclear “ash”). Given the amount of heat claimed, these should be easily detectable.⁵ No convincing evidence of radiation nor transmutations have been reported⁶ and the calorimetry results are sometimes called into question.⁷

As unidentified sources of anomalous heat appear to be the major signature of this process, we investigated the heat production in a gas loading system - a simpler system than electrochemical loading - with the goals of: (1) reproducible heat production, (2) careful attention to heat measurements and energy losses and inputs, and (3) understanding of substrate matrix preparation and instrumentation.

Gas loading experiments have the advantage that the system can be reversible – the heat generated upon pressurization due to the work of pressurization of the gas and the uptake of hydrogen/deuterium into the palladium matrix and spillover of that hydrogen to the support is subsequently taken-up upon evacuation. Any net energy (endothermic or exothermic) from a pressurization/depressurization cycle must come from an irreversible event such as a chemical reaction. Typical reactions and processes that must be considered are the initial reduction of PdO to Pd metal and water, water absorption by the matrix,⁸ oxidation of the hydrogen/deuterium by adventitious oxygen in the gas or absorbed on surfaces, water in the gas binding to the matrix, the Joule-Thompson effect⁹, a change in the matrix lattice with pressure, or D-H exchange with water in the matrix or surface hydroxyls. Most chemical reactions produce gaseous materials that can be monitored by sampling the gas in the cell, or they consume the pressurization gas and cause a pressure drop and thereby signal their presence. Thus, all the reactions listed above should make themselves known, or their effect (such as a change in lattice structure) should quickly be lost during

pressurization/depressurization cycles. Additionally, except for D-H exchange, pressurization with deuterium should produce similar amounts of heat as pressurization with hydrogen *i.e.* any chemical isotope effect should be small.

The consideration that the D/Pd ratio must be near 0.9 for anomalous heat to appear² puts constraints on the size of the palladium particles for gas loading at reasonable pressures. In 1908, Paal and Gerum reported H/Pd of 0.98 measured volumetrically at atmospheric pressure using palladium black prepared with hydrazine.¹⁰ Since that report, most H/Pd ratios on pressurized palladium particles fall in the range of 0.6-0.8 at room temperature (similar to bulk palladium) – increasing at lower temperatures and decreasing at higher temperatures.³ Recently, two groups have reported that they can reach H/Pd ratios near one by decreasing the particle size on certain supports, but this ratio appears to be highly size dependant.^{18,19} A summary of data calculated from Huang, *et al.*, is shown in Table 1.

Table 1. Estimated particle sizes and H/Pd ratios as calculated from the data in reference 19. Note the sensitive dependence of the loading ratio with particle size and the rapid increase in particle size with percent Pd. The more chemically accessible particles (> 5 nm) show a loading similar to bulk palladium of 0.6.

Preparation	Estimated Particle Size (nm)	Heat of Hydrogen Adsorption (kJ/mole)	Ratio H:Pd @ 0.2 bar
Pd Powder	9	94	0.55
1.86% Pd/SiO ₂ (IW)	~4	92	0.68
1% Pd/SiO ₂ (SG)	1.1	131	0.9
0.5% Pd/SiO ₂ (SG)	1	183	1.05

It is difficult to prepare palladium colloids less than 5 nm in diameter as palladium tends to catalyze its own growth.^{11,12} Possibility, Paul and Gerum had a procedure to prepare sufficiently small palladium particles that they absorbed large amounts of hydrogen.¹³ Rather than prepare palladium colloids with their inherent irreproducibility, we focused on preparing nanoparticles in an oxide matrix where the growth is limited by the pore size and availability of atoms. We focused on zeolites because the pore size is about 1 nm and should allow growth of more uniform particles. Also, zeolites are thermally stable so that the high temperatures potentially reached by the particles during pressurization do not degrade the support and the zeolites should help isolate the particles and prevent their coalescence with pressure/temperature cycling.

This paper describes the preparations of some matrices that show an anomalous amount of irreversible heat produced in gas loading and discusses that this heat could be due to Deuterium-Hydrogen (D-H) exchange. Trace levels of neutrons and tritium above background have been seen in some gas loading experiments by other authors.¹⁴ Long term heat also has been reported by other authors that is difficult to explain using conventional chemistry.^{15,16,17} We have been unable to confirm any of these observations in our gas-loading systems.

2. Experimental

We constructed our own data acquisition interface so that we had control over all the design parameters. Two basic systems were designed (GC oven and Hart calorimeter) with a common data acquisition interface. Each component and some of the design parameters will be discussed elsewhere. The deuterium gas was from various suppliers over the course of this project and of varying cylinder ages (which affect the tritium impurity concentrations). The main suppliers were Cambridge Isotope Laboratories, Inc., Praxair, and Matheson. The source of the gas did not appear to affect the results. In earlier experiments, the deuterium was passed through Supelco gas purifiers to remove water and oxygen and produced comparable results to unpurified gases. For the results reported here, all gases were used directly. Weak X-Rays and intense light emission has been observed from these matrices during pressurization, which will be discussed elsewhere. Briefly, these have been shown to be artifacts of the measurement technique or uncorrelated to heat production and therefore likely of chemical origins.

Preparation of the palladium-loaded matrices.

The majority of the matrices were made using zeolite 13X from Aldrich (cat #283592) and chromatography grade Alumina from Fischer (cat #A-540). Other zeolites were purchased from Zeolyst International. High Alumina

Zeolite (Code name NaKX(2.0)) was a gift from Praxair, Inc. As these other zeolites produced similar data to 13X, they will not be reported here.

Two variations were employed to prepare the palladium loaded matrices – wet impregnation for alumina^{18,19} and ion exchange for zeolites.^{20,21,22} Palladium chloride came from several sources but for large scale preparations, it was synthesized by dissolving Suisse 99.95% Pd in *aqua regia* and evaporating to dryness. The palladium-amine solution was prepared fresh each time by dissolving 1 g PdCl₂ in 16 mL of water + 4 mL of concentrated HCl and warming. To this deep red solution was slowly added 20 mL of concentrated ammonium hydroxide (an excess ammonia is used but the reaction is in an open beaker so some ammonia is lost). A pink precipitate formed that slowly redissolved upon warming to generate the light yellow Pd(NH₃)₄Cl₂. If the ammonia concentration is too low, Pd(NH₃)₂Cl₂ may form instead.²³ The percentage palladium is based on palladium metal where PdCl₂ is assumed to be 60% Pd metal by weight. Typically 100 g of zeolite powder was placed in a 500 mL flask with 200 mL of distilled water and the required amount of palladium solution. The flask was refluxed overnight. The zeolite was filtered and washed three times with warm water. The material was either air dried overnight then dried at 120°C or dried at 120°C directly. Air drying overnight appeared to produce material with the best characteristics especially when the palladium concentration was decreased below 0.25%. Allowing the water to be slowly lost may preserve the zeolite crystalline structure. The palladium loaded alumina was made by wet impregnation. Alumina (100 g) was placed in a 500 mL flask and slurried with water. The palladium solution was added and the excess water removed on a RotoVapor system under aspirator pressure to a semi-dry, flowing powder. This was air dried overnight and then dried at 120°C for varying lengths of time. Upon oven-drying, the zeolites lost approximately 15% of their weight and the alumina about 11%.

When samples were dried at 450°C they initially were pink and quickly became yellow when cooled in air or in a desiccator. The palladium in these samples reduced to the nanoparticles faster than the matrix dried at 120°C, but drying the matrix at higher temperatures (450°C) appeared to be detrimental for excess heat production.

Higher loading appears to decrease the percentage of heat produced (see Figure 1), likely by growing larger particles. This particle size effect sets apart our approach from that of Kitamura, *et al.*, where he employed high loading 6-30% and high heat that produces multi-nanometer palladium particles.^{16,24} We have tested material produced using Kitamura's recipe¹⁶ with our protocols. Although the heat generated is large because the percentage of palladium is large, we see neither excess heat nor long-term heat. Why our results should differ from that of Kitamura is unknown but similar results to ours have been presented by Hioki and colleagues.²⁵ However if the hypothesis is correct that <2 nm particles are necessary for anomalous heat generation, their production can be difficult and may depend on the exact sample preparation conditions or impurities in a given preparation.

Pressurization and Depressurization Cycles.

A picture of the manifold and peripheral equipment used with the Hart calorimeter is shown in Figure 2. The automated valves are controlled by a custom LabView program that is managed by macros. A summary of the macros for the pressurization and depressurization of the sample cell are given in Table 2.

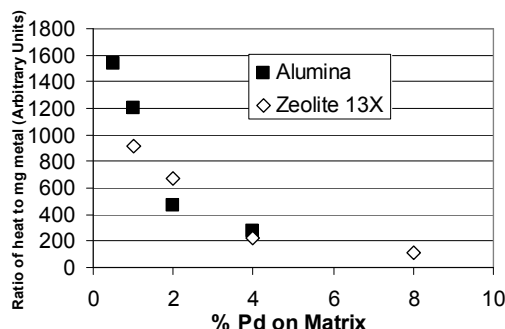


Fig. 1 – Effect of palladium loading of the matrix on excess heat produced. These samples were tested in the GC oven system, which produces relative heats only. The second pressurization cycle with deuterium was used in the calculations. Because these samples were run at different times, direct comparison between matrices is not possible. The percentage Pd on zeolite may vary from the nominal value depicted due to losses during washing.

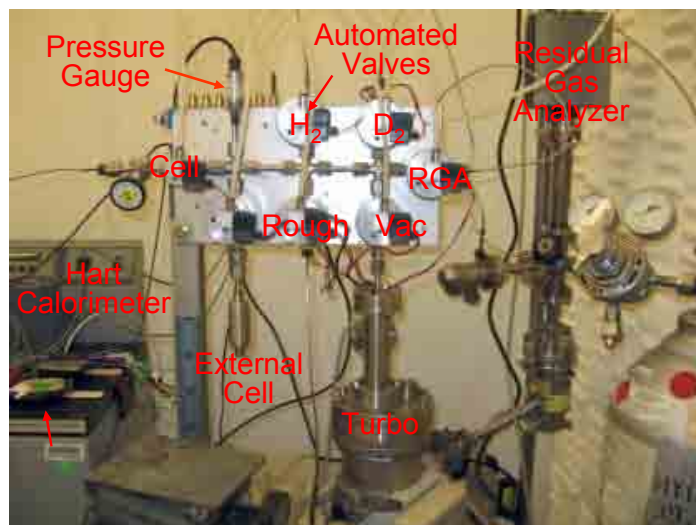


Fig. 2 – Photograph of the manifold and peripheral equipment.

Table 2- Pseudo-macros used to control the automated valves. The timing is in ticks x10, which are acquisition cycles somewhat over a second in length and related to time. The macros in this table were simplified for illustration purposes. The depressurization cycle was done in steps to more accurately measure the D-H exchange. This measurement will be discussed in a subsequent paper.

Pressurization Macro	
Ticks x10	Action
0-120	Close all valves
140	Open RGA
160	Open D2 into manifold
180	Open Cell and fill
1080	Close Cell
1100	Close RGA
1120	Close D2

Depressurization Macro	
0-120	Close all valves
140	Open RGA
160	Open Cell
960	Close Cell
1000	Rough-out the manifold
3000	Close Rough
3020	Open Cell
3100	Close Cell
7000	Rough-out the manifold
9000	Close Rough
9020	Open Cell
9100	Close Cell
13000	Rough-out the manifold
15000	Close Rough
15020	Open Cell

3. Results and Discussion

Figure 3 shows a reversible gas-loading system - five pressurization/depressurization cycles with helium on a Pd-alumina matrix. Integration of all five cycles gives a total heat of $0 \pm 1\text{J}$. The average measured heat of pressurization from the five cycles is $-13.4\text{J} \pm 0.1\text{J}$, whereas the calculated heat of pressurization from PV work is -13.4J .²⁶ This example shows that our approach can have good accuracy and precision. In some matrices, we can directly observe the heat of pressurization because the chemical reduction and subsequent uptake of deuterium is delayed. The delayed chemical reduction is also seen in the pressure recordings, where a pressure drop is observed when the reduction occurs. Like helium, if matrices are initially pressurized with hydrogen, the hydrogen also shows reversible chemistry, where $\text{heat}_{\text{in}} = \text{heat}_{\text{out}}$.²⁷

In contrast to the reversible heat from pressurization with helium (Figure 3) or hydrogen (Figure 4a), is pressurization by deuterium as shown in Figure 4b. With deuterium, the heat released during pressurization (-76.6J) is not equal to that absorbed during evacuation (26.4J) for a difference of -50.2J .²⁸

In one test series, the matrix was cycled many times and the integrated heat ($\text{heat}_{\text{in}} + \text{heat}_{\text{out}}$ and thus excess heat) is shown in Figure 5. The heat from the first pressurization was large due to chemistry occurring. The abrupt decrease in heat after 11 cycles has an unknown cause but it may be due to depletion of a chemical reactant or growth of the palladium nanoparticles above a certain size where anomalous heat is no longer generated.

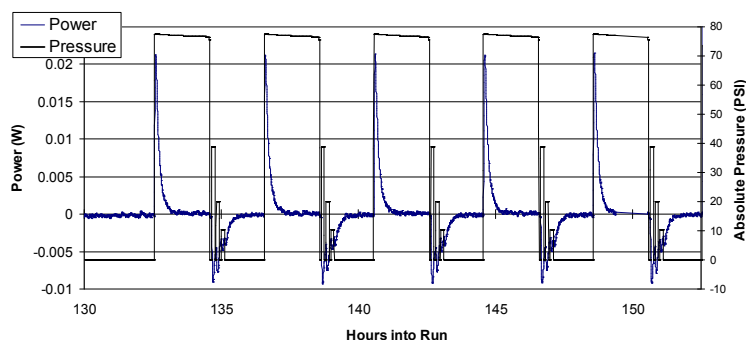


Fig. 3 – Pressurization/Depressurization Cycles Showing Reversible Heat. Pressurization of Pd on alumina with helium: $\text{heat}_{\text{in}} = \text{heat}_{\text{out}}$. The pressurization and depressurization cycles are given in Table 2. The automatic, membrane valves leak deuterium slightly if the pressure is reversed from the normal flow path. To minimize this leakage in the sample cell, the sample cell valve is closed after pressurization and the manifold pressurized. The slight decrease in pressure in the manifold, which is read by the pressure transducer, is due to a leak from the manifold into the turbo system, not due to consumption of the helium in a chemical reaction.

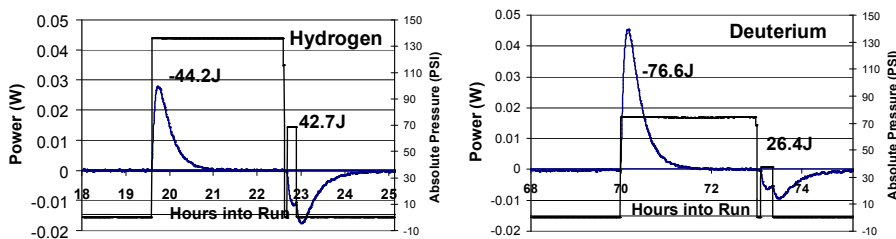


Fig. 4 – Comparison of Hydrogen and Deuterium pressurization cycles. The matrix was 0.5% Pd on zeolite 13X. The hydrogen was pressurized first to avoid possible reverse D-H exchange. Deuterium pressurization shows irreversible heat whereas hydrogen pressurization integrates to near zero (-2.5J). The pressure for hydrogen was larger, but this extra PV work is recovered in the depressurization cycle. In this case, the depressurization cycles were done in two steps rather than four as in Figure 3.

Figure 6 shows a pressurization/depressurization series ($\text{heat}_{\text{in}} + \text{heat}_{\text{out}}$) using zeolite 13X with 1% palladium loading. In this case, the pressurization and depressurization cycles were rapid, which was detrimental to production

of excess heat (see below). The heat decayed with time in a fairly linear manner. More importantly, pressurization with hydrogen produced an endothermic reaction rather than zero (recall that all reversible heat from PV work and hydrogen uptake by the matrix is accounted). This indicates that chemistry must be occurring and, in the case of pressurization with hydrogen, H-D exchange

Consider the reactions in Scheme 1. Palladium-loaded zeolites are known to catalyze D-H exchange.^{29,30} If D-H exchange was occurring in our system, then the chemistry would be exothermic until all the protons in the H₂O and zeolite hydroxyl groups were exchanged. Then, this irreversible energy (due to chemistry) would stop. Pressurization with hydrogen would reverse the exchange making normal water and be endothermic (reverse reactions in Scheme 1). Upon restarting deuterium pressurizations, heat should be produced as the H₂O present would be reconverted to D₂O. Partial restoration of heat appears to occur, as illustrated in Figure 6.

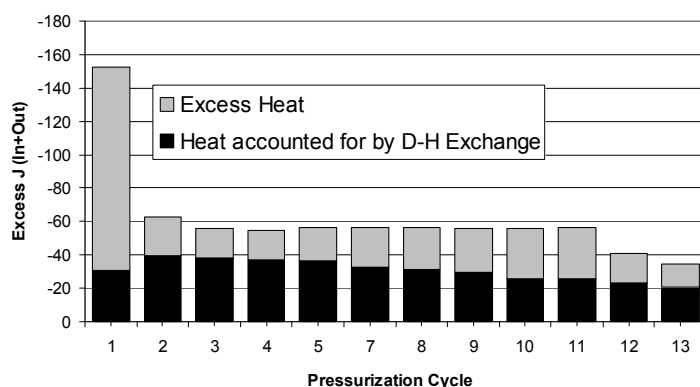
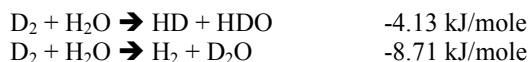


Fig. 5 – Integrated heat for each cycle for 15.42 g of 1% Pd on alumina. The alumina was dried at 120C for 3 hr before use. Note that the calculated heat from D-H exchange (dark bars) is not a constant fraction of the total heat. From step 9 and on, the evacuation time was increased to 10 hr from 6 hr.

D-H exchange should produce a signature in the gas phase because the excess gas overpressure (cells were typically filled to ~5 bar) would be enriched in HD or H₂. This enrichment should be observable using the in-line RGA (see Figure 2). When we first took gas samples, very little D-H was observed. Given the amount of deuterium present and the percentage of HD formed, we concluded that at most 7 J of excess heat could come from D-H exchange. However, later we sampled the gas in pulses (see Table 2 and Figure 5) that allowed sampling at various pressures.³¹ The lower pressure samples were enriched in HD and H₂ and these percentages were used in calculating the excess heat shown in Figures 5 and 6. With these updated numbers, D-H exchange can account for 60-62% (average for initial FDeuterium 7-16 60.7% ±0.56%, n=10) of the heat as calculated from the heats of formation in the pressurization series shown in Figure 6. Other sources (or sinks) of heat can come from the hydrogen bonding of the water and hydroxyls in the zeolite. One complication is that normal water forms stronger hydrogen bonds than does D₂O.^{32, 33} Converting normal water to D₂O should absorb heat and make the discrepancy even larger. Thus, the source of this discrepancy is unknown.

Scheme 1. Possible D-H exchange reactions and the calculated enthalpy. Exchange of the hydroxyls on surfaces should have similar thermochemistry.



Although the calculations of the energy from D-H exchange using the values in Scheme 1 do not quantitatively agree with the measurements, D-H exchange is the dominant mechanism to explain Figure 6 because: (1) the percentages of excess are constant, (2) the hydrogen is negative – also by a constant amount, although slightly different (64.3% ±0.87%, n=15) than that of the deuterium, (3) after the hydrogen pressurization/depressurization cycles, the deuterium returns to similar heat and similar percentage of D-H exchange (after = 60.9% ±0.33% n=4) as was observed initially, and (4) the total heat from D-H exchange of the first 22 pressurization cycles is consistent with the amount of water possible in the zeolite (total = -288 J, 0.6 g water, 4.4% water).

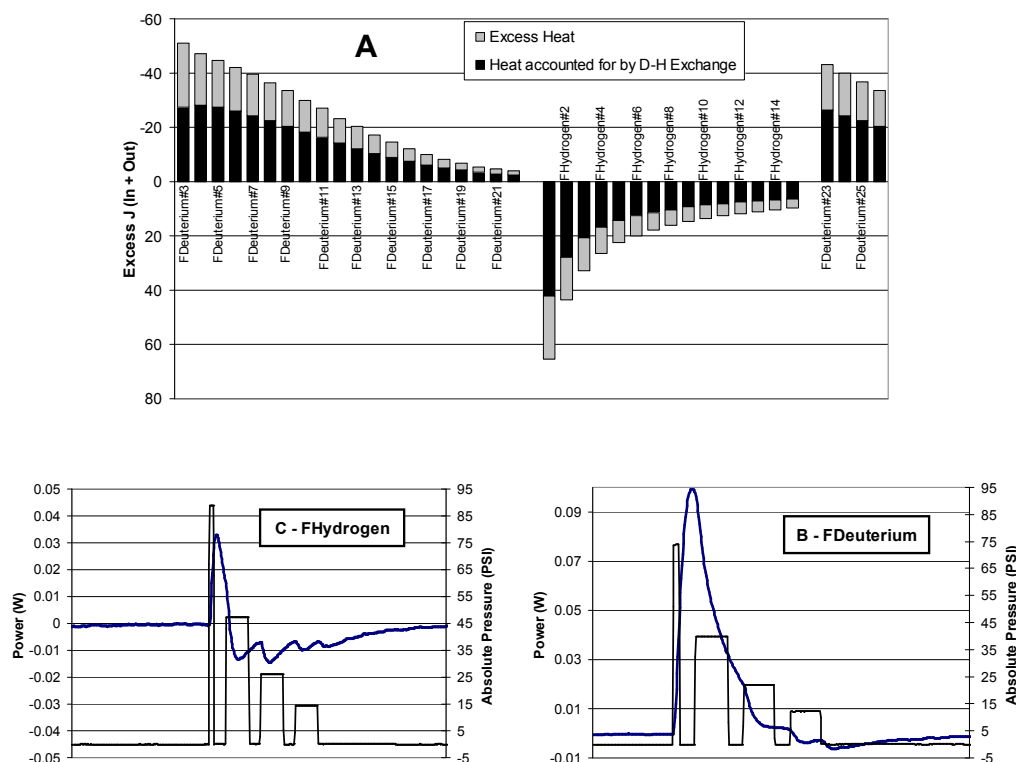


Fig. 6 - (A) Integrated heat for each pressurization/depressurization cycle for 13.5 g of 0.5% Pd on zeolite 13X. This series was started after two normal cycles. The letter F indicates a fast pressurization cycle, which are rapid in-out pulses (which was later hypothesized to be detrimental) where the depressurization period overlaps the pressurization period. Any net positive or negative peak measured is irreversible energy. The depressurization is done in steps (see B & C light lines) to better sample the excess gas with the RGA for calculating the amount of D-H exchange. For an inert gas, the net heat is almost zero. Figure 6 B and C show the cycles for deuterium (cycle FDeuterium #7) and hydrogen (cycle FHydrogen #2). The deuterium cycle is mostly above the baseline – exothermic – whereas, the hydrogen cycle is mostly below the baseline – endothermic. The D-H exchange appears to have a rapid time constant otherwise the heat of pressurization pulse in C should be more evident.

The structure of palladium inside zeolites is complex and depends on preparation conditions.³⁴

We have tried to dry the matrix before the pressurization. However, Type X zeolites contain up to 30% water and can retain considerable water (and OH groups on the surface), except under severe conditions.^{8,35} Also, water and ammonia (left-over from the preparation) may be important to observe anomalous heat generation (they would certainly be important for D-H exchange), as these species can coordinate to the nanoparticles and modify their electronic structure. Heating the zeolites in air to 450°C for 8 hr and adding D₂O reduced the excess heat but did not eliminate it. However, the exchange may have been incomplete and normal water still could have been present.

What is interesting is that the explanation for D-H exchange does not account for the excess heat observed in FDeuterium#3 and FDeuterium#4 (Figure 6). Statistically, FDeuterium#4 at 59.8% of the heat accounted for by D-H exchange is two standard deviations from the mean expected of 60.7%, whereas FDeuterium#3 at 53.8% is 12 standard deviations from the mean. The initial chemical reactions of reduction of the PdO to Pd nanoparticles may take several cycles. Therefore, the excess heat observed in FDeuterium#3 and FDeuterium#4 MAY be due to an incomplete reduction of the PdO rather than unusual chemistry.

Referring to Figure 5, the D-H exchange heat decreases as was observed in Figure 6. This decrease would be expected as the H₂O gets converted to D₂O. However, the excess heat stays the same out to pressurization cycle 11. Thus, in this pressurization series, the D-H exchange is NOT a constant percentage of the total heat, and is not as easily explained as the pressurization series shown in Figure 6. One possibility is that the surface is changing as it becomes more deuterated, and the amount of heat released as H₂O goes to D₂O somehow increases with surface coverage. The major difference between Figures 5 and 6 is in the timing of the pressurization pulses. After many

tests, it appears necessary to restore the particles to their original form without deuterium. This takes considerable time at room temperature given the poor vacuum pumping speed to the cell (Figure 2). Even the 6 hr evacuations used in Figure 5 did not remove all the deuterium from the sample.³⁶ Faster pressurization cycles (2 hr intervals) as used in the sample depicted in Figure 6 would not be sufficient to remove much of the deuterium. Thus, any excess heat due to other causes would no longer be apparent and the D-H exchange reaction would dominate, as in Figure 6.

There may be two reasons for why low deuterium levels in the nanoparticles are necessary to observe anomalous heat: (1) upon absorbing deuterium, small particles heat (but this heat is reversible). One can estimate the expected temperature rise. For example, assume that the enthalpy of formation of nanoparticles of PdD is approximately 100 kJ/mole.³⁷ If all this energy were deposited in one second³⁸ and not transferred quickly to the matrix (as the matrix is an oxide insulator), each particle could heat to 3849°C³⁹ – substantially above the melting point of palladium (1554°C). This high temperature would help catalyze conventional chemical reactions, such as D-H exchange, or it may catalyze an anomalous heat production. and (2) some authors have suggested that anomalous heat production is flux driven.² This could require a particle without much deuterium/hydrogen present each time to reach sufficient flux into the particle during pressurization.

These two hypotheses also suggest why small particles are necessary for this effect to be observed. Larger particles would not load to as high of deuterium levels AND would not load as quickly and thereby not reach as high of temperatures.

4. Conclusions

Low concentrations of palladium in oxide matrices appear to produce sub-nanometer palladium particles which allow high and rapid deuterium gas loading at easily reachable pressures. Gas loading produces anomalous amounts of heat in a reproducible manner in the presence of deuterium but not in the presence of hydrogen. This anomalous heat appears to be sensitive to the size of the palladium particles and rate of loading. The excess heat is reduced during repeated pressurization-depressurization cycles, pointing towards a source of chemical energy that is diminished. Alternatively, the particles may grow with repeated cycling beyond a range that is easily loaded with the parameters employed. In some matrices and pressurization conditions, the likely source of the anomalous heat is D-H exchange with the water present in the matrix. In other cases, this explanation is incomplete and other sources of heat must be considered.

Acknowledgements

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[39] (100 kJ/mole)/(Specific heat capacity of 25.98 J·mol⁻¹·K⁻¹) provides a ΔT of 3849K. This assumes that the heat capacity is constant and heat transfer to the matrix is at a rate much less than the heat production. Both are unlikely situations so this calculation provides an upper limit.

Low Temperature Gas Loading of Deuterium in Palladium

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Abstract. One of the most established features of the phenomenon known with the name of “Cold Fusion”, with reference to the system palladium (Pd) – deuterium (D), is that a condition necessary (even though not sufficient) to be satisfied in order for these phenomena to take place is that the content of D in Pd, called also the D/Pd ratio X , approaches the value of 1 (understanding by this quantity the atomic ratio between the two species in the Pd lattice). In order to reach such an high value of X , extensive use of electrolysis of heavy water with a Pd cathode has been made.

The present experiment is aimed at obtaining high loading ratios of deuterium in palladium without using electrolysis. The idea is to have deuterium gas in contact with palladium. The use of low temperatures has the purpose of increasing the equilibrium loading ratio for a given gas pressure.

A first test experiment, performed at ENEA Frascati in 2002, showed that it was possible to have D/Pd ratios as high as 1 at 150 K with a pressure lower than 1 bar [1]. The experiment has been rebuilt at LNF/INFN and the first results are reported here.

An anomaly in the loading dynamics will be also reported.

1. Introduction

The idea is to realize a conceptually simple experiment, reproducible, and with straightforward answers:

- To start with, measuring the D/Pd ratio, aiming to high values.
- Possibly detecting excess heat.
- Analyzing the gas, looking for ^4He .
- Studying the loading dynamics.

We refer to Ref. [1] for the description of the apparatus and the report of the first results. Here we will limit ourselves to describe the calorimetric technique and to report preliminary results on the loading dynamics.

2. The calorimeter

In Fig. 1 is reported the general scheme of the apparatus. The cell containing the sample is surrounded by a shield: both are made out of copper, and can be considered isothermal. With the help of a Cryodyne closed-cycle refrigerator [2], both can be kept at a constant temperature, from a minimum of 20 K to almost room temperature. The thermoregulator [3] assures a temperature constant within ± 1 mK.

The cell is held at a temperature higher than the shield: thus, heat power has to be dissipated in the cell heater in order to keep the assigned temperature. This power is measured and recorded with the help of a LabVIEW data acquisition system. Should an independent heat source become active within the cell, the thermoregulator has to reduce the amount of energy fed to the cell heater. This decrease, with the opposite sign, gives the value of the heat produced by the independent source.

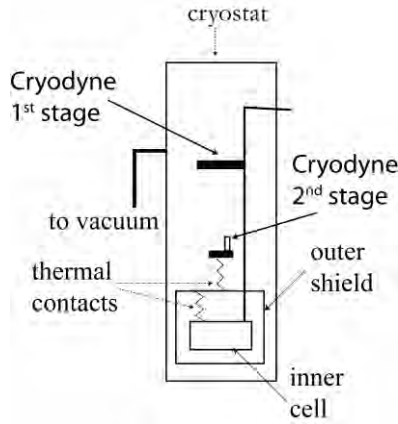


Fig.1 - Schematic view of the apparatus.

In order to validate this method, tests have been performed by mounting within the cell a dummy heater (an evanohm wire in which to create Joule heating), and the power sent into the dummy heater is compared with that detected by the calorimeter. A typical example is shown in Fig. 2. Note the oscillation of the signal of W_c (the power sent by the thermoregulator into the cell heater), both when the heat starts and when it stops. However, when the oscillation is quenched, the agreement between the calculated power (W_{calc}) and the experimental one (W_{exp}) is quite satisfactory, on the order of 1 %.

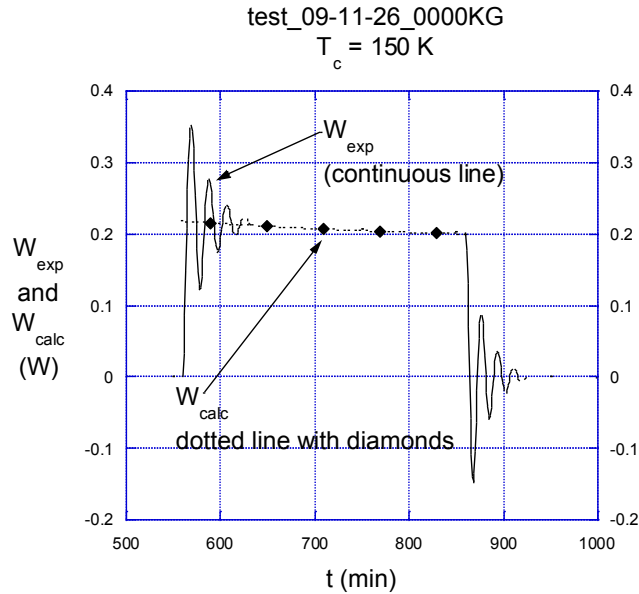


Fig. 2 - Validation of the calorimeter.

It is also possible to measure the total heat produced by the independent heater, by integrating the W_c graph versus time.

3. Preliminary tests of loading dynamics

The geometry of the first samples used for this experiment – the same used in [1] - is shown schematically in Fig. 3a.

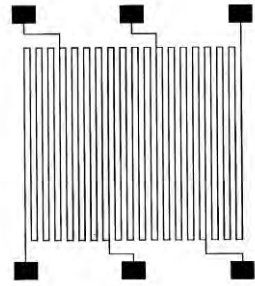


Fig. 3a - The sample used for loading dynamics tests.

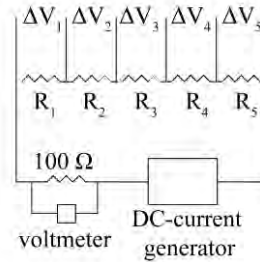


Fig. 3b - The circuit used to measure the resistances R_i .

The real sample is constituted by a Pd film, of thickness 0.5 to 3.5 μm , 80 μm large, and 2.5 m long, deposited on a glass support, 1 mm-thick, 25 x 35 mm^2 area. Its resistance can vary, as a function of thickness, temperature and loading ratio, from a few hundreds to many thousands ohms.

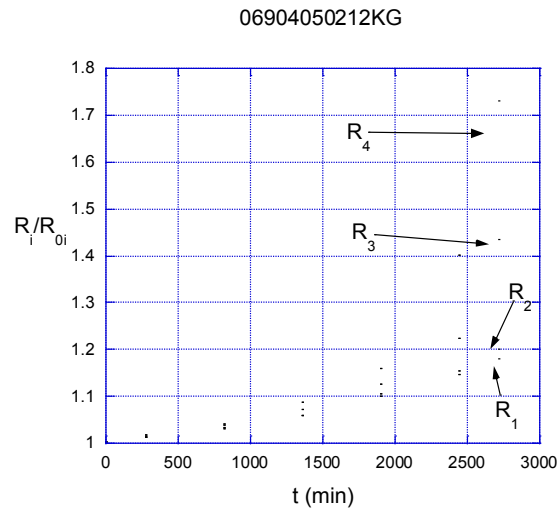
The geometry is such that the total resistance is divided in 5 sections, all in series. In Fig. 3b is reported the scheme of the circuit used to measure the five resistances R_i . The voltmeter in the figure permits measuring the current circulating in the sample, and thus the measurement of the ΔV_i 's, made by the LabVIEW system, gives the resistances. They are measured and recorded as a function of time, at the rate of one value every minute.

Bearing in mind also the suggestion by Giuliano Preparata, the “Preparata Effect” [4], which envisages the possibility that the loading ratio can be influenced by the value of the electric potential on a Pd cathode (in an electrolysis experiment), we have looked at the behavior of the 5 resistances described above during the loading of Deuterium gas. In our case the “electric potential” was that used to measure the resistances. The results are at present quite poor, because of the difficulty of having good Pd samples (“bad” ones tend to detach themselves from the glass support when absorption starts), but nevertheless they are quite suggestive. We will report them here.

The first run we consider is that performed in 2002 [1], at the temperature of 150 K. In order to keep track of the changes of loading ratio, the value of the resistance is considered: it is well known that the resistance grows linearly with increasing X [5]. At room temperature, when $X \approx 0.75$, the resistance is doubled (it increases by a factor 2.6 in the same interval at 150 K).

In Fig. 4 the behavior of the ratio between the value of the resistance while absorbing deuterium (R) and the value of the unloaded sample (R_0) is shown as a function of time for the various sections of the sample during the first phase of the absorption process. Note that R_5 was broken after about one day, and then short-circuited, so that this measurement is reported only for the remaining four sections of the sample.

Table 1. The loading ratio (X) reached by the four sections of the sample.



	R/R_0	X
R_1	1.18	0.13
R_2	1.20	0.14
R_3	1.42	0.29
R_4	1.75	0.52

Fig. 4 - R_i/R_{0i} vs t (2002, 150 K)

The behavior of the four resistances almost two days after starting loading is quite dramatic. In Table 1 the final values of the R_i/R_{i0} are listed, together with the corresponding values of $X = D/Pd$. In this run R_4 was the most negative and R_1 the most positive among the four sections. The absolute value of the voltage used was 0.2 V.

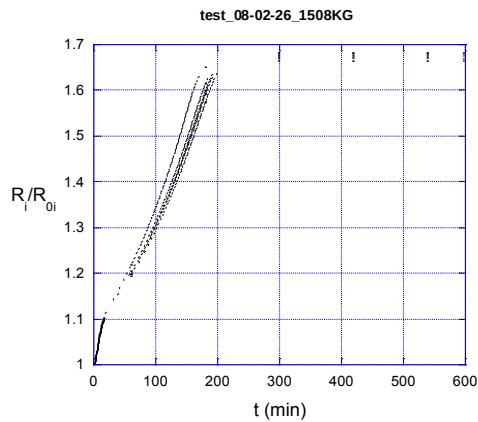


Fig.5a

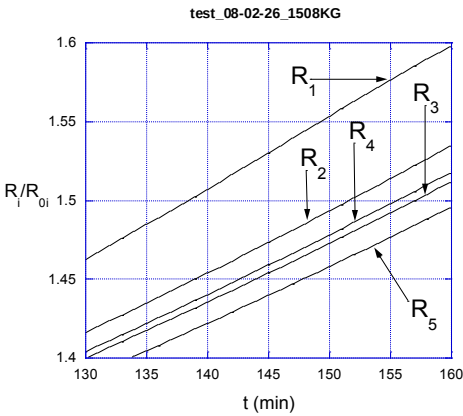


Fig. 5b

The different behavior among the sections becomes much smaller when approaching the maximum value of the loading. This is shown in a Fig. 5a, were another run, this time at room temperature, is considered. In

Fig 5b the same results are reported, by emphasizing the effect at the beginning of the loading. Here R_1 the most negative, R_5 is the most positive. The absolute value of the voltage used was 8 V.

Thus, it seems that a negative potential favors the absorption, at least at the beginning of the loading process.

The data are scarce, even though suggestive. More tests are needed and will hopefully be performed. The main problem is having good quality samples, in the sense that they do not detach from the support when they absorb deuterium. A collaboration is under way with this purpose with David Knies of the NRL of Washington DC, USA.

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The experiment reported here would not have been possible without the skillful help of Franco Campolungo, Mauro Iannarelli, Livio Bettinali and Lorenzo Martinis: also to them goes the Author's gratitude.

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Proposal of an Experiment Aimed at Charging Deuterium in Palladium at the Temperature of Liquid Nitrogen

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Abstract. One of the most established features of the phenomenon known with the name of “Cold Fusion”, with reference to the system palladium (Pd) – deuterium (D), is that a condition necessary (even though not sufficient) to be satisfied in order for these phenomena to take place is that the content of D in Pd, called also the D/Pd ratio X, approaches the value of 1 (understanding by this quantity the atomic ratio between the two species in the Pd lattice).

In order to reach such an high value of X, extensive use of electrolysis of heavy water with a Pd cathode has been made. An alternative line that has been followed by the Author [1] consists of trying to obtain high values of X by the direct interaction of Pd with D₂ gas. The use of low temperatures has the purpose of increasing the equilibrium loading ratio for a given gas pressure.

The proposal of an experiment which requires little attention is presented here.

1. Introduction

When facing the task of loading deuterium (or hydrogen) in palladium, with the aim of reaching high values of the loading ratio $X = D/Pd$, the following parameters have to be considered:

- temperature: X increases as temperature decreases;
- pressure: X increases as pressure increases;
- minimum linear size of the sample: diffusion regulates the distribution of D within the lattice of Pd, and the coefficient of diffusion decreases as temperature decreases; conversely using low linear size samples shortens the diffusion times;
- as a consequence of the latter, time becomes an important parameter when planning an experiment.

To give an idea, in the quoted experiment [1] a value of $X = 1$ was obtained with a pressure slightly lower than 1 bar, at the temperature of 150 K, with a sample 3.6 μm thick. The time necessary in order to reach thermodynamic equilibrium starting from the moment in which D₂ went in contact with Pd, was in the order of one week.

The idea at the base of this proposal is to have a much simpler experiment, able to run for a long time substantially unattended, in order to handle long lasting runs. It consists of using a sample of larger mass and lower dimensionality than the one used in [1], held at the temperature of liquid nitrogen (LN₂), while in touch with D₂ gas at a rather high pressure, and realizing a very simple calorimeter, so that the possible excess heat be the only parameter to be measured and recorded. In this way, it would be possible to perform very long runs, lasting weeks, or even months.

It has been said that another necessary condition to satisfy in order to have cold fusion phenomena, is to have a motion of the D ions in the lattice of Pd: in the system presented here diffusion should be able to provide this kind of dynamic regime.

The calorimeter will be described here.

2. The calorimeter

The calorimeter is based on the use of an “old style” Supairco dewar, designed to contain either liquid helium or liquid hydrogen. It is well known that these liquids have a very low latent heat of evaporation; thus, in order to keep them in liquid form, their container has to be well protected from heat inlets of various types. In particular, in order to reduce the heat inlet by radiation coming from the outer envelope at room temperature, modern dewars have both MLI (MultiLayer Insulation) and metallic shields cooled by the evaporating He/H₂. However, till the years ‘sixties these techniques were not yet applied: the way in which the radiation heat inlet was cut down consisted of having a liquid nitrogen dewar (77 K) surrounding the liquid helium (hydrogen) container, of course both in a good insulating vacuum. The reduction in heat power inlet due to radiation was thus cut by a factor $300^4/77^4 \approx 230$. In Fig. 1 a schematic drawing of such a dewar is shown.

For the calorimeter described here the idea is to put liquid nitrogen (LN₂) also in the inner dewar, the one designed to contain liquid He/H₂. In this way the radiation heat coming from the surrounding container is cut to zero. The only heat inlet remaining is that by conduction through the stainless steel pipe sustaining the inner dewar, which is quite small, since a thin-walled pipe is used.

This remaining heat will produce a small constant evaporation of nitrogen from the inner dewar. Should any independent source of heat appear, there will be an increase in the evaporation rate, which will take place at a substantially constant temperature. The measurement of the increase of the evaporation rate will be easily transformed into heat inlet, since the latent heat of nitrogen is well known.

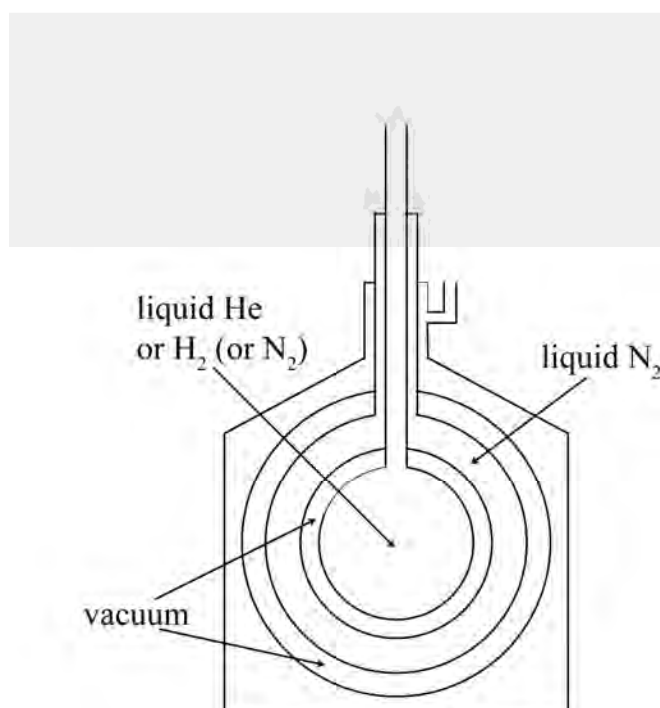


Fig. 1 - Schematic drawing of a Supairco “old style” liquid He/H₂ dewar.

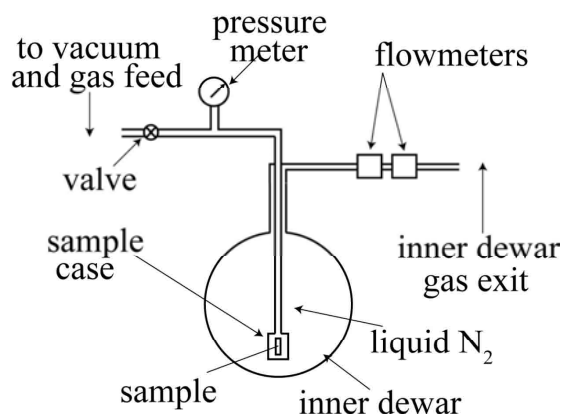


Fig. 2 - Scheme of the experimental set-up.

Thus, provided that the the nitrogen evaporation from the inner dewar is measured and recorded, the experiment can be run substantially unattended. The only operation to perform is, from time to time, to refill LN2 in the outer dewar.

3. The proposed experimental set-up

In Fig. 2 a scheme of the experimental set-up proposed is shown.

The sample is in a vacuum-tight case immersed in LN2 in the inner dewar. In the case high pressure (tens of bars) D_2 gas is put. Evaporation from the inner dewar is measured by a series of two flow meters of different full scale range and recorded with the help of a LabVIEW data acquisition system. Care is taken that the outer dewar be always at least half-full of LN2.

Excess heat in the sample will produce an increase in the evaporation rate of LN2, and will be detected by the flow meters. It will be easy to transform these data into heat or power.

4. A preliminary test

A test was performed, using gas meters, rather than flow meters. The outer dewar was filled with LN2, only 3 liters of LN2 were put in the inner dewar (this was a Supairco 10-liters dewar).

The (residual) heat input in the inner dewar, calculated from the evaporated gas, was constant in time, and amounted to 10 mW (it would take about 19 months to evaporate all the 3 liters of LN2).

The two flow meters in series that will be used will have 20 and 500 sccm (standard cubic centimeters per minute) range full scale. The first will give a reading of 2.47 sccm (the 10 mW quoted above) in the absence of heat excess. The second would give a reading of 240 sccm in the presence of a heat excess of 1 W.

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Wave Nature of Deuterium Flux Permeating through the Palladium Thin Film with Nanometer Coating Layers --- (I) Experimental Observation

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Abstract. Wave nature of deuterium flux permeating through the palladium thin film is revealed using nanometer coating layers. Three sets of experimental data [1,2,3] agree with wave in multiple-layer theory quantitatively or qualitatively. Other than granular particle diffusion model and surface catalyst model, the wave nature of deuterons inside the coating layers must be included in order to explain the experimental phenomena.

1. Introduction

The anomalous deuterium flux permeating the thin wall of palladium tube showed a peak while the temperature of Pd tube was monotonically decreasing through 150°C to 120°C [1]. It was a hint that other than the diffusion there must be some different mechanism governing the deuterium flux permeating the thin Pd film, otherwise diffusion coefficient was supposed to be a monotonic function of temperature. When deuterium molecule dissociated into 2 atoms, and entered the Pd surface as if a granular particle, it would be reflected by the single surface layer only. However, if its behavior was similar to that of a wave; then, it would feel more layers behind the surface layer. The reflecting wave from the surface would be determined not only by the surface layer, but also by the layers behind the surface. Then the reflection of wave should depend on the interference of several reflecting waves from several layers, and manifest itself a peak-wise behavior. This distinct feature might be tested by a deuterium flux permeating through a palladium thin film with multiple nanometer coating layers.

2. Experimental results

Fig.1 shows the schematics of the apparatus. We loaded deuterium gas to Pd film through coating layers while pumping on other side, and then heating the Pd film. Thus deuterium flux formed in Pd had to go through multi-coating layers on the surface of Pd first. By the analysis of the experimental data, we can identify relationship between deuterium flux and coating layers on Pd film.

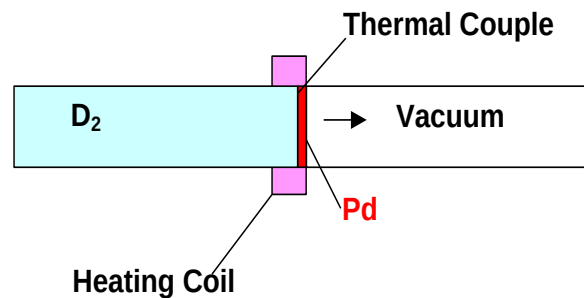


Fig. 1 – Schematics of the deuterium flux apparatus.

The following plots show some results of observation. Under the same conditions, the Pd film with

coating layers (Pd-TiC-Pd) has greater deuterium flux than Pd film without coating layers has unexpectedly.

Fig. 2 and Fig. 3 show a set of comparative results of the experiment. These two experiments have almost the same gas-loading procedure, and the only difference between these two experiments is the sample of Pd film. The first sample is a Pd film ($\phi 20\text{mm} \times 0.1\text{mm}$) without coating layer, while the second one was coated with a layer of titanium carbide (Pd / TiC). The substrate is a Pd film of $\phi 20\text{mm} \times 0.1\text{mm}$, while the Pd / TiC coating layer is 20/2nm. In two experiments, we were first using mechanical pumps to evacuate both sides of the Pd film, and then turned off the pumps. After that we loaded deuterium gas into Pd film from the side with coating layer. At that time deuterium gas pressure reached 80kPa, right in the measuring range of pressure gauge. We heated Pd films in a stepwise way, (changing the heating power every 80 minutes, such that the temperature rose to 120°C thermal equilibrium first; then to 200°C thermal equilibrium, and then dropped back to 120°C thermal equilibrium and room temperature thermal equilibrium)(see temperature curves in Fig. 2 and Fig. 3).

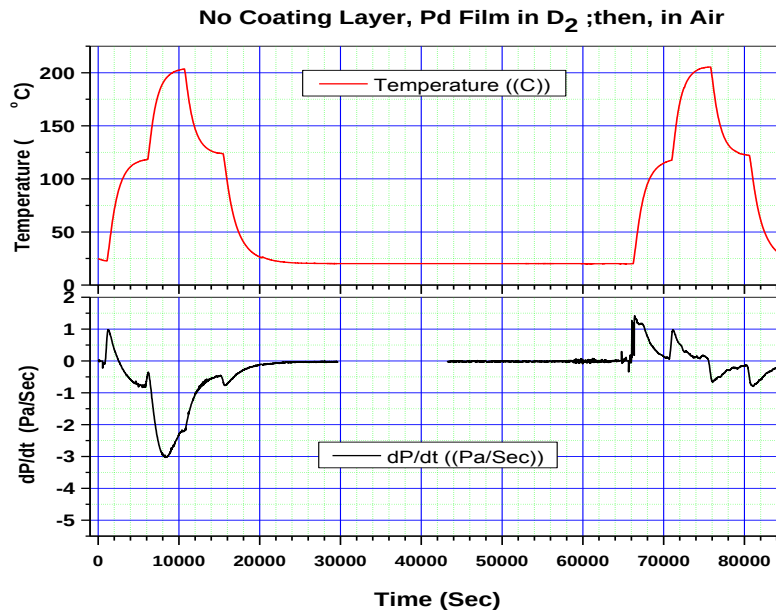


Fig. 2 – Pd film without coating layer.

At the same time we used the multi-channel data acquisition system (Keithley 2700) to record the pressure data. In order to analyze data of pressure change, we calculate deuterium gas chamber pressure derivative to get pressure change rate. The negative peak of pressure change rate represents the rapid decrease of deuterium gas pressure (lower plots in Fig. 2 and Fig. 3 for dP/dt). After deducting the pressure changes caused by temperature, we use the curve to watch deuterium flux.

In order to compare with loading deuterium gas, we loaded air instead of deuterium gas with the same procedure. After heating and cooling in air, we also got temperature and pressure change rate in air as well (Fig. 2 and Fig. 3).

On both figures data after 45,000 seconds are loading air procedure. The positive and negative peaks of dP/dt curves indicate pressure change rate accompanied with temperature changes. We can see from the loading air part, every time Pd film temperature changes, there will be a correspond peak on the pressure change rate curve.

The heating and cooling corresponds separately to the positive peak and negative peak, regardless of the Pd film with or without coating layer. What's more, at the loading air part the positive peak shape of pressure change rate curve is almost the same as the negative peak shape, and peaks height are roughly equal. This shows the air inside chamber acts as the ideal gas isochoric change following the gas state equation. The air does not permeate through the Pd film. However, loading deuterium gas procedure is completely different. After thermal equilibrium pressure change rate is larger than that of loading air, and positive and negative peak are not asymmetric. A wider and higher negative peak indicates more reduction of deuterium gas pressure. Deuterium flux appears. The puzzle is that Pd film with coating might have much more deuterium flux than Pd film without coating at the same temperature, although Pd film with one coating layer is thicker than Pd film without coating layer. This phenomenon conflicts with classical diffusion theory. (In Fig. 2 the peak of deuterium flux reaches -3.0Pa/s, while in Fig. 3 it reaches

-5.0Pa/s).

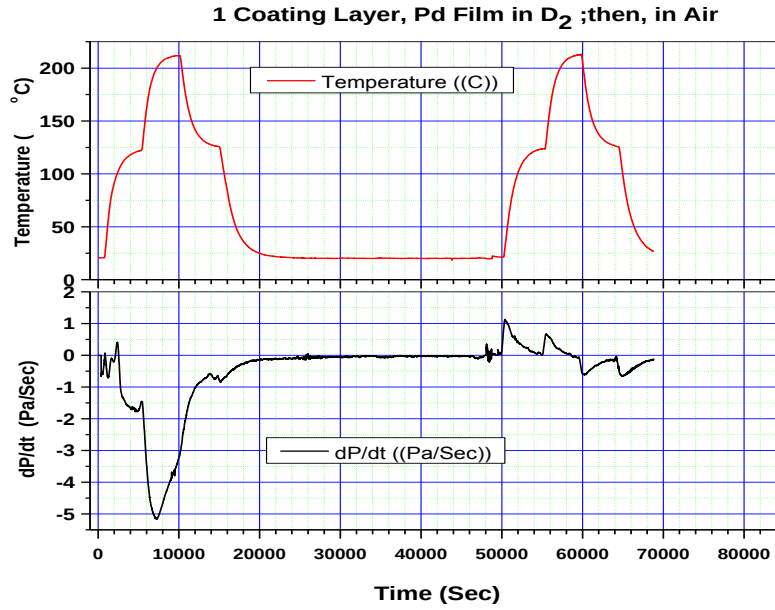


Fig. 3 – Pd film with coating layer.

Further more, we use different numbers of coating layer Pd film to run the same loading procedures. The results show the deuterium flux with different coating layer numbers is not monotonic. Fig. 4 indicated that at the different number of Pd/TiC layers on Pd film with the same experimental conditions, the peak value of deuterium flux changes. All the experiments run with the same deuterium gas pressure (80kPa), and the substrate of Pd film was $\phi 20\text{mm} \times 0.1\text{mm}$, each Pd/TiC layer thickness was 20/2nm. We repeated experimental procedures as abovementioned experiments. Different coating layer number Pd film reaches the peak deuterium flux at slightly different temperature. We found that the deuterium flux through the multilayer films was not monotonic with the number of coating layers, and there comes the peak in a certain layer.

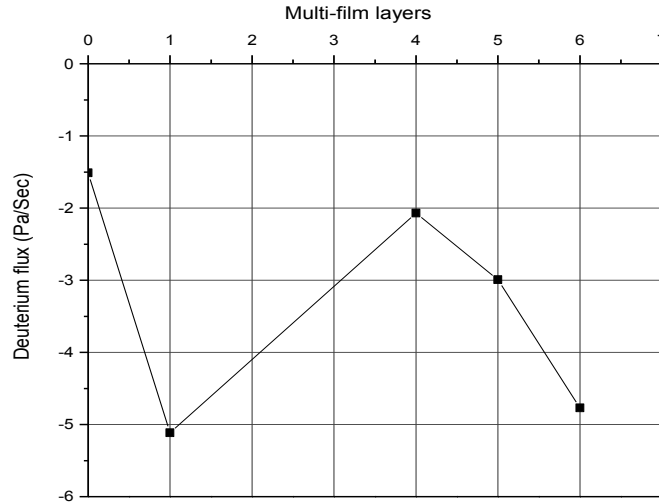


Fig. 4 – Deuterium flux in different coating layer number.

3. Discussion

In 1858, reference to the Fourier thermal equation in 1822, Fick established the quantitative formula to describe the matter migration from high-density area to low-density areas. [4] With low concentration, during unit time and through unit area, material quality (flux) determined by the concentration gradient:

$$\vec{J} = -D\vec{\nabla}n \quad (1)$$

Here D is constant coefficient, called the diffusion coefficient. The concentration n can be expressed as the number of diffusion atoms per unit volume, or other physical quantity represents amount of material like gram atoms. (diffusion flux also takes the appropriate units) Equation (1) is often called as Fick's first law. Equation (1) shows that, keeping the Pd film with the same pressure, the diffusion of deuterium flux through the Pd film usually monotonously decreases when thickness of Pd film increases.

The work of this experiment shows that, accompanied with the variation of the number of coating layers The peak of deuterium flux appears. That is to say, the deuterium flux reaches peak value at the certain number of coating layers. According to the wave nature of deuteron motion, although individual reflected waves on each scattering body is not zero, the summation of reflected waves may be smaller than that of single scattering body. In another words, with the appropriate number of coating layers the different reflected waves might have destructive-interference which would lead to a very small reflectivity. Deuterium flux peak would occur at this condition.

Based on above discussion, permeating characteristics of Nano-system materials can not be fully explained by traditional diffusion theory. The wave nature of deuteron motion can qualitatively describe some anomalies in D-Pd/TiC/Pd multi-layer systems.

Acknowledgments

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Wave Nature of Deuterium Flux Permeating through Palladium Thin Film with Nanometer Coating Layers --- (II) Theoretical Modeling

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Abstract. Two sets of experimental results are analyzed using the wave nature of the deuterons inside the palladium film. An identity for the ratio of absorption to transmission rate is derived to qualitatively explain the correlation between the deuterium flux and heat flow in experiments. In addition, a peak-wise behavior is shown for the permeation of deuterium flux through the palladium thin film as a function of the number of nanometer coating layers in experiments and in theory. This peak-wise variation is the characteristic behavior due to the wave nature of the deuterons.

1. Introduction

The studies on deuterium/palladium system have been conducted for more than 20 years in order to search for the anomalous phenomena. One of the subjects has been if we should treat the deuterons inside the palladium as granular particles or as a wave. S. Chubb and T. Chubb proposed early in 1990 that the deuterons inside the palladium should be treated as a wave based on the similarity with the electrons and the experimental facts [1, 2]. In 1995, the selective resonant tunneling model was proposed to explain the tunneling of Coulomb barrier between deuterons based on the wave mechanics [3, 4]. This wave model explained also why there was no accompanied commensurate neutron and gamma radiation for excess heat. Indeed the hot fusion data for 6 major fusion cross sections justified this wave model [5, 6] as well. The verification of three deuteron fusion reactions [7, 8, 9] has further supported this wave resonance model inside the metal-hydrides. In this paper, we provide two additional analyses of experimental data which show the wave nature of the deuterons inside the palladium thin film.

The correlation between deuterium flux and heat flow provides the first set of experimental data [10]. The permeation of the deuterium through the palladium thin film with nanometer coating layers provides the second set of experimental data [11, 12, 13]. Two theoretical derivations are presented accordingly to explain these two sets of data, and show clearly the wave nature of deuterons.

2. The identity of (A/T) and correlation between deuterium flux and heat flow

A, the absorption rate, and T, the transmission rate, are two important rates to describe the permeation process of deuterons through palladium film. A is defined as the ratio of the number of absorbed deuterons to the number of injected deuterons. T is defined as the ratio of the number of permeated deuterons to the number of injected deuterons. If the deuterons are treated as granular particles, we may expect that the transmission rate might decrease when the absorption rate increases while the injected number is fixed.

However, the experimental result showed differently. The deuterium flux (solid line in upper plot of Fig.1 (blue, right coordinate)) increased when the heat flow (dash-dotted line (red, left coordinate)) increased. Since the deuterium flux and heat flow are supposed to be related to transmission (T) and absorption (A), respectively, the summation of (T+A) is supposed to be equal to (1-R). Here R is the reflection rate which is defined as the ratio of the number of reflected deuterons to the number of injected deuterons. If the deuterons are treated as granular particles and the permeation is treated as a diffusion process of random walking particles; then, the number of the reflected deuterons on the palladium surface is fixed or increases slowly when temperature decreases (the solid line (pink) in the lower plot of Fig.1). Thus, we might expect (T+A) is fixed or decreases slowly. Then any peak up in T would be accompanied a spike down in A. In contrary, the experimental data showed that peaks in T are accompanied by peaks up in A. It implied that (T+A) has a peak there, or more deuterons are entering palladium there. This conflicts with the diffusion model which implies less diffusion flux through palladium when temperature goes down.

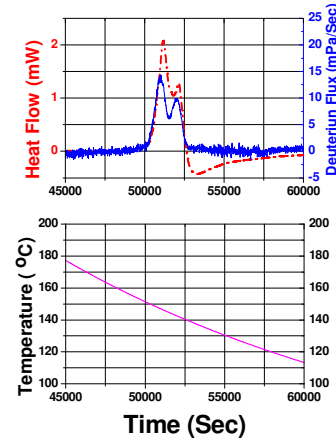


Fig.1—Correlation between deuterium flux and heat flow

In a word, diffusion model allows only a monotonic decreasing deuterium flux when palladium is cooling down, and allows only a negative correlation between the deuterium flux and heat flow. It does not allow such a peak-wise behavior of deuterons permeating through the thin film of palladium, and does not allow a positive correlation between the deuterium flux and heat flow. We have to modify the diffusion model in order to explain this phenomenon. That is to say: deuterons are not random walking granular particles in permeation through the thin palladium film.

A slab model based on the wave nature of the deuterons is proposed to describe the interface between deuterium gas and palladium surface in Fig.2. A thin layer (PdO or any coating layer) is assumed on the surface of palladium. Two sets of rates, (T_0, A_0) and (T_1, A_1) are defined to describe the surface layer and the palladium substrate, respectively.

An identity has been proved to calculate the transmission and absorption rates of compound system (see Appendix A):

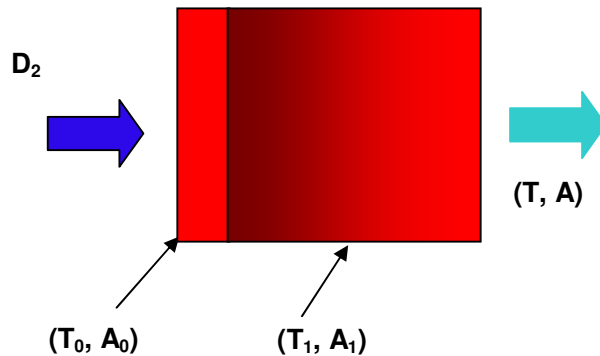


Fig. 2. - Slab model for coating layer on surface of Pd substrate

$$\frac{A}{T} \equiv \frac{A_0}{T_0} + \frac{A_1}{T_1} + \frac{A_0}{T_0} * \frac{A_1}{T_1} \quad (1)$$

It is a direct result of wave property: (1) The injected wave may be reflected not only by the first layer, but also by the interface between the first layer and the Pd substrate; (2) the total reflection is determined by the summation of these two reflected waves; (3) the wave phase angle between these two reflected waves may lead to a zero summation of wave amplitude and greatly reduce the total reflection. As a result, the ratio of $\frac{A}{T}$ is always greater than each individual ratio ($\frac{A_0}{T_0}$ or $\frac{A_1}{T_1}$), because the multiple reflections

in the interface between the first layer and the Pd substrate always enhance the total absorption (A) and reduce the total transmission (T). On the contrary, if the deuterons act as the granular particles, the total reflection, (1-(T+A)), is always greater than each individual reflection; then, (T+A) must be reduced. Thus any peak in T must lead to a spike downward in A.

Consequently, the positive correlation between the deuterium flux and the heat flow just denies the simple diffusion model of granular particles and reveals the wave nature of the deuterons permeating through the thin film of palladium. A series of experiments were designed to further verify this wave nature [11, 12, 13].

3. The permeation of deuterons through palladium film with nanometer multiple coating layers

In order to verify this wave nature of deuterons permeating through palladium film, we may add more coating layers on the surface of palladium substrate (Fig.3). Instead of changing temperature, we may change the number of coating layers and see if the total reflection might be reduced by interference of reflected waves from several interfaces. If the wave model is correct; then, at certain number of coating layers, we are supposed to see the total transmission would be enhanced to higher than the transmission with no coating layers.

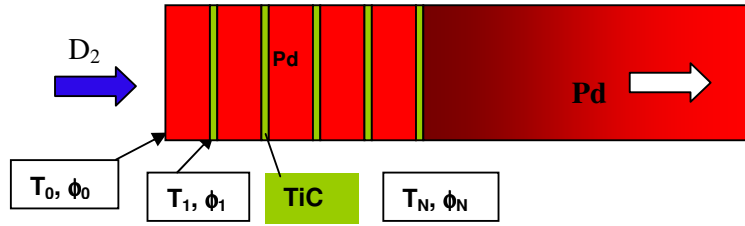


Fig. 3. - Multiple coating layers on the surface of Pd substrate

On the palladium substrate a TiC layer of 2 nm is coated first by ion sputtering. Then a palladium layer of 20 nm is coated. These alternatively coated Pd-TiC-Pd films were used to measure the deuterium flux near 120°C [13]. Since the phase angle plays key role in the wave phenomena, we assign the change of the phase angle (ϕ) for each Pd-TiC-Pd compound layer. The transmission rate (T) is assigned also to describe the feature of each Pd-TiC-Pd compound layer. The task is to find the total transmission rate (T_N) for a palladium substrate with N Pd-TiC-Pd compound layers, and compare it with the experimental data.

Based on the matrix algebra(Appendix B), we may reach 3 conclusions:

- (1) The Transmission rate of the palladium coated with nanometer TiC-Pd layers is

$$T_{0N} = \frac{T_0 * T_N}{1 + (1 - T_0)(1 - T_N) + 2\sqrt{(1 - T_0)(1 - T_N)}\cos(\phi_0 + \phi_N)}. \quad (2)$$

Here, (T_0, ϕ_0) is assigned for the first palladium layer facing deuterium gas. (T_N, ϕ_N) is assigned for the N compound layers TiC-Pd facing the first palladium layer (see Appendix B.)

(2) (T_N, ϕ_N) can be written as an explicit function of the number of compound layers TiC-Pd...TiC-Pd:

$$T_N = \left| \frac{\sin \alpha_1}{\sqrt{\frac{1}{T_1} e^{-i\phi_1} \sin(N\alpha_1) - \sin[(N-1)\alpha_1]}} \right|^2 \quad (3)$$

$$\phi_N = -\text{Arg}[\sqrt{\frac{1}{T_1} e^{-i\phi_1} \sin(N\alpha_1) - \sin[(N-1)\alpha_1]} / \sin \alpha_1] \quad (4)$$

(3) An eigen angle, α_1 , is introduced in eqs.(3) and (4) based on the (T_1, ϕ_1)

$$\alpha_1 = \text{ArcCos}[\sqrt{\frac{1}{T_1}} \cos \phi_1] \quad (5)$$

Here, N is the number of nanometer coating layers.

Using 4 input parameters, T_0, ϕ_0, T_1, ϕ_1 , it reproduces the experimental data, the ratio of $\left(\frac{T_{0N}}{T_0}\right)$. In

Fig.4, the red stars are the results of the experimental measurement, and the open circles are the result of calculation using eqs. (3), (4), (5) for $T_0 = 0.0031$, $\phi_0 = 0.1123$, $T_1 = 0.7629$, $\phi_1 = 2.4026$. These open circles are connected by dotted lines because N is supposed to be integers only. The predominate

feature is that: (1) This ratio $\left(\frac{T_{0N}}{T_0}\right) > 1$ at N=1, and N=6. It implies the reduction of reflection due to

interference of several reflected waves.

This is the characteristics of wave model.

(2) A peak-wise behavior of $\left(\frac{T_{0N}}{T_0}\right)$

versus N implies the failure of diffusion model of random walking granular particles in palladium.

4. Discussion

This wave model is originally based on the similarity between electrons and deuterons in the palladium-deuterides. However, the de Broglie wavelength of deuteron is much smaller than that of electron. Can we still apply the wave model to deuteron? The low energy electron diffraction (LEED) experiments show that the electron

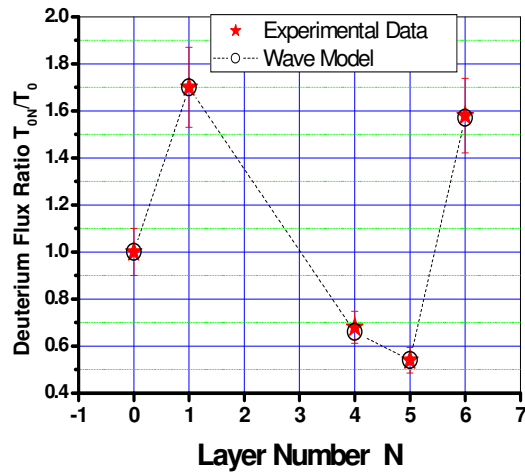


Fig. 4. - Comparison between experiment and slab model

diffraction pattern appears even if the electron energy reaches 267 eV [14]. The electron wave length at this energy is similar to that of a deuteron at thermal energy. Hence, we might expect the characteristics of deuteron waves in the palladium deuteride at room temperature. Indeed we checked once and once

again this peak-wise dependence of $\left(\frac{T_{0N}}{T_0}\right)$ versus N by different experiments: measure the changing

rate of deuterium pressure in vacuum side of palladium film[12], and in the high pressure side of palladium film[13]; compare the behavior of air and deuterium to assure the peak-wise characteristics of deuterium flux[13]. All these experiments have confirmed the peak-wise behavior in Fig. 4. Hence, the wave nature of deuterium flux permeating through palladium thin film is confirmed.

The great success in superwave triggering, and in ultrasonic wave work has implied the wave nature of metal deuterides as well [15,16,17] although we need to figure out the underlined mechanism. Chemical catalyst model failed in this peak-wise feature because its effect depends only on the first surface layer.

The ratio $\frac{A}{T}$ may be enhanced by multiple nanometer coating layers on the surface of palladium. If we increase the transmission T by certain number of coating layers; then, we may increase the absorption of deuterons inside the palladium deuteride. In this way we may enhance the loading ratio and the possibility of having “excess heat”. Indeed, this is using the reflection waves among interfaces to enhance the confinement of deuterons inside the palladium.

Acknowledgments

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Appedix A, Identity of $\frac{A}{T} \equiv \frac{A_0}{T_0} + \frac{A_1}{T_1} + \frac{A_0}{T_0} * \frac{A_1}{T_1}$

A useful identity may be derived just based on the wave properties. The wave mechanics may be expressed by matrix algebra as follows.

The injected wave coming from the left-hand-side of the slab. Part of it is reflected, and part of it penetrates the slab. We may use the 2 plane waves as the base functions to describe the outgoing wave and the incoming wave. Then the outgoing wave on the right-hand-side may be assigned as a wave vector:

$$\Psi_0 = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

The wave on the left-hand-side may be written as

$$\Psi_1 = M \Psi_0$$

$$M = \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix}$$

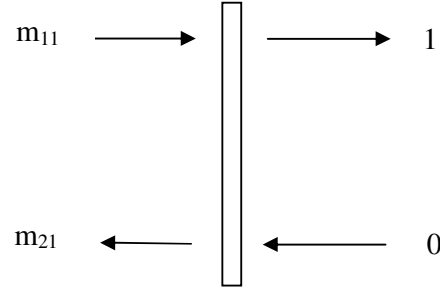


Fig. A1. - Slab model

M is the matrix to describe the slab. Because of the conservation of the probability current, and the symmetry of the slab, we have:

$$M = \sqrt{\frac{1}{T}} \begin{bmatrix} e^{-i\phi} & -i\sqrt{1-T-A} \\ i\sqrt{1-T-A} & e^{i\phi} \end{bmatrix};$$

Here, $T \equiv \frac{1}{|m_{11}|^2}$ is the transmission rate, $R \equiv \frac{|m_{21}|^2}{|m_{11}|^2} = (1 - T - A)$ is the reflection rate, and A is the absorption rate, respectively. M is defined as the compound layer composed of layer 1 and 2. Similarly, M_1 and M_2 are defined for individual layer 1 and 2, respectively.

$$M_1 = \sqrt{\frac{1}{T_1}} \begin{bmatrix} e^{-i\phi_1} & -i\sqrt{1-T_1-A_1} \\ i\sqrt{1-T_1-A_1} & e^{i\phi_1} \end{bmatrix}; \quad M_2 = \sqrt{\frac{1}{T_2}} \begin{bmatrix} e^{-i\phi_2} & -i\sqrt{1-T_2-A_2} \\ i\sqrt{1-T_2-A_2} & e^{i\phi_2} \end{bmatrix}.$$

ϕ, ϕ_1 and ϕ_2 are defined as the change of phase angle of the wave across the corresponding layer, respectively.

This leads to the identity directly using $M=M_1*M_2$ and matrix algebra.

$$\frac{A}{T} \equiv \frac{A_0}{T_0} + \frac{A_1}{T_1} + \frac{A_0}{T_0} * \frac{A_1}{T_1}$$

Appendix B, Permeation through multiple coating layers

$$T_{0N} = \frac{T_0 * T_N}{1 + (1 - T_0 - A_0)(1 - T_N - A_N) + 2\sqrt{(1 - T_0 - A_0)(1 - T_N - A_N)}\cos(\phi_0 + \phi_N)}. \quad (\text{B.1})$$

Same matrix algebra may be applied to show: The transmission rate, T_{0N} , of a compound layer composed of layer 0 and layer N, may be expressed by the individual parameters, (T_0, A_0, ϕ_0) and (T_N, A_N, ϕ_N) as eq.(B.1). (T_0, A_0, ϕ_0) defines the first layer on the surface (Fig. B1). (T_N, A_N, ϕ_N) defines the compound layer behind the first layer. It is composed of N layers, each of which is same with the parameters (T_1, A_1, ϕ_1) . In reality, each individual layer was composed by a thin TiC layer (2nm) and a thick Pd layer (20nm) in our experiments. (T_N, ϕ_N) may be expressed by (T_1, ϕ_1) and N as well (A_0, A_1 are assumed zero in calculation because it is negligible in our experiments).[18]

$$T_N = \left| \frac{\sin \alpha_1}{\sqrt{\frac{1}{T_1}} e^{-i\phi_1} \sin(N\alpha_1) - \sin[(N-1)\alpha_1]} \right|^2,$$

$$\phi_N = -\text{Arg}\left[\left(\sqrt{\frac{1}{T_1}} e^{-i\phi_1} \sin(N\alpha_1) - \sin[(N-1)\alpha_1]\right) / \sin \alpha_1\right],$$

$$\alpha_1 = \text{ArcCos}\left[\sqrt{\frac{1}{T_1}} \cos \phi_1\right].$$

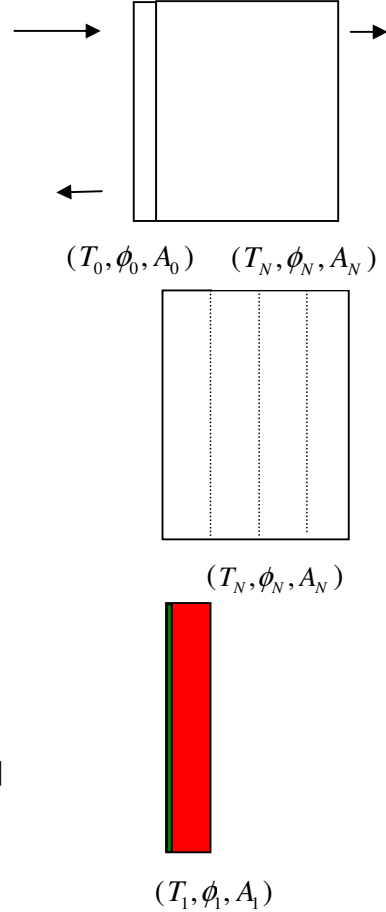


Fig. B1. - Multiple coating layers on the surface of Pd substrate

Self-Polarisation of Fusion Diodes: Nuclear Energy or Chemical Artefact?

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Abstract. The authors discusses the results of the testing of a new fusion device : the “Fusion Diode”.

The cold fusion community has been trying to justify cold fusion on the basis of empirically produced excess heat for nearly two decades. [1], [2] The science world has continually resisted the possibility, citing the heat as not conclusive. Some problems of chemical reactions can interfere with calorimetry. [3]

The authors have sought a different approach, whereby the device has no input energy, relying on the only energy produced from the device. We are using diodes, made of palladium as the metal, and silicon as the semiconductor. We have also tried other semiconductors. But we describe here our experiments with silicon. The palladium is loaded with deuterium simply by the gas-loading method. We don't know the effective loading value, but it is probably rather high, because of the micrometer size of the palladium powder.

A diode is basically a surface of contact with a metal (electronic conductor) and a semiconductor (hole conductor).

We think that the deuterium nuclei which are in the palladium will be driven in the direction of the electric field. Once these deuterium cores will arrive at the interface between palladium and the semiconductor, they will accumulate there. The probability of fusion probably will increase. [4]

Better: if reactions of fusion take place into the junction, an excitation of the electrons will occur at this level (as in the junction zone of a photovoltaic cell). A solar cell is a diode with a large surface. When photons fall on the junction zone, certain atoms are excited, and electrons pass from a low energy level to a higher energy level. A spontaneous electric voltage thus will appear. It is what we observed.

In order to get a surface of junction as large as possible, our fusion diodes are made as powder diodes, with a large surface junction made up of a semiconductor powder in contact with palladium powder charged with deuterium. (Fig. 1) [5] The weight of palladium powder is comprised between 1 g and 2 g by diode.

The suspected fusion reactions take place in the junction between the semi conductor and the Palladium powder, which produces an excitation which is transmitted to the electrons. This excitation increases their energy and allows them to cross the bandgap of the semiconductor and pass into the conduction band, as in a photovoltaic cell. This energy very quickly appears as a spontaneous potential difference which can reach over 0.5 volt per junction. (open circuit)

Diodes comprising of a stack of junctions were made, making it possible to obtain over 1 volt at the poles of a very compact device of a few centimeters length. The released power remains very low for the moment, (in the nanowatt range) but it should be noted that it is presented in the form of directly usable electrical energy, and not of thermal energy.

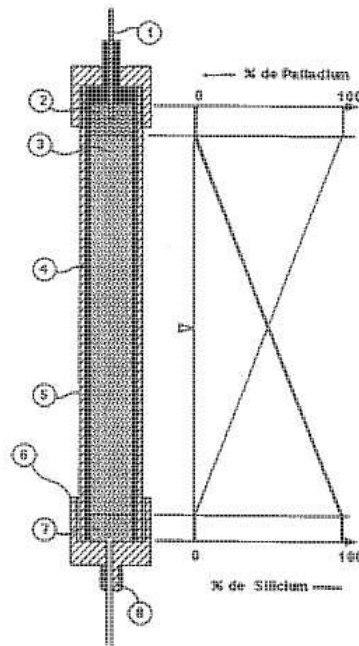


Fig. 1 - Our fusion diode : 1 Electrical connection; 2 End cap with threading; 3 Mix of silicon and palladium powder (at the bottom pure palladium and then an increasing concentration of silicon; at the middle of the diode: 50% silicon, 50% palladium; at the top: pure silicon. The result is a very large surface rectifier diode); 4 Plastic tube for insulation; 5 Aluminum or machined nylon container; 7 End cap; 8 Swagelok valve.

Of course, we have made blank and control experiments. We have built three diodes, one filled with pure deuterium (1.5 bar) another filled with hydrogen at the same pressure, and another filled with pure argon (Fig. 2). The black plastic tubes are 6 cm long.

We observed no voltage with argon filling, a little voltage with hydrogen, twice the voltage with deuterium. We think that the observed voltage with hydrogen is generated by the little amount of deuterium in the hydrogen. (0.015%)



Fig. 2 - Three diodes, one filled with pure deuterium (1.5 bar) another filled with hydrogen at the same pressure, and another filled with pure argon.

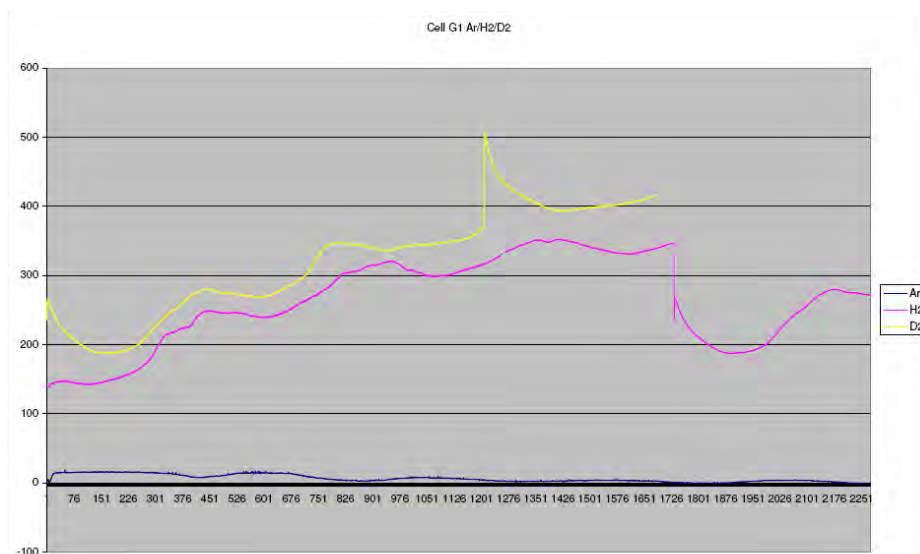


Fig. 3 - Yellow line : voltage at the ends of the deuterium filled diode; Cyan Line : voltage at the ends of the hydrogen filled diode; Blue line : voltage at the ends of the argon filled diode. Vertical axis: millivolts; Horizontal axis: minutes.

Our lab is not air-conditioned : the diurnal oscillation of the voltage is probably caused by the variation of the temperature of our lab, so we can exclude a “Allais Effect”.

Is the observed release of energy due to the fusion of the deuterium nuclei, or is it an electrical voltage produced by an electrochemical reaction? (For example, oxidation of deuterium by the little amount of adsorbed oxygen on the powder) The authors plan to prove the origin of the energy measured over several months with the help of various methods. First of all, we plan to seal our fusion diodes inside glass containers, to avoid leak of deuterium.

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***In Situ* Energy-Dispersive X-ray Diffraction Study of Thin Pd Foils at D/Pd and H/Pd ~1**

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Abstract. Time resolved, *in-situ*, energy dispersive x-ray diffraction was performed in a modified Fleishman-Pons electrolytic cell during electrochemical loading of palladium foil cathodes with hydrogen and deuterium. Concentrations of H:Pd (D:Pd) up to 1:1 in 0.1 M LiOH (LiOD) in H₂O (D₂O) electrolyte were obtained, as determined by both the Pd lattice parameter and cathode resistivity. In addition, some indications on the kinetics of loading and deloading of hydrogen from the Pd surface were obtained. The alpha-beta phase transformations were clearly delineated but no new phases at high concentration were determined.

1. Introduction

Since the discovery in 1886 by Graham [1] that Pd can absorb relatively large amounts of hydrogen, palladium hydrides and deuterides have been extensively studied. Metal hydrides have generated much interest among a variety of scientific disciplines, particularly in hydrogen storage in recent years [2-3], because of the limited supply of fossil fuels and growing worldwide demand for energy. Palladium and its alloys are also materials extensively used for hydrogen purification [4], which is applicable to fuel cells. Although current research on hydrogen storage has shifted from transition metals to light elements to gain a high gravimetric density of hydrogen, palladium still plays an important role in the study of metal hydrides.

The phase diagram of Pd-H shows this system to have two phases, α and β , separated by a miscibility gap for temperatures below about 300°C and a hydrogen pressure below about 20 bar. At room temperature, the solubility limit for H in the dilute α phase is about 0.03 H/Pd, while the lower limit for the concentrated β phase is 0.58 H/Pd. In between is a two-phase region with a mixture of α and β at these H concentration limits. Both α and β are FCC interstitial solid solutions, but with different lattice parameters. In both, hydrogen atoms randomly occupy the four octahedral interstitial sites present per FCC unit cell containing four palladium atoms. So, when fully loaded with H, stoichiometric PdH forms the B1, or rocksalt structure. The Pd lattice parameter increases from 3.889 Å for pure Pd up to 4.102 Å for PdH at room temperature, an increase over 5.5%.

However, deviations from this simple structural model have been reported. For nanocrystalline palladium, a narrowing of the Pd-H miscibility gap has been observed using *in-situ* synchrotron x-ray diffraction measurements [5]. The phase boundary change is associated with a larger ratio of the value of the entropy of mixing to that of the enthalpy of mixing in nanocrystalline samples than in coarse-grained samples. At low temperature (50-80K) in the concentrated β phase of PdH, there is the so-called 50-K anomaly, associated with a structure change [6]. At high hydrogen pressures, a hydrogen-induced superabundant-vacancy phase can be produced in the palladium metal lattice [7] and stabilized at room temperature and normal pressure [8].

At high H (D) concentrations, there is some evidence for additional structure changes. Tripodi et al. suggested a new γ phase to explain the temperature coefficient of resistance (TCR) increase for electrochemically loaded palladium when the composition H/Pd approached one [9]. Recently, they showed the TCR decreases when H/Pd exceeds one [10]. In the Pd-D system, new phases were reported from deuterium thermal desorption spectra taken from Pd samples [11]. In addition, there was a report showing oscillating resistivity for palladium hydrides at a high concentration range of H/Pd > 0.9 [12].

All these recent experiments suggest that something must happen in palladium with a ratio of H/Pd approaching unity or above, which is currently not understood. Moreover, these proposed phase transitions are only based on indirect experimental data and have not been structurally determined yet. In fact, while loadings of H and D approaching 1:1 D:Pd and H:Pd have been measured *in situ* at 77K on Pd powder [13] the highest loading of D/Pd that has been measured at room temperature by *in-situ* x-ray diffraction is 0.76 [14,15]. For these reasons, we have undertaken this *in situ* x-ray diffraction (XRD) investigation of Pd highly loaded with H and D at near room temperature.

2. Experimental Procedure

Fig. 1 shows a schematic representation of the experimental geometry used with the wiggler beam line X17C at the National Synchrotron Light Source, Brookhaven National Laboratory.

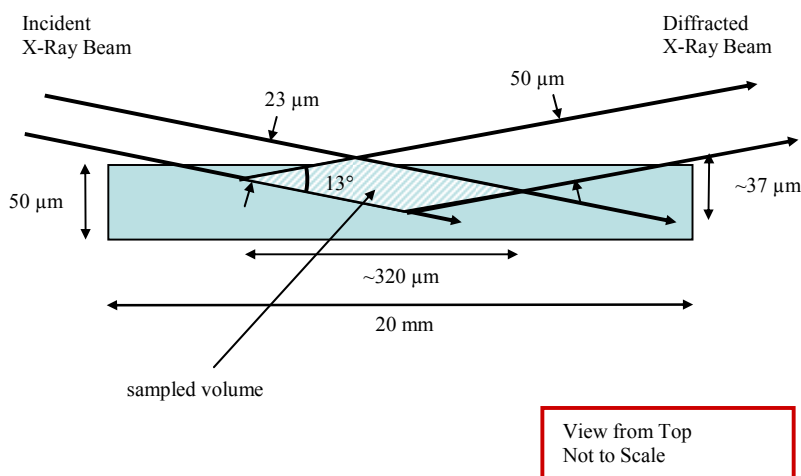


Fig. 1. - Schematic representation of experimental geometry used. Beam widths collimated to dimensions shown, with an incident beam height of 12-15 μm, resulting in a sampled volume of ~70 pL, with maximum dimensions as shown. A high resolution Ge detector was positioned at a diffraction angle of 13° (2θ).

A collimated, high-intensity, white-radiation x-ray beam with energies of 10-100 keV entered from the left and impinged upon the center of a sample stage that provided x-y-z translation and two axes of rotation, ω for the sample and 2θ for the detector. The incident x-ray beam was collimated to a shape 12-15 μm tall and 23 μm wide. The diffracted beam was collimated to 50 μm width by tungsten slits, and detected by a high resolution Ge x-ray detector. Nominally symmetric reflection diffraction conditions were used with $\omega \approx \frac{1}{2} 2\theta = 6.5^\circ$, meaning grazing incidence and a shallow sampling volume applied. As a guide, the x-ray path length in Pd is almost 18 times its depth of penetration with this geometry. For energies just above the Pd K absorption edge at 24.35 keV, the short absorption length in Pd (i.e., $1/\mu$) of about 14 μm limits sensitivity to depths very near the surface. Just below the Pd K edge and up to 47 keV, $1/\mu$ is 83 μm, allowing sensitivity to the top 10 or so μm of the foil. Only for energies > 80 keV (where $1/\mu = 335 \mu\text{m}$) is the entire thickness of the foil accessible, as selected by positioning the sampling volume within the foil. We employed the Pd K_α x-ray fluorescence at 21.13 keV ($1/\mu = 55 \mu\text{m}$) to position the sample surface in the diffraction sampled volume, based on the intensity of this x-ray fluorescence. Diffraction data from high energy x-rays was sometimes obtained even when the Pd K x-ray was not observed, because it would be totally absorbed by the cathode at depths greater than ~30 μm ($10 \times 1/\mu \div 18$). The original Pd grain size of the cathodes averaged 100 μm, so that most spectra sampled a mixture of two or three grains that the sampled volume straddled during the measurement.

The 2θ diffraction angle was set to 13 degrees to transmit the x-ray beam between the cathode and anode, and to enable diffraction from a broad range of d spaces. The diffraction angle was calibrated using a gold target substituted for the cell. The experimental procedure was to take x-ray spectra prior to beginning electrolysis, and to

also establish the starting resistance to enable measurement of R/R_0 , where R is the measured resistance and R_0 is the starting value. The x-y-z stage and ω were used to align the cathode within the sampled volume and to establish the Bragg diffraction condition.

The electrochemical cell, fabricated at ENEA, consisted of a 26-mm-OD glass tube with 1-mm-thick walls and an electrolyte volume of 25 mL. The x-rays passed through the glass wall and about 12 mm of electrolyte to reach the cathode and another 12 mm of electrolyte and the glass wall before emerging from the cell. This limited the detection of diffracted x-rays to energies greater than ~ 20 keV. The cathode was positioned at the center of rotation of the sample stage and initial alignment was performed with a microscope. The parallel-plate, dual-anode-geometry electrochemical cell is illustrated in Fig. 2. The two anodes were 50- μm -thick Pt foils and the cathodes were nominally 50- μm -thick Pd foils. All electrodes were 20 mm wide and 40 mm in height. The anodes and cathode were separated by 4-mm-thick Teflon spacers, used to clamp the electrodes together at each end.

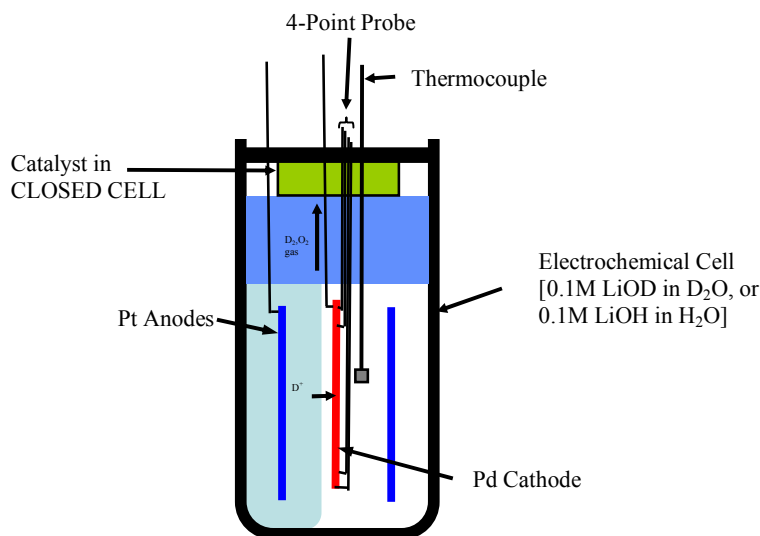


Fig. 2. - Schematic representation of the modified Fleischman-Pons electrolysis cell. This was a closed cell with self-contained catalyst for H_2 and O_2 recombination, and was instrumented to measure cathode resistance and cell temperature and pressure.

Five Pt wires were spot-welded to the Pd foil: one contact for the cathode current and four for the four-point probe measurement of resistivity at a frequency of 1 kHz. Initial resistance of the Pd was a few m Ω . The cell was hermetically sealed, and had a Pt basket containing a catalyst in the upper region to recombine the evolved hydrogen and oxygen generated by electrolysis. A valve was set to release at 1.4 bar to ensure safety from explosion, and a temperature-controlled, high-precision pressure sensor monitored cell pressure and enabled termination of electrolysis if the pressure reached 1.4 bar. The measured pressure was very stable throughout the experiments, indicating that the catalyst performed well.

The electrolyte was composed of either 18M Ω H_2O containing 0.1M LiOH or 98+ atomic% D_2O with 0.1M LiOD. Thermocouples measured the electrolyte temperature and the temperature of the x-ray cabinet at 5 different positions. Input electrolysis power to the cells varied but never exceeded 14 watts. The electrolyte temperature was highly correlated to the input power. The cell electrolyte temperature increased to as much as 51 $^\circ\text{C}$ from a starting temperature of 29 $^\circ\text{C}$ during experiments due to this heat source.

Electrolysis was begun using 0.2 to 1.2 mA/cm 2 current density under current control and required a starting voltage of about 2.2 V to drive the current. The voltage steadily increased with the degree of loading as the chemical potential of the PdH system increases with loading. The degree of loading was estimated using the resistance ratio R/R_0 calibration curves for H or D shown in Fig. 3. Spectra were collected during ~ 5 -minute intervals. The error in the R/R_0 measurement is estimated to be $<1\%$.

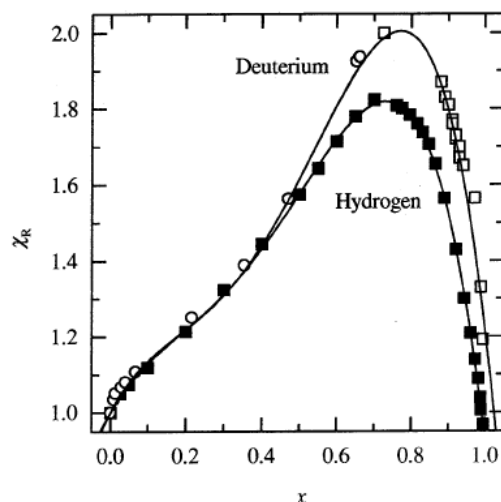


Fig. 3. - Resistance ratio R/R_0 or χ_R versus H(D)/Pd ratio x . Data taken from Zhang et al. [16], and references therein. Data was digitized then fit using fifth order polynomials.

However, the Pd resistance changed during a run from factors other than just hydrogen content, such as changes in dislocation density, grain size, and lattice strain, so that when the resistance ratio peak is retraced, the maximum can unpredictably change by as much as 6%. Therefore, the R/R_0 measurement is considered a semi-quantitative *in-situ* indicator of loading of the foil. Additionally, R_0 was always measured at room temperature, but the temperature upon reaching the peak in resistance was always higher due to the input power into the cell. Therefore, the peak value of R was temperature corrected to room temperature prior to forming the R/R_0 ratio, using a temperature coefficient of resistance value of 0.004 K^{-1} taken from the value for pure Pd. Nevertheless, the peak value of the R/R_0 ratio generally differed from literature values (1.8 for H and 2.0 for D), due to extraneous factors as mentioned above. Consequently, the peak value was scaled to the literature value by multiplying R_0 by an appropriate factor.

When R/R_0 approached the peak in Fig. 3, the current was increased in stages to produce a higher loading ratio. At appropriate times when the loading stalled, either the current was increased, or the current set to zero for several minutes and then restarted at a current 20% greater than prior to shutting off the current. These procedures sometimes resulted in a new surface condition where the loading would increase.

Due to the large lattice expansion of Pd when it is loaded with hydrogen (up to 5% lattice parameter increase, 16% volume increase), the cathode began to warp and move immediately upon initiation of electrolysis. This required continuous use of the x-y-z stage and ω to reengage the cathode, since it moved as much as 2 mm as it adjusted to the strain from loading. The problem was less acute at high loadings due to the slower change in H/Pd value and lattice constant with time. The problem was so severe that little data was taken at low loading ratios. In the last run with H_2O , the cathode was deloaded in steps by lowering the current systematically so that some x-ray spectra could be taken at smaller H/Pd ratios.

During each run, additional x-ray fluorescence lines appeared in the spectra that were identified as Sn and Pb. The origin of these impurities was most likely from solder used in wire connections to the feed-through at the top of the cell. Conceptually, the solder dissolved in vapor condensed onto the solder, then dripped back into the electrolyte. The surface of the cathode became coated with impurities from the electrolyte, because metallic ions in the electrolyte will plate out on the cathode during electrolysis. This was confirmed by visual observation of the cathode when the cathodic current was removed. Immediately a cloud of material came off of the cathode turning the electrolyte black in color. Then, the electrolyte cleared in only a few seconds as the material dissolved back into the strong base.

Four cathodes prepared at ENEA were run in the cell. Details of their preparation are described elsewhere [17]. Briefly, cathodes of 0.9995 purity were rolled to 50- μm thickness, annealed at 850°C for 1 hours, etched in Aqua

Regia, and recleaned with alcohol and DI water just prior to insertion into the cell. In one case, a cathode (B) was reused with another batch of electrolyte, after first deloading and recleaning.

All x-ray spectra were least-squares-error fit to obtain peak positions, widths, and intensities. These were analyzed to obtain d spacings and hkl values, then lattice parameter a. At the beginning of loading, few diffraction peaks were found, consistent with few grains being sampled, and the Bragg diffraction condition not readily being satisfied. As the loading progressed, more peaks were observed, consistent with subgrains being formed due to the large lattice strains generated by the hydrogen loading of Pd. In many cases, a single lattice parameter could match all the diffraction peaks observed. However, in some cases the loading was heterogeneous, typically resulting in pairs of peaks at the same hkl value. In those spectra we identified two different lattice parameters.

The D (H) composition of the cathode in the β phase of PdD_x (PdH_x) was determined from the measured lattice parameter using the 77K composition versus lattice parameter data from Schirber and Morosin [13], combined with an extrapolation of the thermal expansion data of Hemmes, Geerken and Griessen [18] provided from 10-250K.

3. Results

Table 1 summarizes results for the four cathodes run over a 9-day period. Table 1 shows that high maximum loadings ($0.86 < \text{H(D)}/\text{Pd} < 0.98$) were obtained from the lattice parameter a for all four cathodes; that the thinnest cathodes (with larger R_0) loaded to the highest H(D)/Pd ratios; and that the R/R_0 method slightly underestimated the maximum loading fraction for the D case, but overestimated it for the H case. The discrepancy was about 2%. Fig. 4 shows the current, voltage and power values needed to obtain the minimum R/R_0 for a D loaded cathode, plotted versus the minimum R/R_0 . Higher values of all 3 parameters promote better loading, but the strongest correlation is for input power and input current. For all cathodes, higher powers were attempted after the minimum R/R_0 (max. loading) was reached, but the cathodes deloaded and never returned again to the lowest R/R_0 values. For 3 of the 4 cathodes, the electrolyte temperature clearly decreased upon initial loading, caused by the endothermic heat of water hydrolysis combined with the dissolution of D (H) in Pd and the creation of orphan oxygen, preventing their recombination at the catalyst. For the fourth, very low current was initially used so that the thermal signal was below the sensitivity of the measurement.

Table 1. Cathode Loading Descriptions.

Cathode	Electrolyte	R_0 (m Ω)	Time (h:min)	Charge (C)	Energy (kJ)	Maximum	Maximum
						D(H)/Pd From R/R_0	D(H)/Pd From a
NRL#2	D ₂ O	3.69	46:15	6337	22.14	0.85	0.856
L23	D ₂ O	3.82	30:15	5974	18.32	0.87	0.893
B2	D ₂ O	10.08	48:22	110947	783.24	0.95	0.977
L5	H ₂ O	5.24	09:56	4354	18.19	0.97	0.946

Figs. 5a and 5b show x-ray spectra for Cathode B2 (D loaded) and cathode L5 (H loaded), respectively. The intensity falls off at low energy due to absorption in electrolyte and at high energy due to x-ray beam intensity fall-off. Diffraction from multiple hkl orientations are identified in the plots, and indicate that the incident x-ray beam intercepted multiple subgrains within the nominal 3 original grains inside the sampled volume. The D/Pd ratio in (a) is 0.913 from the lattice parameter, while R/R_0 indicated a ratio of 0.936 for cathode B2/spectra_154. From (b), the H/Pd ratio is 0.933, which matches the value obtained from R/R_0 for cathode L5/spectra_229. Pd, Sn, and Pb fluorescence peaks are also identified in the spectra, as are satellite escape peaks from the escape of Ge x rays from the detector, and diffraction peaks likely from Sn deposited on the surface in (a).

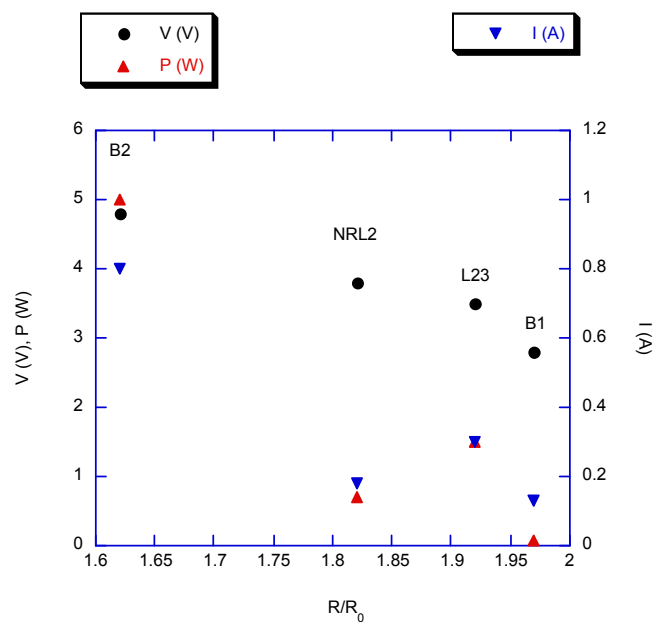


Fig. 4. - Cathode operating conditions to obtain the minimum R/R_0 at the highest D loading: current, voltage, and power, versus the minimum R/R_0 obtained.

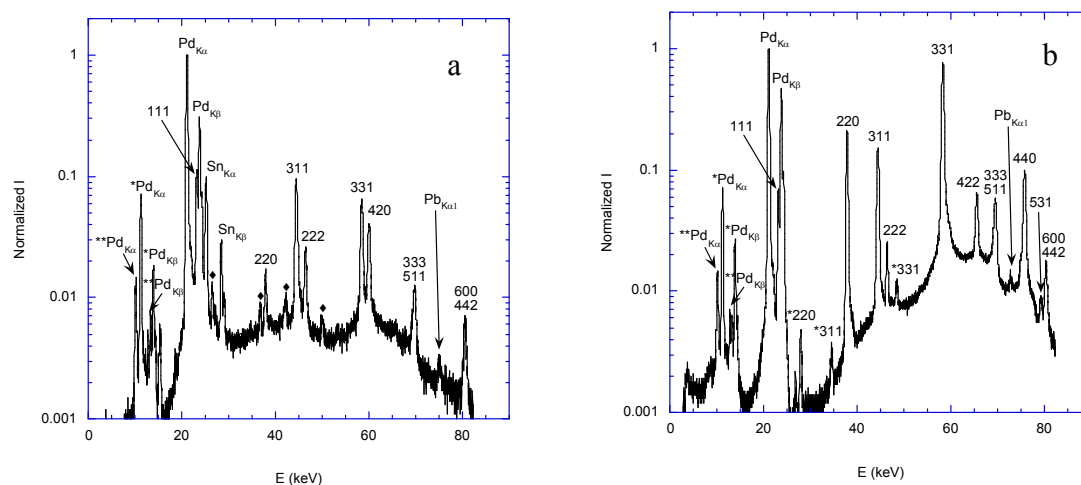


Fig. 5. - Typical x-ray diffraction spectra obtained, a) from cathode B2 (D loaded, spectra 154), and b) from cathode L5 (H loaded, spectra 229). Besides diffraction peaks marked by their hkl values, there were also fluorescence peaks from Pd, Pb, and sometimes Sn present in spectra, as well as escape peaks caused by escape of $Ge_{K\alpha}$ or $Ge_{K\beta}$ x rays from the detector (marked by * or **, respectively). Extra diffraction peaks from white Sn deposited on the cathode could sometimes be observed, as indicated by the diamond symbols shown in a).

Figs. 6a and 6b display a time history of the lattice constant, R/R_0 , and cell current for Cathode B2 (D loaded) and cathode L5 (H loaded), respectively. A general observation is that the deuterium-loaded cathodes displayed variability in the lattice constant upon large current changes (Fig. 6a, 4E4 s and 1.0 E5) while the one hydrogen-loaded cathode did not show this variability (Fig. 6b, 2.2 E4 s). The highest D/Pd ratios occur at the beginning of the electrolysis, and in one case occurred when the R/R_0 ratio had not yet even reached the peak (not shown). A possible explanation is that some orientations of the crystallites have faster kinetics than others and may load to high values

unconstrained by neighboring grains. Eventually, the other grains equilibrate, but by then compression prevents all the grains from obtaining the highest value. A second possible explanation is that the Pb and Sn surface impurity build-up over time may reduce the H fugacity and therefore the chemical potential pressure on the surface. This behavior was not observed in the one cathode run with H₂O.

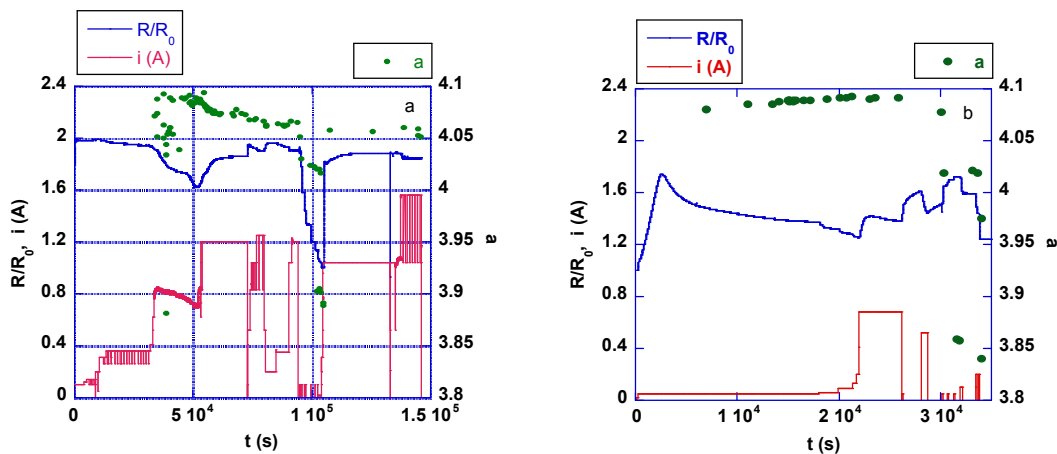


Fig. 6. - Time history of (a) cathode B2 loaded with D, and (b) cathode L5 loaded with H. R/R_0 , cell current, and measured lattice parameter a are shown.

Figs. 7a and b plot the R/R_0 ratio versus lattice constant for Cathode B2 and Cathode L5, respectively. These data have several features to note. First, there is a very clear delineation between the lattice constants for the α phase ($a \sim 3.9$) and the β phase ($a > 4$). Second, the collection of data does not appear to follow a smooth curve, especially near the peak in R/R_0 for the B2 cathode. This is largely caused by the heterogeneous loading of subgrains in the Pd foil. While R/R_0 is a bulk average for the foil, XRD was measuring individual subgrains, whose composition varied from subgrain to subgrain during some measurements. In those cases, the diffraction spectra showed multiple peaks for a given hkl for PdD_x, leading to multiple lattice parameters corresponding to the single R/R_0 value. These multiple values of a are plotted in Fig. 7. These cases were most common when the current changed by a large amount.

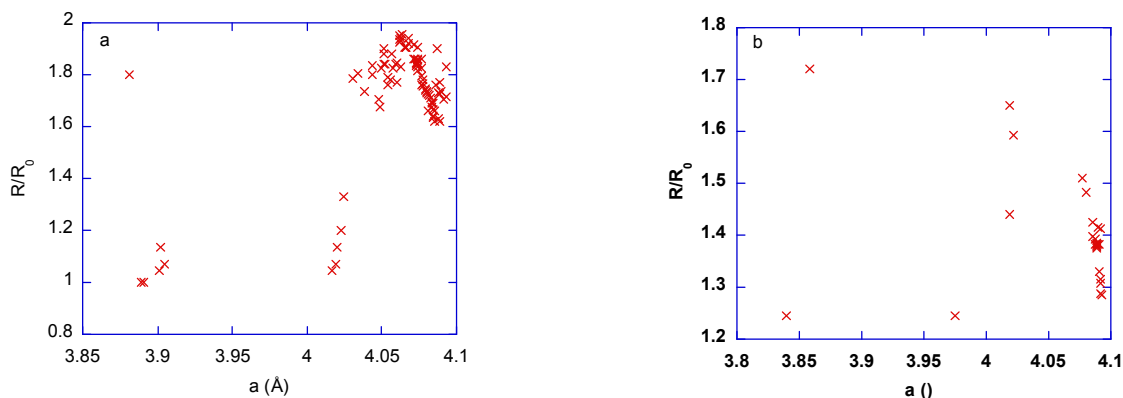


Fig. 7. - Comparison of measured R/R_0 with lattice parameter for (a) cathode B2 loaded with D, and (b) cathode L5 loaded with H.

4. Summary

For the first time, time resolved, *in-situ*, energy-dispersive x-ray diffraction was performed on modified Fleishman-Pons electrolytic cells during electrochemical loading of palladium foil cathodes to high levels with hydrogen and

deuterium. Concentrations of H/Pd (D/Pd) up to nearly 1 in 0.1 M LiOH (LiOD) in H₂O (D₂O) electrolytes were obtained with lattice parameter data monitored throughout the range of concentrations.

A number of observations regarding the electrolysis of F-P cells were consistent with the literature. These include: it is more difficult to load deuterium than hydrogen into palladium, large amounts of impurities are deposited on the cathode from the electrolyte, the *in-situ* relative-resistance measurement of the cathode provides only a semi quantitative guide to the hydrogen concentration, and once a cathode has been loaded to high hydrogen concentration, it is difficult to repeat this high concentration upon subsequent loading. Potential new observations in the electrolysis of FPE cells include: higher starting resistivity foils (thinner foils) loaded to higher D concentration, the highest loading fractions occurred during times of large current and/or concentration change, and all 4 cathodes produced at ENEA loaded very well.

Observations regarding *in situ* XRD during electrolysis in F-P cells were consistent with the literature in that only the well-known alpha-beta phase transition was observed. New observations from the *in situ* XRD during electrolysis in F-P cells include: data obtained for high D/Pd ratios up to 0.98, the relative resistivity measurement R/R_0 slightly underestimates the XRD measurement of the maximum D/Pd ratio by $\sim 2\%$, there is no obvious new PdD phase at D/Pd ~ 1 , and nonuniform loading of hydrogen can occur. Tentative new observations from the XRD data include evidence of rapid loading and deloading ($\sim$ minutes) of the surface while R/R_0 was virtually unchanged, and very few x-ray spectra contained both alpha and beta phases together. This implies that the phase change snaps from Alpha to Beta, and vice versa, within the time resolution of the data, or about 5 minutes.

The research work demonstrated for the first time with *in situ* XRD that a loading near D(H)/Pd = 1 may be achieved at room temperature, and can be reasonably controlled.

Acknowledgments

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Material Database for Electrochemical Loading Experiments at ENEA

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Abstract: A large number of palladium cathodes have been crafted, in many years, to perform chemical loading experiments. These cathodes underwent, very often, different production processes, characterization procedures and experimental conditions. The need to keep trace of all the steps of the “life” of a cathode was the starting point for the creation of a database. The information stored in this useful archive puts us in condition of easily compare different cathodes and try to correlate their experimental behavior with their history.

1. Introduction

The research activity carried out in ENEA on the field of the Fleischmann and Pons (F&P) effect includes different aspects regarding the palladium cathodes used in the electrochemical experiments. One of these concerns the best way to sort and classify the huge quantity of information produced by the large number of experiments carried out and by the enormous number of variables that can be introduced in the manufacture process and in the characterization of each cathode. An efficient method to do so could both easily allow to run through the steps that led to the generation of a cathode again, and help correlating one or more peculiar characteristic with the results of an experiment.

2. The Database

Each electrode undergoes, during its “life”, different processes, some of which are needed for its manufacture (figure 1), and others for its characterization (figure 2). Each detail of the manufacture of the cathodes has to be recorded into a database.

A lot of data, result of the characterization procedures used on the cathodes before and after the electrolysis process, needed as well to be stored in the database.

The first thing to do in order to classify different electrodes, and all the information about them, is to give to each one a name that will allow to:

- Discriminate it from all the others.
- Discriminate different stages of its own (temporal) manufacturing path.

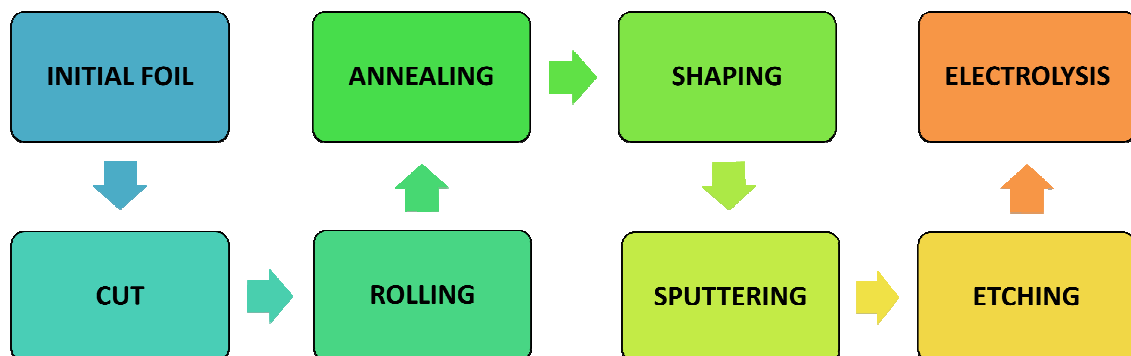


Fig. 1 – Example of some of the processes a cathode can undergo during its manufacture.

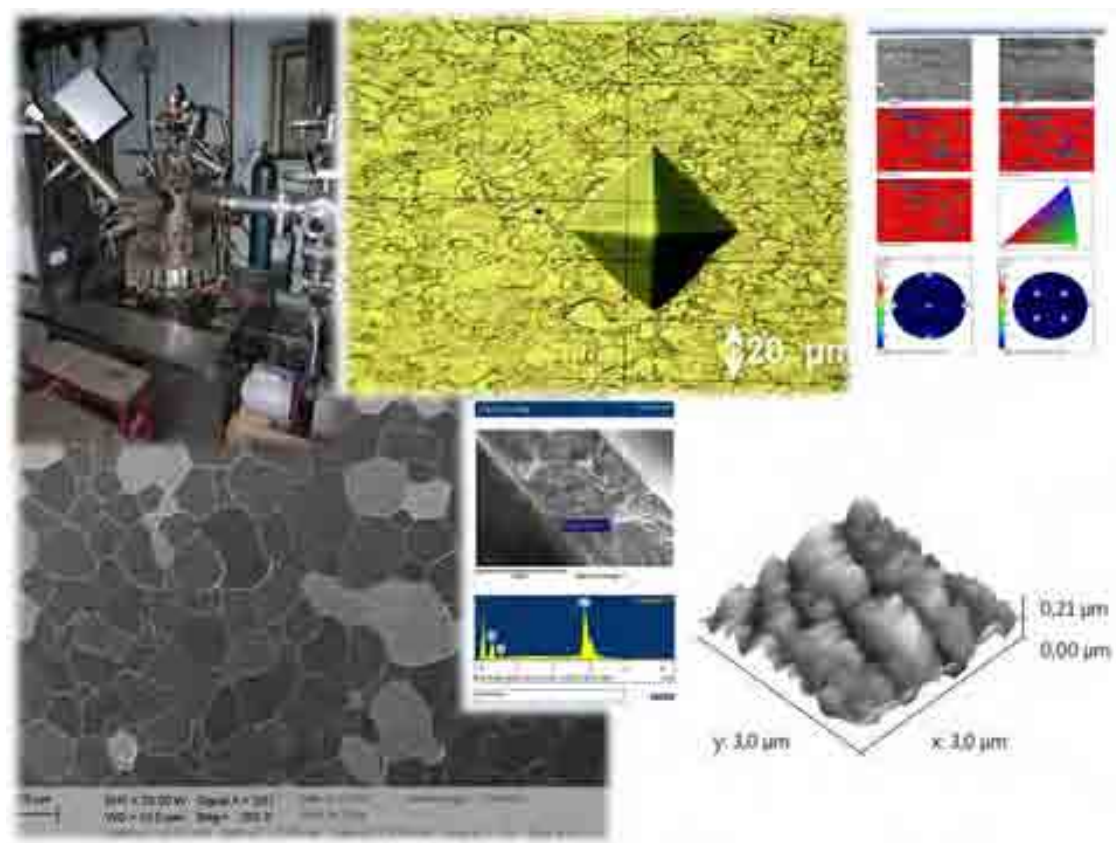


Fig. 2 – Example of some of the techniques used to characterize the cathodes. Starting from the upper left corner, moving clockwise: S.I.M.S., Vickers indenter, E.B.S.D., S.E.M., E.D.X., atomic force microscope.

To do so we thought up a very efficient nomenclature that matches these two requirements and consists in naming each cathode with an abbreviation that increases as the electrode goes on through its manufacturing process. Each cathode name is unique and contains information on which production processes the electrode underwent, and on the position the electrode took up on the rolled foil. Such nomenclature allows to discriminate each stage of the cathode “life” and to store information stage-related. An example is shown in Figure 3.

The database has been made using Microsoft® Access®. Its structure is time organized, newer cathodes are added sequentially from top to bottom and newer operations done on them are added from left to right in the corresponding row. A scheme of its structure and contents is shown in figure 4. All the information stored for each electrode can easily be accessed through a simple interface as shown in figure 5.

L54 (189-227) RAEF					
L54: means that the electrode comes from a certain rolling process	(189-227): shows the point of the rolled foil, in millimeters, the cathode was cutted from	R: means that the rolling process has been recorded into the database	A: means that the annealing process has been recorded into the database	E: this letter can change and represent the etching process	F: this letter can change and represent the cell in wich the cathode was electrolyzed

Fig. 3- Example of a cathode’s name.

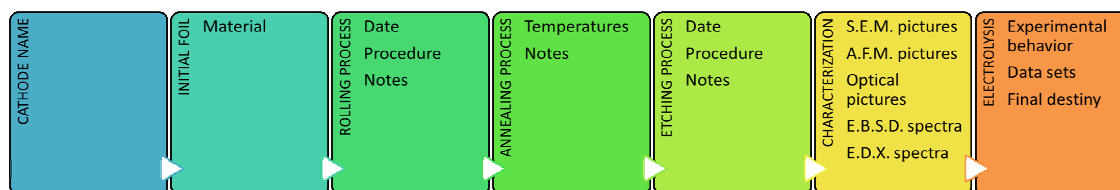


Fig. 4 – Structure of the database.

ENEL CAMPIONE Excess Heat: Si

Nome Campione:

Data:

Sistema di Prolungamento:

Dettagli Annealing:

ANNEALING			
1° RAMPA		2° RAMPA	
TEMP	TIME	TEMP	TIME
		900°C	1h

Note Annealing:

Data Etching:

Dettagli Etching:

ETCHING			
TEMP	TIME	TEMP	TIME
67%	30sec	50%	90sec

Note Etching:

Ultrasuoni:

Note Ultrasuoni:

Immagini Microscopia Ottica:

Immagini SEM:

Immagini AFM:

Spettri EDX:

Fig. 5 – Database interface.

3. Conclusions

Our database holds, until now, over 550 records and is updated almost daily, the oldest entry is from the 29th of June 2005 and since the 21th of November 2007 the cathodes were named using the new nomenclature. The large number of information, spanning over a wide period of time, have put us in conditions, as done in other works, to try to statistically correlate the experimental behavior of the cathodes with their measured properties or with the production processes they underwent. However a lot of additional work is still required to improve it, both in terms of variety of information stored and in terms of capability to sort the electrodes who share one or more characteristics. Time will allow us to increase the number of information and to ameliorate our database so that it could become, more than it is today, an absolutely necessary tool for a systematic approach to the problem we try hard to solve.

Interaction of the Electromagnetic Radiation with the Surface of Palladium Hydride Cathodes

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Abstract. The change of the electronic density of metallic Pd due to the hydride formation and to the build-up of the double layer, rising at the metal-dielectric interface when an electric field is applied, is involved in the variation of the metal dielectric function. A model including also metal surface roughness has been developed to take into account such modifications.

1. Introduction

The dissolution of hydrogen within a metal lattice and the formation of a metal hydride greatly perturb the electrons and phonons of the host material. Several are the relevant observed effects:

- The generally observed expansion of the lattice, often including a change in the crystal structure, involves a modification of the symmetry of the states and a reduction of the band width
- The attractive potential of the protons affects those metal wave-functions which have a finite density at the H site and leads to the so called metal hydrogen bonding band below the metal d-band
- The additional electron brought by the H atoms into the unit cell produces a shift of the Fermi level
- H-H interactions leads new features in the lower portion of the electron density of states.

One can affirm that the *1s* electron bonded with the hydrogen ion enters into *s* and *d* bands of the considered material, thus modifying the states density on Fermi surface and the energy bands structures itself^[1].

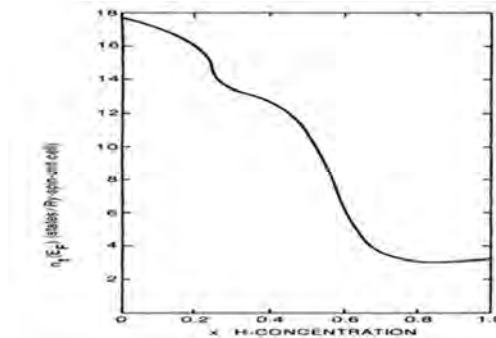


Fig. 1 - Total Density of States at the Fermi level plotted versus hydrogen concentration in Pd.

In Ref. [2] the total density of states (DOS) of palladium versus hydrogen concentration is shown, expressed for unit cell, spin and Rydberg (1 Rydberg, R_y , ~ 13.6 eV).

To estimate the electrons concentration n_e at Fermi energy for pure Pd and for $\text{PdH}_{x=1}$ we have to integrate the DOS with respect to such energy.

By considering that the volume of the unit cell in the reciprocal lattice is

$$V_{\text{cell}} = \frac{a^3}{4} \quad (1)$$

Where a is the lattice parameter, we can write for n_e the expression:

$$n_e \approx \frac{2\text{DOS} \cdot KT}{R_y} \frac{1}{V_{\text{cell}}} \quad (2)$$

Where K is the Boltzmann constant and T is the room temperature. By assuming a lattice parameter of 0.348 nm for pure Pd and of 0.406 nm for $\text{PdH}_{x=1}$ we obtain $n_{\text{ePd}} = 6.5 \cdot 10^{21} \text{ cm}^{-3}$ and $n_{\text{ePdH}_{x=1}} = 6.8 \cdot 10^{20} \text{ cm}^{-3}$. As expected, the electron concentration at Fermi energy strongly decreases in palladium hydride.

2. Electrochemical Surface Model

In the considered system, an electrochemical interphase has to be taken into account, as the hydrogen is introduced into metal lattice via electrolysis by a cathodic polarization of the metal.

The chemical interface is characterized by the presence of a strong electric field.

Recently, techniques based on the resonant excitation of surface plasmons (SPR) have been developed in order to study the effect of the electrochemical double layer electric charges redistribution on the thin metallic film dielectric properties^[3].

Substantially, the application of a electric potential modifies the dielectric properties near the metal-liquid interphase, and consequently the SPR signal is modified.

It has been demonstrated that the Helmholtz double layer formation deeply influences the SPR answer.

A model has been developed to take into account such modifications^[4].

Several effects, rising at a metal-dielectric interface when an electric field is applied, are involved in the angular shift of the SPR. In particular, the electronic density variations due to double layer and to the hydride formation are taken into account.

Modification in Palladium real and imaginary dielectric function components after deuterium solubilisation in metal lattice are shown in Fig.2 e Fig.3

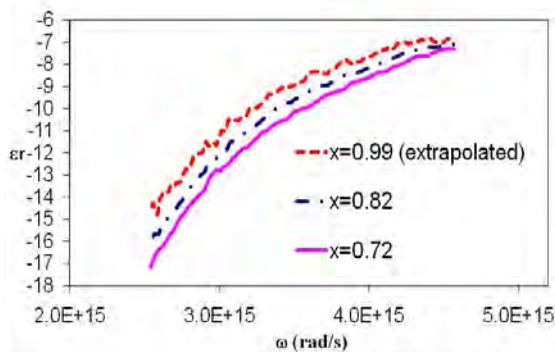


Fig.2 - Dielectric function real component, palladium

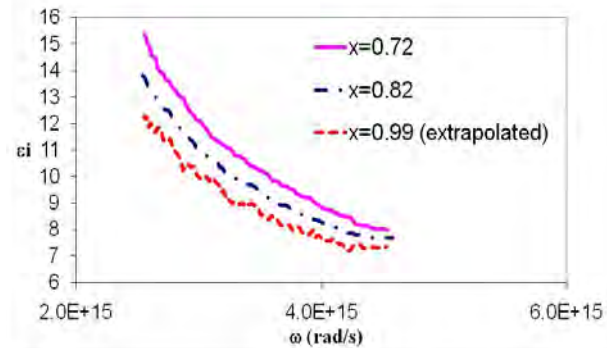


Fig.3 - Dielectric function imaginary component, palladium hydride.

Surface charge density σ , which can be calculated by the Stern's theory^[4], by varying the electronic configuration of the material, affected dielectric function value too^[5].

The dielectric function variation $\Delta\epsilon_{\text{PdH}_x}$ related to surface charge density is

$$\Delta\epsilon_{\text{PdH}_x} = \left(\epsilon_{x_{\text{free}}} - 1 \right) \frac{\Delta Ne \sigma_{\text{PdH}_x}}{Ne_{\text{PdH}_x}} \quad (3)$$

Where $\epsilon_{x_{\text{free}}}$ is palladium hydride dielectric function free electrons contribute, Ne_{PdH_x} is the free electrons concentration in palladium hydride bulk and $\Delta Ne \sigma_{\text{PdH}_x}$ is the free electrons excess on its surface, defined as:

$$\Delta Ne \sigma_{\text{PdH}_{0.99}} = \frac{\sigma^m}{q \cdot d} \quad (4)$$

Where q is the electron electric charge modulus and d the electric field penetration inside metal, defined in c.g.s. units as^[6]

$$d = \frac{c}{\sqrt{8\pi\mu_{0Pd}\rho_{PdH_{0.99}}^{-1}}} \quad (5)$$

Where c is light velocity in vacuum, $\rho_{PdH_{0.99}} \approx 5 \cdot 10^{-5} \Omega cm$ is palladium hydride samples resistivity and $\mu_{0Pd} = 1$ is palladium magnetic permeability.

The total surface palladium hydride dielectric function in electrochemical condition ε_{PdH_xTOT} can be expressed as:

$$\varepsilon_{PdH_xTOT} = \varepsilon_{PdH_x} + \Delta\varepsilon_{PdH_x} \quad (6)$$

Where ε_{PdH_x} is palladium hydride dielectric function if no excess of charge is on the metal surface, i.e. no electrochemical processes are running.

In Fig.4 and Fig.5 the profile of PdH_x dielectric function real and imaginary components versus angular frequency is presented, in the range of validity of the proposed approximation. Also the total dielectric function, obtained taking into account the presence of an excess of electric charges due to electrochemical operating conditions is shown. As expected, the presence of surface charge density makes the material to acquire a more metallic behaviour.

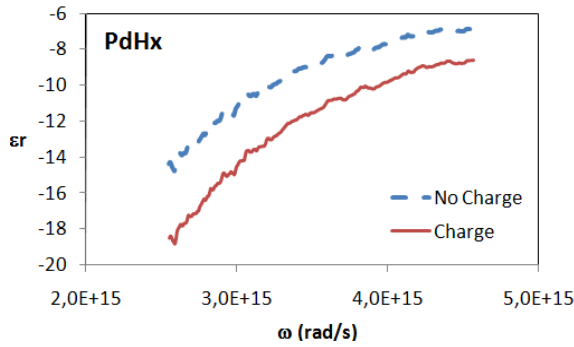


Fig.4 - Dielectric function real component, palladium hydride under cathodic polarization.

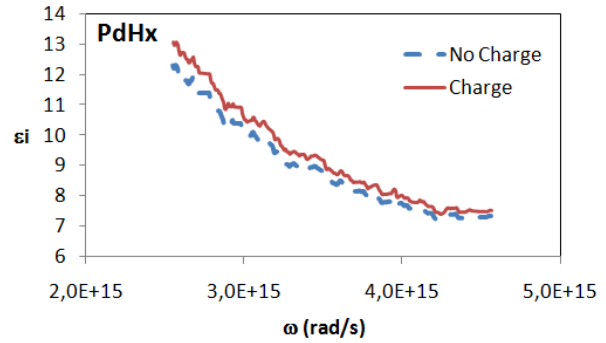


Fig.5 - Dielectric function imaginary component, palladium hydride under cathodic polarization.

Surface Plasmons resonance could give rise to a huge local field enhancement, due to a focusing effect: a broad e.m. wave is confined in a surface. Enhancement of about 10^2 factor could be obtained in this classical calculation. Using appropriate structures and quantum mechanical computation the enhancement factor could be equal to several magnitude orders. No matching condition results to be possible between light lines and surface plasmon dispersion curve at an air-Pd interface: the matching condition can not be satisfied on smooth surface, because the interaction between photons and plasmons can not simultaneously satisfy the energy and momentum conservation^[7]. It is possible to obtain s.p. excitation both using a corrugation lattice or by corrugating the metal surface itself: such a corrugation increases the surface parallel component of the laser beam wave vector, making thus possible the coincidence with s.p. wave vector^[7].

As Pd cathode are chemically etched before electrolysis, their surface is quite rough, with roughness parameters highly depending both from etching procedure and starting material properties. In Fig.6 and Fig.7 Atomic Force Microscope (AFM) three-dimensional images of two Pd etched samples are shown. The differences in surface morphology are quite evident.

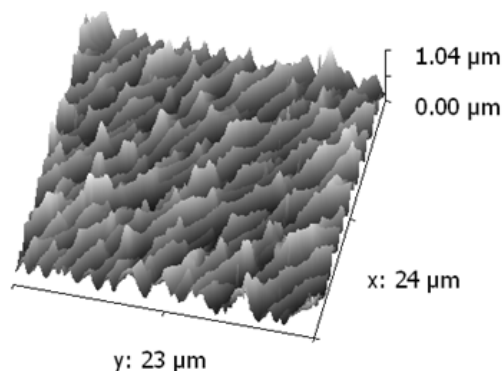


Fig.6 - Dielectric function real component, palladium hydride under cathodic polarization.

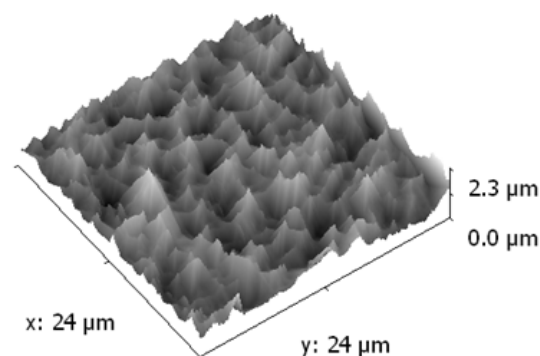


Fig.7 - Dielectric function real component, palladium hydride under cathodic polarization.

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The Role of Cathode's Surface Properties in the Electrochemical Deuterium Loading of Pd Foils

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Abstract. Recent experimental evidences clearly indicate that the reproducibility of excess heat production is correlated with the cathode surface properties. To support the results, a theoretical frame has been also developed, that suggests that a relevant role in the excess heat production is played by the electro-dynamics processes at the cathode interface. In particular, one of the mechanisms involved is the enhancement and spatial localization of the electro-magnetic field at the metal/electrolyte interface, promoted by proper surface roughness and morphology.

A further point to be considered is the dynamic character of the metal/electrolyte interface during electrochemical deuterium loading, that derives from the coupling between the different interface characteristics. Surface reconstruction of the metallic cathode is expected to happen, due to corrosion-deposition mechanisms, D/H transport, stress relaxation and defect production, and so on. All these mechanisms both affect and are affected by the surface properties, such as the morphology of the metal/electrolyte interface, the metallurgical and crystal structure of the cathode and the presence of contaminants.

1. Introduction

In the last years, an increasing amount of experimental evidences has been reported, pointing out the correlation between the material properties of the palladium cathodes used in the Fleischmann and Pons (F&P) excess heat experiments and the reproducibility of the effect [1-3]. Replication of calorimetric results in different laboratories was achieved according to the fact that the cathodes had undergone the same manufacturing process and were belonging to the same commercial Pd lot [4]. Some cathodes features have been preliminarily identified to be relevant to the occurrence of the effect, in particular the polycrystalline structure and the surface morphology on micrometer scales.

Recently, a systematic study has been carried out by the authors, aimed to characterize the surface properties of the cathodes and to correlate them with the excess heat occurrence [3]. The results supported the preliminary observations, showing further evidence of the dependence of the anomalous heat effect on the crystallographic orientation, impurity contamination and microscopic features of the cathodes' surface. As concerning this last observation, an extended characterization of the surface morphology at the microscopic scale have been carried out by Atomic Force Microscopy (AFM) [2]. This study was also inspired by a theoretical frame suggesting that electro-dynamical effects (plasmons excitation) could be involved the excess heat production of F&P experiments [5,6].

Based on these recent experimental results and considerations, in this article we analyze some possible scenarios through which the microscopic surface morphology of the Pd cathodes could affect the electric field distribution at the metal/electrolyte interface during the electrochemical deuteride formation.

2. Experimental methods

The Pd samples used as cathodes in the electrolysis experiments were obtained from different commercial lots of pure Pd, having nominal purity above 99.95%. They have been processed by

mechanical, thermal and chemical treatments, well described elsewhere [3], in order to reduce foil thickness and to improve metallurgical properties and surface morphology. The typical manufacturing procedure consists in the following steps: 1) cold rolling of the raw 1 mm thick material to produce foils thinner than 50 microns; 2) annealing at temperatures ranging from 800 to 900°C for about 1 hour, to relax defects and induce re-crystallization into a proper polycrystalline structure, optimized for achieving maximum deuterium loading; wet chemical etching by nitric acid and aqua regia, to remove impurities and native oxide, and to produce a specific surface roughening.

Atomic Force Microscopy was used to investigate the surface morphology of the samples. AFM gives a direct measurement of the tri-dimensional (3-D) surface height profile. For each sample, several images have been taken at different points on the surface, excluding grain boundaries. Details of the AFM instrument used can be found elsewhere [2]. To make easier the comparison between different samples, the images were acquired on the same length scale (typically $24 \times 24 \mu\text{m}^2$) and with the same number of pixels (typically 257×257). Scanning of the same sample zone on different scale was also performed, in order to select the magnification factor more convenient to observe the surface features of typical samples.

The height profiles of the investigated samples were generally characterized by random fluctuations superimposed on periodic or quasi-periodic patterns. These surface features are hard to recognize in direct space, but can be effectively revealed in reciprocal space of the spatial frequencies (k_x, k_y), by computing the Power Spectral Density (PSD) of the height profile, that provides a decomposition of the surface profile into its spatial wavelength. Although the computation of the PSD is a quite common practice in isotropic random surface characterization, because of the anisotropic texture of our samples, we have defined a dedicated set of (1-D) PSD functions, which were more appropriate to extract the more relevant patterns embedded in the surface profiles, without missing the information relative to surface anisotropy. Details of image processing and analysis can be found in previous publication [2].

3. Results and discussion

It's well known that nano-metric surface features of a metal/dielectric interface can induce collective oscillations of the free electron gas (surface plasmon polaritons (SPP) or localized surface plasmons (LSP)), which can be associated to strong amplification of the local electromagnetic field [7].

The electromagnetic (EM) field can be enhanced close to a metal-dielectric interface via the excitation of surface plasmon (SP) modes. Surface roughness and isolated surface features make it possible the coupling of a EM field source with the SP modes, because they provide additional wave-vector to the source EM field that is necessary to fulfill the required momentum conservation. Thus, the role of the surface morphology in the electric field enhancement is played by the wave-vector content of the surface morphology. The Power Spectral Density is just a tool to quantify such a “wave-vector content” of the height profile, since it represents the distribution of the intensity of the sinusoidal components of the surface morphology. The correlation between the shape and intensity of the PSD curves and the anomalous thermal behavior of the Pd cathodes, observed in ref. [2], supports this scenario.

SPP modes can be excited on rough metal surfaces by electromagnetic radiation of suitable frequency and polarization to fulfill simultaneously energy and momentum conservation laws. In the specific case of a plane wave of wavelength λ impinging on a sinusoidal corrugated metal surface of wave-vector $\mathbf{G}$, this condition implies that

$$\mathbf{G} = \mathbf{K}_{sp} - \mathbf{K}_i \quad (1)$$

where $\mathbf{K}_{sp}$ is the wave-vector of the SP mode given by

$$\mathbf{K}_{sp} = (2\pi/\lambda)^2 \text{Real}(\epsilon_m / (\epsilon_m + \epsilon_d)) \quad (2)$$

where $\mathbf{K}_i$ is the projection of the incident wave-vector into the surface plane, ϵ_m is the metal dielectric constant and ϵ_d is the dielectric constant of the adjacent dielectric medium (see for example, ref. [7] pag.8).

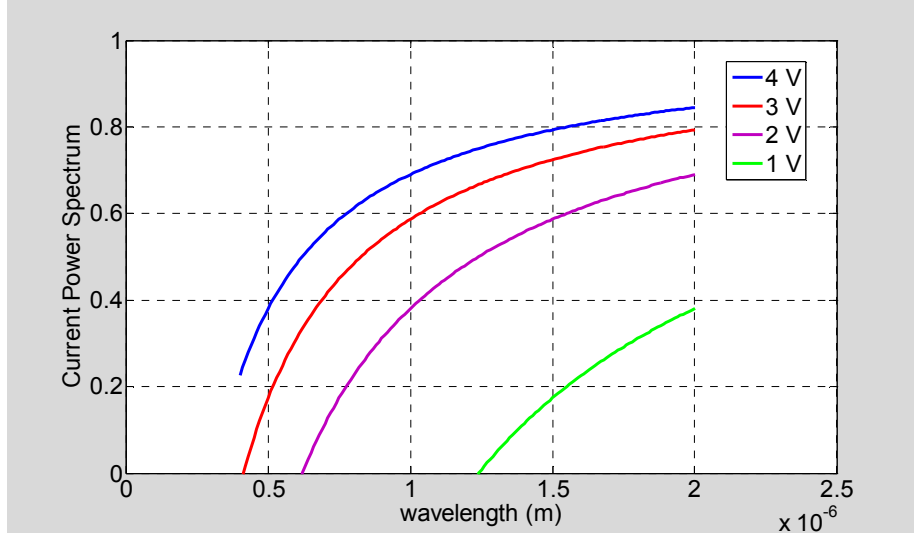


Fig. 1 Power Spectrum of the DC Current fluctuations at the interface of a DC polarized tunnel junction; different colored lines refers to different values of the DC polarizing voltage.

Typical experiments have been performed by using laser radiation to excite surface plasmons modes confined on the surface of thin metal films during electrolysis [8]. Electrochemical F&P experiments have been also carried out, in which laser irradiation of the metallic cathode was performed during deuterium loading [9]. Anyway, most of the F&P-type electrolytic experiments do not usually employ external sources of electromagnetic radiation, because they operate under direct current (DC) control.

An interesting case that presents some similarities with the typical situation occurring in the F&P experiments is the SPP excitation by microstructures on tunnel metal/insulator (or metal/semiconductor) rough junctions [10]. The effect was well known from the literature since more than 30 years ago and it consisted in the observation of light emission by tunnel junctions DC polarized, when the metal/dielectric interface presented a rough morphology. A DC bias voltage across a tunnel junction causes a DC tunnel current to flow across the dielectric barrier. Although this current is continuous, its time dependent fluctuations have a frequency spectrum ($C(\omega)$) extending from DC to a cutoff frequency (ω_c); then, such time fluctuations can drive SPP modes. In ref. [10] the tunnel current spectrum and cutoff frequency were reported:

$$C(\omega) = \frac{eV}{2\pi R_0} \left(1 - \frac{\hbar\omega}{eV} \right). \quad (3)$$

where e is the electron charge, R_0 is the DC junction resistance, $\hbar$ is the Planck's constant V is the DC voltage across the junction and $\omega_c = eV/\hbar$.

In a typical F&P experiment we could depict the double layer zone at the metal/electrolyte interface as the equivalent of the metal/dielectric interface of a tunnel junction. Under the DC current flow across the junction, the SPP modes localized at the metal interface can be excited by the time dependent fluctuations of the electric current. The frequency spectrum of the fluctuations depends on the particular type of noise by which they are produced: in the case of the tunnel junctions described above it was assumed to be that typical of “shot” noise, due to the discrete nature of the electrons flow, which has been shown in fig. 1; in the case of an electrolysis experiment different sources of noise can be imagined to be involved, such as “thermal noise” or “bubble noise”.

Once a driving EM field is available to excite SPP, the amplitude and frequency spectrum of the SPP field depends on the coupling between the source spectrum and the characteristic modes of the rough surface. The linear theory [11] offers a simple approach to compute the total field enhancement due to SPP.

We have followed this approach in order to get an approximate estimate of how much the SPP effect can be relevant to the surface morphology of our investigated samples.

In the following section, we briefly illustrate the linear method and its main assumptions and we report the results of the calculations of the electric field enhancement relative to the surface profiles of the cathodes measured by AFM technique.

3.1 The linear model

The surface profile z of the metallic cathode is described as the superposition of several sinusoidal diffraction gratings [11]:

$$z = \zeta(x, y) = \sum_{\vec{G}} \zeta_G e^{i\vec{G} \cdot \vec{R}} \quad (3)$$

where $\vec{R}$ is the position vector of Cartesian coordinates (x, y) , the average value of the profile is zero (i.e. $\langle \zeta(x, y) \rangle = 0$), $\vec{G}$ is the wave vectors of the surface profile, belonging to the reciprocal space of the Cartesian plane.

Under the hypothesis of “small roughness”, (i.e. $\sigma \ll \lambda$, where $\sigma = [\langle \zeta^2(x, y) \rangle]^{1/2}$ is the surface roughness and λ is the wavelength of the electromagnetic field) the first order approximation can be assumed to be valid, in which the electromagnetic field scattered by a surface having the specific profile $\zeta(x, y)$ of eq. (1) is reduced to the linear superposition of many fields, each scattered by a sinusoidal diffraction grating characterized by an amplitude ζ_G of eq. (1).

Consequently, SPP modes can be excited on the rough metal surface if eq. (1) and eq. (2) are fulfilled, being $\vec{G}$ the wave vectors of the surface profile defined by eq. (3) and $|\vec{K}_i| = (2\pi/\lambda) \cos(\theta_i)$, where θ_i is the incidence angle of the electromagnetic radiation.

In the same hypothesis, it can be shown that the SPP excitation probability (ΔR_{sp}) is given by:

$$\Delta R_{sp} = (2\pi/\lambda) 4 \cos(\theta_i) \int PSD(\vec{G}) \Phi(\vec{G}, \theta_i, \epsilon_m, \epsilon_d) \delta(|\vec{G}|^2 - |\vec{K}_{sp} - \vec{K}_i|^2) d\vec{G} \quad (4)$$

where $PSD(\vec{G})$ is the power spectrum of the surface profile; $\Phi(\vec{G}, \theta_i, \epsilon_m, \epsilon_d)$ is a factor that does not depend on the surface profile; $\delta(x)$ is the Dirac δ function, whose effect in the integration of eq. (4) is to reduce the integration domain to the ensemble of wave-vectors $\vec{G}$ which fulfill the matching conditions stated by eq. (1) and (2).

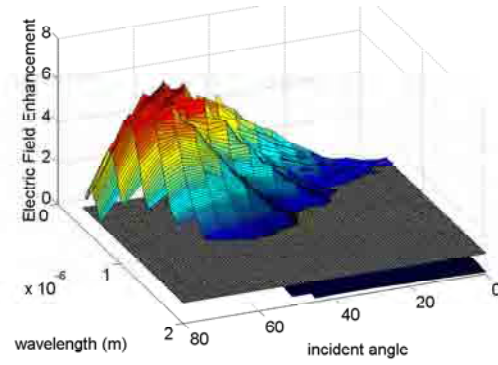
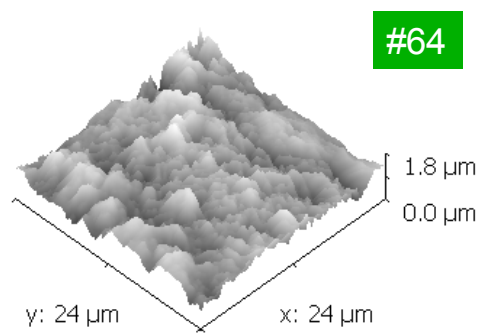
The electric field associated to the SPP charge oscillation is enhanced because of its spatial confinement close to the interface. The enhancement ratio ($|E_{sp}|^2/|E_{inc}|^2$) is given by [12]

$$|E_{sp}|^2/|E_{inc}|^2 = \cos(\theta_i) \Psi(\lambda, \epsilon_m, \epsilon_d) \Delta R_{sp} \quad (5)$$

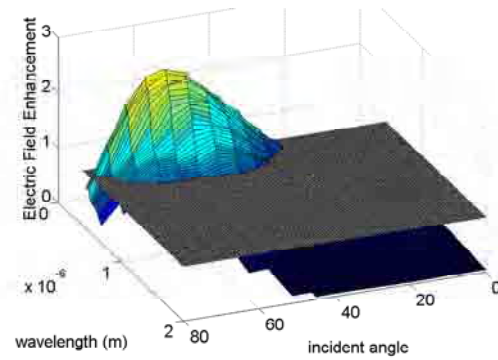
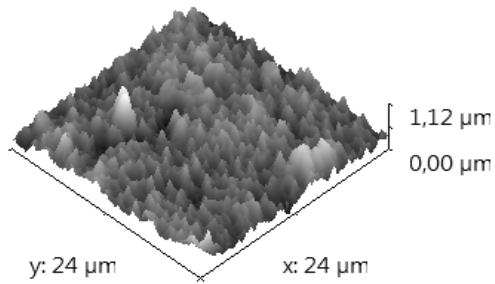
where $\Psi(\lambda, \epsilon_m, \epsilon_d)$ is a factor that does depend only on the dielectric constant of the metal and of the adjacent dielectric and on the wavelength.

3.2 Computation results

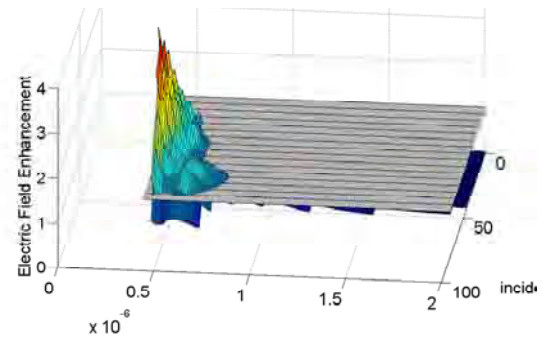
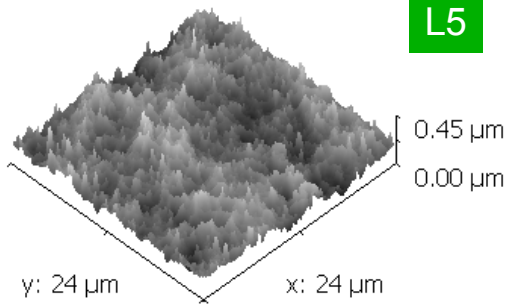
The surfaces of the Pd cathodes used in F&P experiments have been scanned by atomic force microscopy and the collected data have been numerically processed to compute the corresponding bi-dimensional PSD spectra. Such PSD spectra were used to calculate the enhancement ratio of the electric field,



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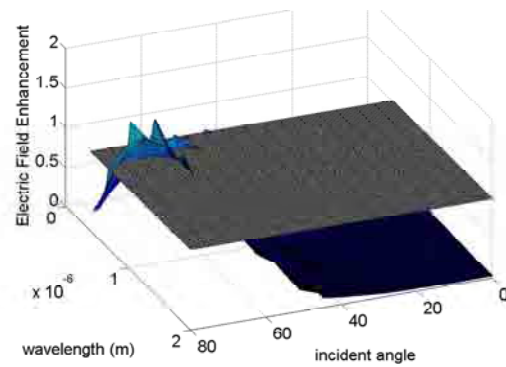
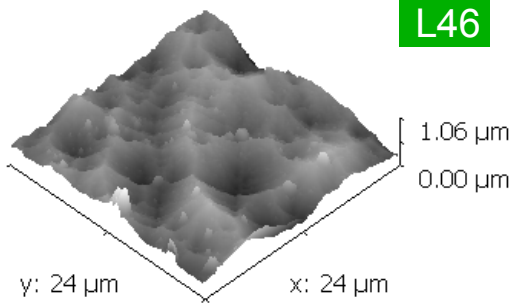


Fig. 2 AFM images (left) and corresponding electric field enhancement (right), computed according to the linear approach described in the text, of samples which gave anomalous excess heat production; the horizontal plane outlines the region in which the enhancement factor is higher than 1.

according to the linear theory described above, by means of eq. (4) and eq. (5), in which the values of the dielectric constants of the metal and the dielectric have been taken from ref. [13] and set to be 1, for the PdH and the electrolyte, respectively.

In fig. 2 the AFM images (left) and the results of the calculations of the enhancement ratio (right), relative to a set of samples which showed anomalous thermal behavior, have been reported; it can be observed that this ratio is higher than 1, in a selected domain of the incident electromagnetic radiation parameters (angle and wavelength). In particular, in going from the top to the bottom of the figure, the measured amount of excess heat produced by the corresponding samples decreased, as expected on the basis of the results reported in ref. [2], showing a correlation between the amount and reproducibility of excess heat and the maximum value of the PSD spectrum (see table I of ref. [2]). In addition, it can be noted that the max values of the field enhancement correspond to values of the incident wavelength in the range of a fraction of to a few microns.

4. Conclusions

The surface morphology of Pd cathodes used in electrochemical experiments has been characterized by atomic force microscopy, after electrochemical loading of deuterium. The electric field enhancement due to surface plasmons excitation has been estimated on the basis of the AFM images and the Power Spectral Density function, following the approach of the first order perturbation theory of the interaction of electromagnetic radiation with a random moderately rough metal surface. The results indicate that the surface morphology of the samples giving anomalous heat production can sustain SPP modes at wavelengths in the range of a fraction to some microns, thus enhancing the electric field at the metal/electrolyte interface up to a factor ten.

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Concentration polarization in Pd-based membranes for hydrogen separation: modeling and simulation

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Abstract. In this study, a new hydrogen permeation model through Pd-based membranes is developed and used to analyze the role of the concentration polarization. According to this new model, the entire hydrogen permeation process is divided into several elementary steps: multicomponent mass transport in the feed and permeate side, adsorption and desorption on/from the membrane surface, absorption and de-absorption into/from the metal lattice, diffusion through the Pd-based bulk and multicomponent mass transport through an asymmetric multilayered porous support. Each of these steps is modeled by means of some equations whose solution provides as result the value of transmembrane flux and the hydrogen partial pressure profile through the membrane. The influence of each step is evaluated as a function of several operating conditions (membrane thickness, temperature, fluid-dynamic conditions, hydrogen partial pressure on feed and permeate side). The effect of the mass transfer in the feed and permeate side is evaluated in terms of concentration polarization effect by defining an opportune coefficient and analyzing its behaviour in different conditions. As results, the investigation shows that the influence of the polarization can be appreciable even for not so thin membranes and provides some “polarization maps”, which are diagrams where the polarization level (in terms of CPC) can be directly visualized and simply estimated once knowing the external operating conditions. Hence, these maps can be very useful in order to predict better the membrane performances and, consequently, reduce the uncertainty during the design step of the membrane modules.

1. Introduction

It is well-known that Pd-based membranes show an infinite selectivity towards hydrogen with respect to the other chemical species. Thus, they are usually employed in processes requiring the selective removal of hydrogen from the reactive zone. In order to optimize their usage, in this work, the H₂ permeation and the concentration polarization phenomena are described by a complex model taking into account all the mass transfer phenomena involved in the H₂ transport through such membranes.

2. Description of the model

The schematic representation of the target system are shown in Fig. 1, where a) an SEM photo of a multilayered Pd-based membrane, b) the scheme of membrane considered here and c) the mechanism rate of each elementary step involved in the permeation, are reported. The Pd-based layer is supported by an asymmetric support characterized by several (five) layers, each one having different thicknesses and pore sizes (Table 2). The whole permeation mechanism has been divided into the following elementary steps: mass transfer in the fluid phase of the film just near the interface on retentate and permeate side; dissociative adsorption and recombinative desorption on the Pd-based layer; atomic hydrogen transition from Pd-alloy surface to Pd-alloy bulk and vice-versa (named “Surface-to-Bulk” and “Bulk-to-Surface”, respectively); diffusion of atomic hydrogen through the Pd-alloy bulk; mass transfer in the multilayered porous support. The detailed mathematical form of such a model can be found elsewhere [1].

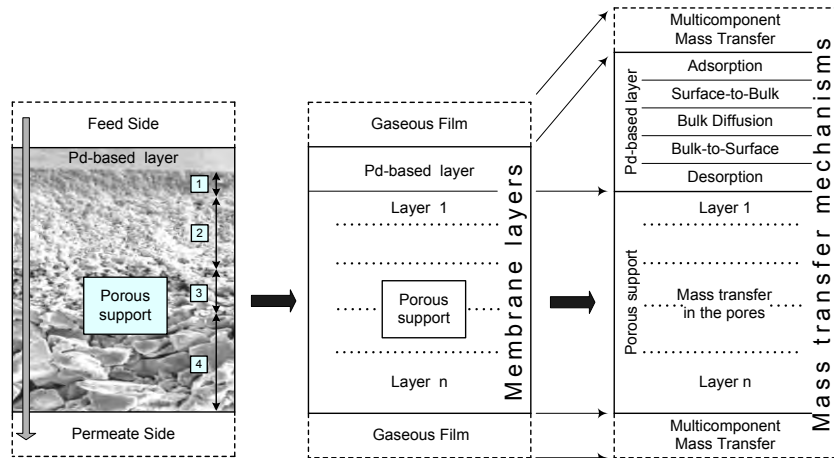


Fig. 1. – Scheme of the multilayered membrane considered and mass transfer mechanisms of all the elementary steps involved in the permeation process.

Table 1. Operating conditions considered.

Side	Pressure, kPa							Reynolds' Number	Total flow rate, mmol/s
	H ₂	N ₂	O ₂	CO ₂	H ₂ O	CO	Total		
Feed	600	75	75	50	50	25	875	1700 - 800	100
Permeate	100	80	20	-	-	-	200	1900 – 950	20

Temperatures, °C = {250; 300; 350; 400; 500; 600}

Table 2. Geometrical data of the Pd-alloy supported membrane considered.

Pd-alloy layer thickness, μm = {1, 10}				
Porous Support Layers	Thickness, μm	Mean pore Diameter, nm	Porosity, -	Tortuosity, -
1	1	5	0.5	1.2
2	50	100		
3	100	1,000		
4	500	10,000		
5	850	50,000		

3. Results and discussion

Fig. 2 shows the transmembrane hydrogen partial pressure profile at different temperatures for a thickness of 1 μm . At 300°C a quite significant pressure drop is found for hydrogen profile in the upstream film. In the adsorption and desorption steps the pressure drop is low but non-negligible, whilst both “surface-to-bulk” and “bulk-to-surface” do not show any appreciable contribution. The diffusion in Pd-bulk and transport in porous support provide important pressure drops, especially in the first two porous layers, which show important resistances even if their thicknesses are very thin. The effect of external mass transfer is also appreciable in permeate side. At higher temperatures, the mass transfer influence becomes more relevant in both gaseous film and in the support, whereas the surface phenomena (adsorption and desorption) and diffusion in the Pd-based layer got to be more rapid steps.

In Fig. 3, the overall resulting flux is plotted together with the step-limited fluxes (dashed-line), each of which is calculated considering a certain step as the only rate-determining one and all the others at the equilibrium. The adsorption and desorption steps have a decreasing slope larger than diffusion, but

obviously in both cases the temperature has a positive effect on the flux. The slopes related to these steps are proportional to their respective activation energies. On the contrary, the curve of the transport in the film on the retentate side is almost flat and the one relative to the transport in the support has even an increasing profile. This means that this last step is not favoured by the temperature and, hence, that Knudsen-type transport prevails on the Poiseuille-type one and on ordinary diffusion, the Knudsen diffusivity decreasing with temperature.

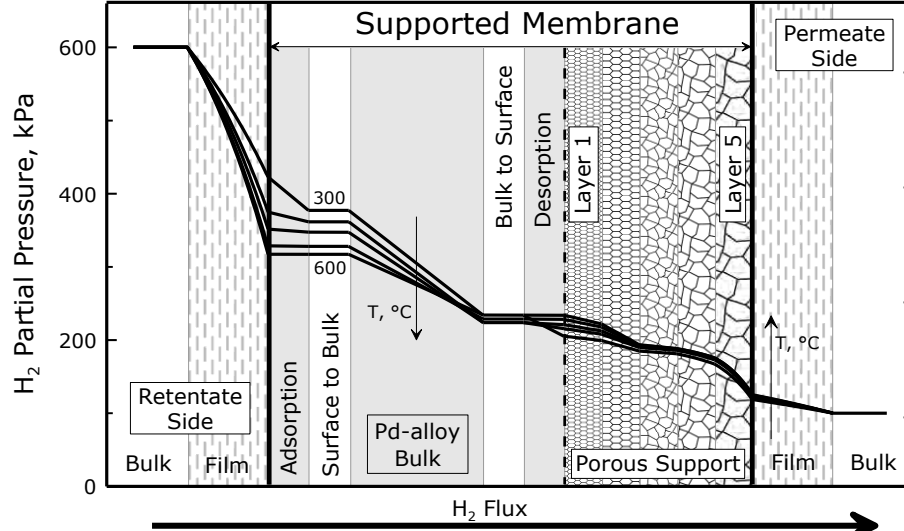


Fig. 2. – Calculated hydrogen partial pressure profiles through the membrane and in the fluid phases adjacent to the membrane for different temperatures in laminar regime at a membrane thickness of 1 μm . The lengths of the permeation steps are not to scale.

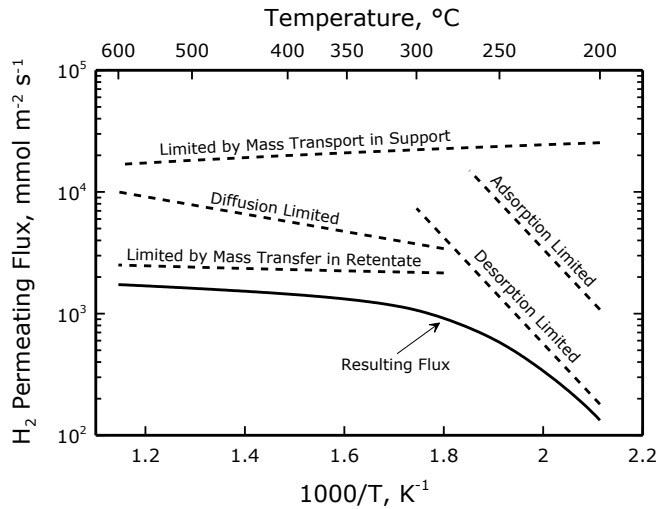


Fig. 3. – Step-limited fluxes (dashed lines) and overall resulting flux (continuous line) as functions of temperature in laminar conditions. Membrane thickness of 1 μm .

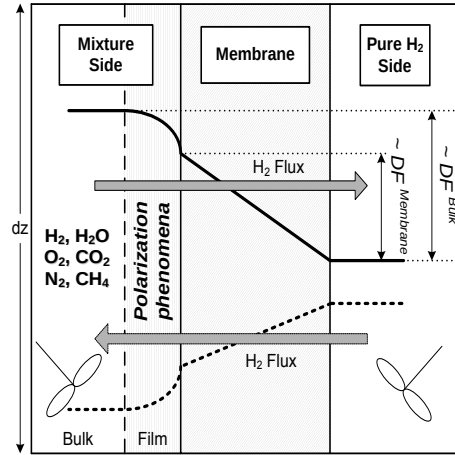


Fig. 4. – Sketch of the system to analyze the concentration polarization phenomena.

Fig. 4 shows the system considered to analyze the concentration polarization phenomena. In this case, the presence of the support has not taken into account in order to focus the attention on the external mass transfer. Furthermore, in the permeate side, only hydrogen is considered to be present. The Concentration Polarization Coefficient (CPC) is defined as shown in Eq. 1, where the value of the flux is calculated by means of the model described above. Further details about its definition are reported elsewhere [2]. The so-defined CPC approaches to zero when the polarization is negligible and to one in the opposite case.

$$CPC = 1 - \frac{H_2 \text{ Flux (ElementarySteps)}}{\pi^{Membrane} \Delta \sqrt{P_{H_2}}^{Bulk}} \quad (1)$$

Fig. 5 shows the effect of the operating conditions on *CPC* is analyzed in details, developing some “polarization maps” useful to determine the level of the polarization in some situations. The influence of six different system variables is considered: 1) temperature, 2) membrane thickness, 3) total pressure of mixture, 4) total pressure in pure H₂ side, 5) hydrogen molar fraction in mixture. In the first plot, considering molar fractions from one to zero, the level of polarization on one hand tends to increase for the larger composition of other components, but, on the other hand, it tends to decrease for the smaller hydrogen permeating flux. Until the first tendency prevails, the curve is convex, whilst it is concave in the opposite situation. This inflection point can be found in correspondence of a higher abscissa as lower temperature is considered. At high contents of hydrogen in mixture (close to unitary value), the polarization tends to be zero, even for high fluxes, because of the absence of other species creating a composition gradient. The other two plots show similar behaviour as regards the effect of mixture and pure H₂ side pressure.

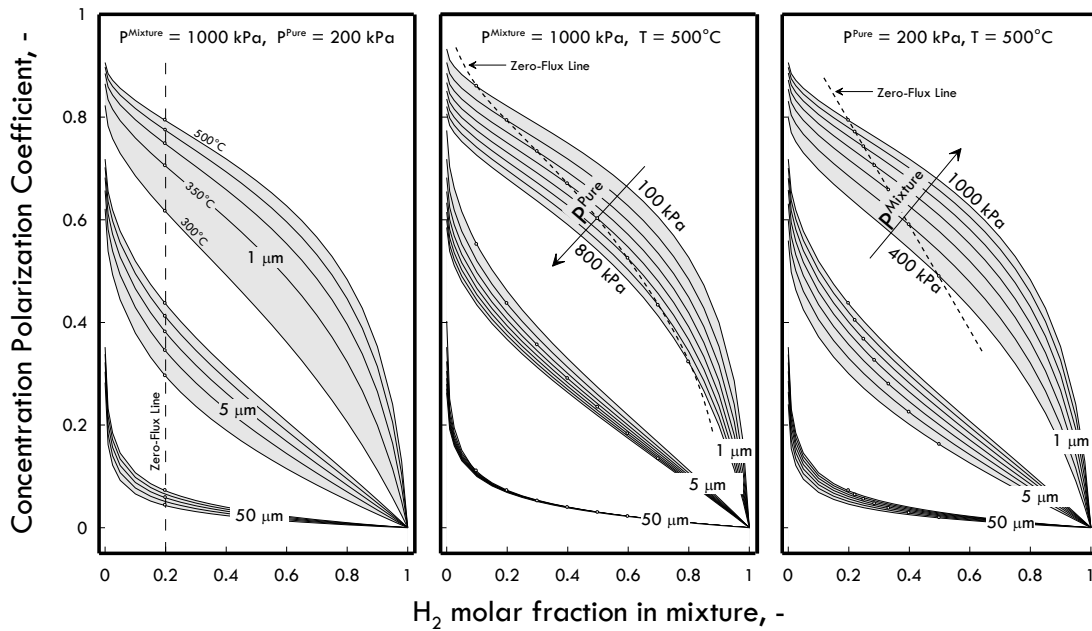


Fig. 5. – Polarization maps in different operating conditions (temperature, feed and permeate pressure).

4. Conclusions

The hydrogen permeation through supported Pd-alloy membranes is described by means of a detailed model involving several elementary steps, among which the external mass transfer on feed and permeate side. After describing this model, the concentration polarization phenomenon is studied in terms of an opportune coefficient, which is evaluated as a function of several operating conditions. This analysis is summarized in some “polarization maps”, which can be built once the fluid-dynamic conditions and the membrane permeation parameters are known. These diagrams can be very useful to avoid as much as possible the inefficiencies of a membrane separation process by minimizing the uncertainty in the step of the membrane-based system design.

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Electrical resistivity and linear expansion of a hydrogenated Pd/Ag permeator tube

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Abstract. The Pd-Ag-H system is of particular importance with respect to the separation and purification of the hydrogen gas. Pd-Ag alloys have high selectivity for hydrogen gas permeation and thus are suitable for manufacturing hydrogen selective membranes. Accordingly, among the technological properties many authors have studied the electrical resistivity and linear expansion of the Pd-Ag-H system, but no data are available in a wide range of temperature and hydrogen pressure. During this activity, the solubility, the linear expansion, the resistivity and the permeability of a Pd/Ag (with Ag 25% wt) permeator tube has been measured in both hydrogenated and non-hydrogenated conditions. The experiments have been carried out in a temperature and in a lumen hydrogen partial pressure range of 50-400 °C and 0-400 kPa, respectively.

1. Introduction

Hydrogen selective membranes are important for technological processes such as separation of hydrogen from gaseous mixtures, purification of hydrogen for fuel cell applications and chemical reactions in membrane reactor [1]: they are even used in hydrogen isotope storage, extracting, purification and separation processes [2].

Palladium membranes have been developed for ultra-pure hydrogen separation because of their high selectivity. However, they have a problem of hydrogen embrittlement, a phenomena in which dissolved hydrogen tends to cause an elongation of the metal lattice as a consequence of the hydrogen uploading thus leading to the membrane failure after repeated thermal and hydrogenation cycles. In order to avoid the embrittlement, alloying of Pd with group IB metals such as silver is generally made. Another advantage of alloying is that the mechanical strength in pure hydrogen atmosphere is higher [3]. In general, a Pd-membrane becomes brittle after certain cycles of $\alpha \rightarrow \beta$ transformations due to the accompanied lattice expansion. For example in palladium-silver alloys, the lattice has already been expanded by the silver atoms, and the Pd-Ag lattice is less influenced by hydrogen uploading and then less brittle than the pure Pd lattice [4]. An optimal value of the hydrogen permeation rate is reached for a silver content around 25 wt. %.

During this activity the electrical resistivity and the linear expansion of a 25 % wt Pd/Ag permeator tube has been measured under both hydrogenated and non-hydrogenated conditions. The experimental measurements have been carried out in a temperature and in a lumen hydrogen partial pressure range of 50-400°C and 0-400 kPa, respectively.

2. Experimental

A Pd-Ag tube of wall thickness 200 μm and length of 12.8 cm has been produced by extrusion. The hydrogen permeator has been obtained by joining via brazing at the ends of the Pd-Ag tube a stainless steel tube and a steel plug. The obtained permeator was assembled inside a membrane module in a finger like configuration (Fig. 1): the membrane tube was gas tight fixed to one end of the module in order to permit its elongation and contraction due to the hydrogenation cycles. In this way, any mechanical stress on the thin wall tube was avoided. In the finger like configuration the feed stream entered the membrane lumen via a stainless steel tube inserted inside the Pd-Ag membrane.

The experimental apparatus used to characterize the membrane is shown in the scheme of figure 2. A mass flow controller sends the hydrogen feed stream into the lumen side, while a nitrogen flux of 500 $\text{N cm}^3 \text{ min}^{-1}$ is used as sweep gas in the shell side. The membrane module is heated by a direct current supply system; the elongation and the resistivity are measured with an optical microscope and a multimeter, respectively.



Fig. 1. - Pd-Ag permeator tube.

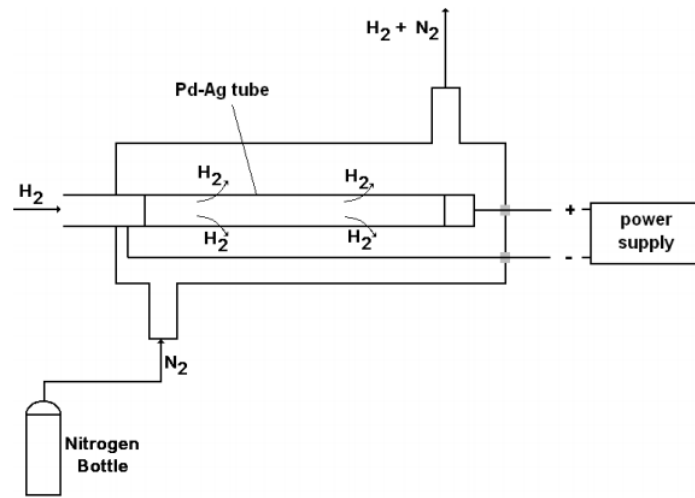


Fig. 2. - Scheme of the experimental apparatus.

3. Results and discussion

3.1 Hydrogen Solubility

The hydrogen solubility, in the investigated operative conditions, has been assessed by applying the Sieverts' law:

$$S = K_s p^{0.5} \quad (1)$$

where K_s [5] is the solubility constant:

$$K_s = 0.182 \exp\left(\frac{19598}{RT}\right) \quad (\text{mol m}^{-3} \text{ Pa}^{0.5}) \quad (2)$$

and p the hydrogen partial pressure into the metal lattice, assessed as the arithmetic mean between the hydrogen partial pressure in the lumen side ($p_{\text{H}_2, \text{lumen}}$) and the hydrogen partial pressure in the shell side ($p_{\text{H}_2, \text{shell}}$).

In figure 3 the effects of temperature and hydrogen lumen pressure on the solubility are reported. By increasing the temperature, the hydrogen solubility decreases for all the hydrogen lumen pressures investigated, although the solubility gap between the various lumen pressures is much larger at low temperature. Particularly, these results show that the hydrogen loading into the Pd-Ag membrane significantly occurs below 150-200 °C where the hydrogen permeation is quantitatively modest as reported below (section 3.4).

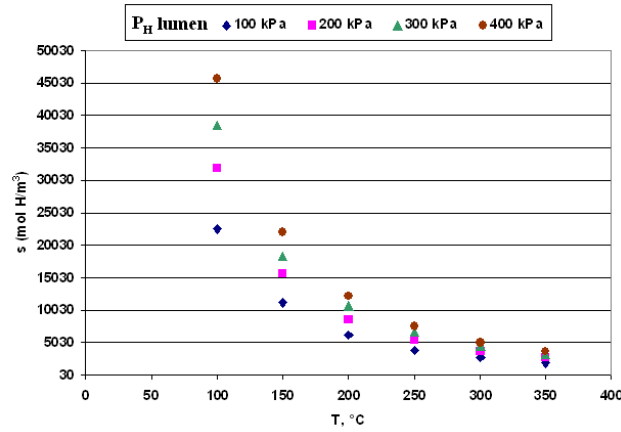


Fig. 3. - Hydrogen solubility in Pd-Ag membrane versus temperature for different hydrogen lumen pressure.

3.2 Linear Expansion

To measure the linear expansion of the membrane a metal cylinder sustained in a pyrex tube has been attached on the free-end of the membrane: the metal cylinder was able to move inside the pyrex tube. In this way the movement of the metal cylinder followed the elongation of the membrane, while the pyrex tube having negligible thermal expansion coefficient has been used as a reference. An optical microscope fixed on the described experimental apparatus has been used to measure the displacement of the metal cylinder, i.e. the linear expansion of the membrane. Figure 4 represents a particular of the experimental set-up viewed by the microscope.

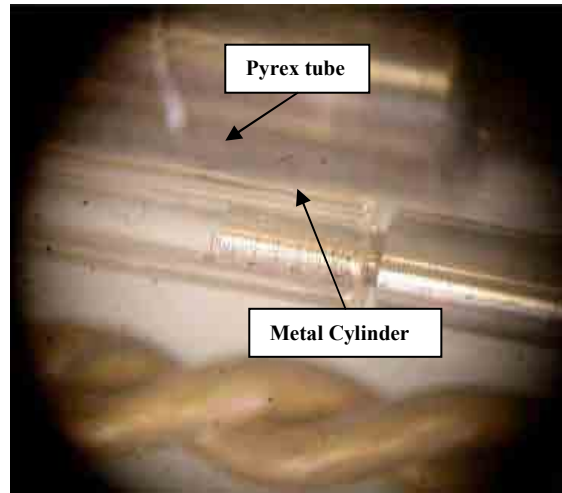


Fig. 4. - Particular of the membrane viewed by the optical microscope.

Figure 5 described the linear expansion ε of the Pd-Ag membrane in different conditions.

$$\varepsilon = \frac{\Delta l}{l_0} \quad (3)$$

Where Δl is the difference between the final and the initial (l_0) length of the membrane tube.

In particular the linear expansion can be considered by the sum of two contributions: the thermal and the hydrogen uploading contribution. In order to put into evidence these contributions, in figure 5 the grey points are referring to the linear expansion measured under nitrogen atmosphere (hydrogen partial pressure equal to zero), that means only thermal contribution, while the other points are related to the total linear elongation (both thermal and loading contribution).

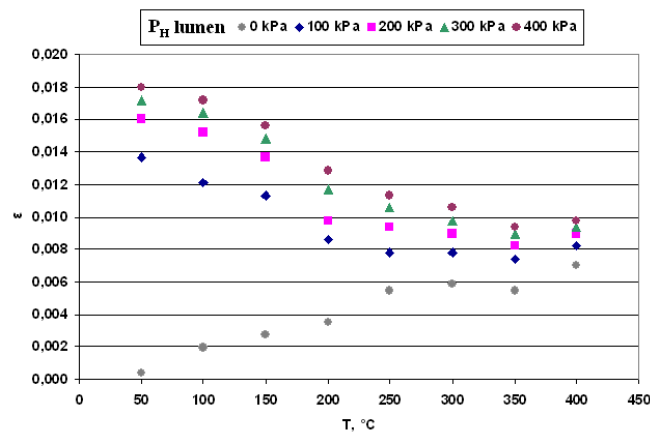


Fig. 5. - Linear elongation of the Pd-Ag membrane tube in a temperature range between 50-450 °C at different lumen hydrogen partial pressures, from 0-400 kPa.

According to the literature, the linear expansion related to the thermal contribution increases by increasing the temperature: in particular at 50 °C the elongation is almost zero, while at 400 °C it is about 0,7%. Under the hydrogenated conditions, the linear elongation decreases by increasing the temperature for each lumen hydrogen partial pressure investigated. Even in this case the gap between the measurements at low temperature is larger than the gap related to the measurements at high temperatures, in particular at 400 °C the gap is almost negligible.

This phenomenon agrees with the assessed hydrogen solubility values: at low temperature maximum hydrogen solubility (uploading) corresponds to the maximum elongation.

3.3 Electrical Resistivity

The electrical resistivity is a Pd-Ag property alloy affected by the hydrogen loading: measurements of this parameter have been carried out under different hydrogenation conditions and temperatures. A DC current has been applied to the ends of the membrane tube through a power supply (HP 6573A) while a multimeter (HP 3458A) has been used in order to measure the voltage in different points of the membrane. The electrical resistivity has been then assessed via the Ohm law.

The connection between the multimeter and the membrane has been realized with Pt wires attached on the membrane surface (Fig. 6).

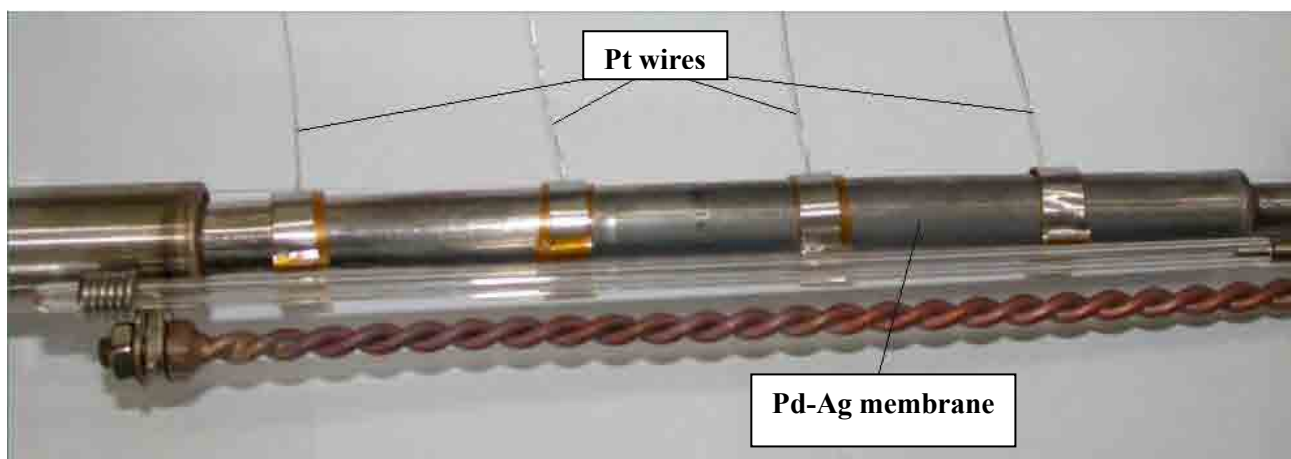


Fig. 6. - Particular of the palladium wires attached onto the membrane surface for the resistivity measures.

Figure 7 reports the values of the Pd-Ag electrical resistivity in the range temperature between 100 and 400 °C, for different lumen hydrogen partial pressure. Especially, for a given temperature the electrical resistivity values change slightly for the hydrogenated material.

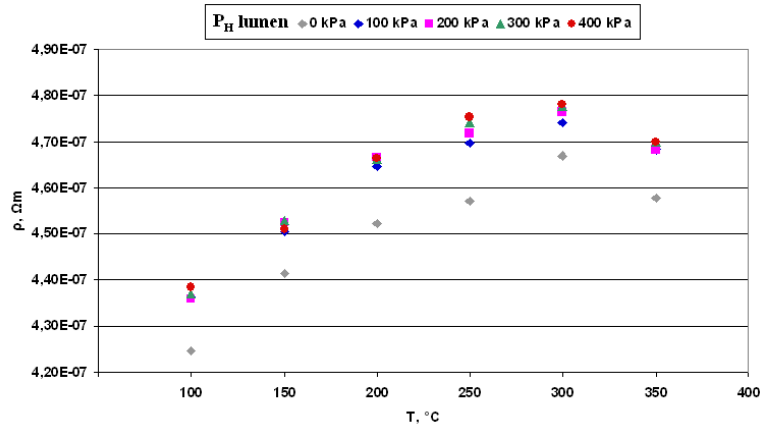


Fig. 7. - Pd-Ag electrical resistivity in temperature range between 100-400 °C for different lumen partial hydrogen pressure.

3.4 Hydrogen Permeability

Permeation tests of the Pd-Ag tube have been carried out under controlled temperature and transmembrane differential pressure conditions: pure hydrogen was fed in the lumen side in the pressure range between 100-400 kPa, while the hydrogen permeated through the membrane was collected in the shell side at atmospheric pressure by a nitrogen stream of 500 Ncm³ min⁻¹, the investigated temperature range was 100-400 °C.

The hydrogen permeability through the Pd-Ag membrane was calculated by the formula:

$$Pe = \frac{Fd}{(\sqrt{p_{H_2, \text{lumen}}} - \sqrt{p_{H_2, \text{shell}}})A} \quad (4)$$

where Pe is the hydrogen permeability (mol m⁻¹ s⁻¹ Pa^{0.5}), F is the hydrogen permeating flow rate (mol s⁻¹), d the wall tube thickness (m), $p_{H_2, \text{lumen}}$ the hydrogen pressure inside the membrane (Pa), $p_{H_2, \text{shell}}$ the hydrogen partial pressure in the shell side (Pa), and A is the permeation surface area (m²).

The permeability data have been collected according to the Arrhenius law:

$$Pe = Pe_0 \exp\left(\frac{-E_a}{RT}\right) \quad (5)$$

where Pe is the hydrogen permeability, Pe_0 the pre-exponential factor, E_a the activation energy, R the gas constant and T the absolute temperature.

By considering the hydrogen permeability values reported in figure 8, there are some considerations to underline. In fact, the activation energy (that can be visualized by the slope of the permeability values line) presents two different values, as reported in table 1. In particular the activation energy at low temperature is higher than the activation energy at high temperature thus meaning that significant hydrogen permeation through the membrane can occur only at temperature over 200 °C. As another important result, despite of the large membrane wall thickness (200 μm) the high hydrogen permeation fluxes measured demonstrated the applicability of such a membrane tube for separating ultra pure hydrogen in laboratory and industrial processes.

Table 1. Hydrogen permeability through Pd-Ag.

Temperature, K	Pressure, kPa	Pe_0 , mol m ⁻¹ s ⁻¹ Pa ^{-0.5}	E_a , kJ mol ⁻¹
373-423	100-400	3.38×10^{-5}	19.7
474-673	100-400	3.43×10^{-7}	3.4

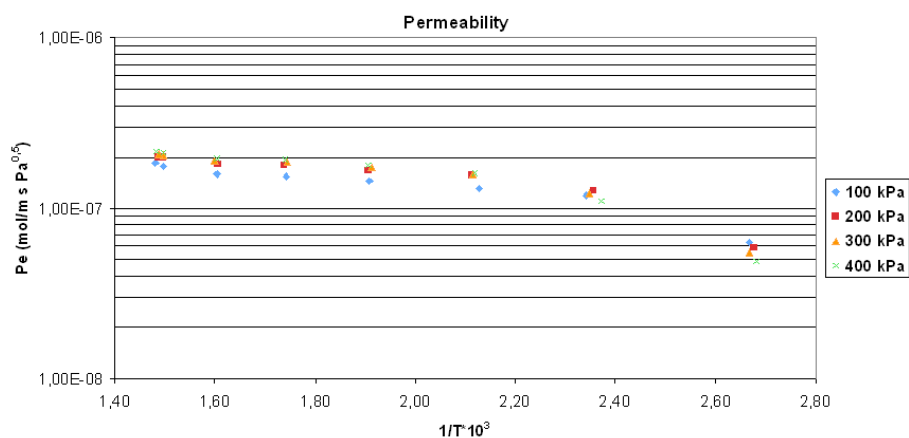


Fig. 8. - Hydrogen permeability through Pd-Ag.

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Synthesis and characterization of BaCe_{1-x}Y_xO_{3-δ} protonic conductor

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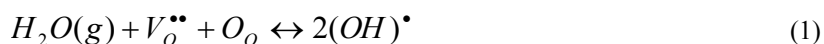
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Abstract. In recent years, doped perovskites such as barium cerates (BaCeO₃), strontium cerates (SrCeO₃) and barium zirconates (BaZrO₃) have been studied as ceramic proton conductors for several technological applications: protonic membranes, hydrogen separation, catalytic support and solid oxides fuel cell components. Among those compounds, yttrium doped barium cerates have the best performances in terms of protonic conductivity at lowest temperature.

In this activity, doped BCY oxide powders was synthesized via novel soft chemical route. The method is based on the formation of a metallorganic xero-gel at room temperature. The structural phase of powders and dense pellets were analyzed using X-ray diffraction (XRD), while the morphology was investigated by field emission scanning electron microscope (FE-SEM). Electrochemical impedance spectroscopy (EIS) measures were performed on dense pellet under synthetic air flux and hydrogen atmosphere in a temperature range between 200-750 °C with a frequency range of 10mHz-10MHz.

1. Introduction

Several oxide with the ABO₃ perovskite structure have shown protonic conductivity between 500-1000 °C [1-4]. These oxides are doped on the B-site by lower valence elements, typically a trivalent rare-earth metal (M), to introduce oxygen defects. The exposure of the doped material to humid atmospheres results in the formation and incorporation of hydroxyl groups to oxygen vacancies followed by the migration of the lone protons by hopping between oxide ions via a Grotthus-like mechanism. The formation of the hydroxyl defects may be written using Kröger-Vink notation (1).



According to Irvine et al. [5] the most technologically promising moderate-temperature proton conductors are those perovskites based upon the cerates or zirconates of barium doped with yttria or lanthanide oxides. Barium cerates generally exhibit the highest proton conductivities; but these materials are unstable at high temperature in the presence of CO₂ and steam, while the zirconates are much more resistant to degradation. The zirconates do not sinter easily, and the highest conductivities are only obtained when sintering occurs at or approaching 1700 °C, in fact the highest conductivities are influenced by some form of phase transformation or segregation or, as suggested by Snijders et al. by a slow kinetic process of water absorption. The stability of doped BaCeO₃ is improved by the introduction of Zr at the B site, but the typical sintering temperature of Zr-replaced BaCeO₃ is still above 1550 °C. However, very significant differences exist in reported values of conductivities, which seem to be related to the synthesis procedure.

In general, the BaCeO₃ powders were synthesized by the conventional solid state reaction, in which oxide precursors are repetitively milled and calcined at high temperature. However, these conventional ceramic powder processes can have several drawbacks such as relatively large and varied grain sizes, inhomogeneities in the chemical composition [6,7], and of course high cost related to the high sintering temperature.

In this view, one possible approach to overcome these difficulties is to employ a soft chemical process which has the following advantages: lower sintering temperature, shorter processing time, and the possibility of obtaining high purity and ultrafine powders. Essentially, these methods can produce nanocrystalline materials, which appear to be a promising approach to combine the superior characteristics of these nanoscaled ceramics with the proton conducting properties of doped perovskite [8].

In this activity a new synthesis route for the BaCe_{0.8}Y_{0.2}O_{3-δ} (BCY20) called sol gel combustion, has been investigated. The method is based on the autocombustion reaction of the gel resulting from a novel sol gel process. The technique involves three different steps: the preparation of a stable and homogenous sol, the formation of a gel, and the

combustion of the so-formed gel. This synthesis procedure allows us to obtain the requisite phase for BCY20 at lower temperature and dense pellet with high conductivity.

2. Experimental

The novel synthesis method consists of the formation of a gel of the nitrate solution using agar powder. The metal nitrates were dissolved in water in the correct stoichiometric ratio, and then the solution was heated to 80 °C. At that temperature the agar powder (20% of weight) was added. Agar is a polysaccharide and it works as a gelling agent. The dissolution process of the agar in the solution was completed by several minutes of stirring at 80 °C. The agar induced the complete gelation at 4 °C in a few minutes. During cooling the viscosity increased rapidly and there was the formation of a self-sustaining gel, then the gel was burned in a reactor. The reactor had two different holes that allowed the continuous flux of air that was essential to ensure the complete combustion of the gel inside. The precursor powders were ground into an agate mortar and calcined at the appropriate temperature in order to have a pure perovskite phase. Then the powders were uniaxially pressed at 4 tons in order to form a 3 mm diameter pellet. The discs were sintered in air in a tubular furnace. The sintering temperature required for the agar method was 1450 °C. After sintering the surface of the pellet were polished and stripped off with a thermal etching.

The precursor powder obtained with the agar method was characterized by simultaneous thermogravimetric-differential thermal analysis (TG/DTA) performed on a NETZSCH STA 409. The sample was held in a platinum holder under air atmosphere. The phase composition was analyzed by X-ray diffraction (XRD). X-ray diffraction data were acquired using a Philips X'PertMPD using CuK α radiation. The phases present in the BCY20 sample at different stage of calcination were analyzed in the Bragg angle range $20^\circ < 2\theta < 85^\circ$. The microstructure of the sample was then characterized by field emission scanning electron microscopy (FE-SEM LEO 1530) after polishing and thermal etching. The densification rate has been determined with samples of 10,40 mm length and a diameter of 8,02 mm, it was sintered in a dilatometric up to 1600 °C using a constant heating rate of 5 K min⁻¹ and cooled down to a room temperature with a rate of 10 K min⁻¹. The shrinkage was recorded during heating and cooling. Finally conductivity measurements on the BCY20 agar sample were performed in order to investigate the electrical property of the material. The BCY20 pellet was assembled in a cell (Fig. 1): the cell apparatus was connected with a frequency response analyzer to measure the conductivity across the electrolyte. The measurements have been performed in a frequency range between 10mHz-10MHz, and in a temperature range between 200-750 °C.

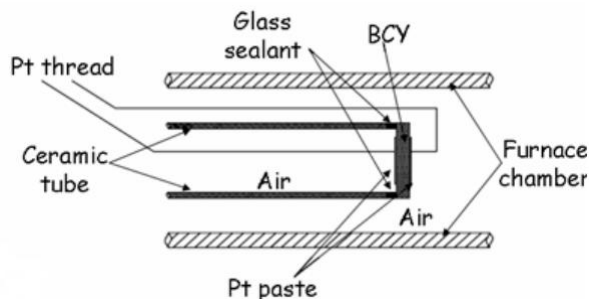


Fig. 1. – Scheme of the cell apparatus.

3. Results and discussion

3.1 TG/DTA

The powders obtained after burning the gels at 200 °C were characterized by Thermogravimetric/Differential Thermal Analysis (TG/DTA), in order to study the crystallisation process and choose the suitable temperature range for calcination. The TG (Fig. 2) revealed that the weigh loss, for a heating rate of 5 °C/min, was completed at 1150 °C with a total weigh loss less than 10%. The results showed two plateaux: between 700-800 °C and over 1200 °C. According to the DTA, from 600-700 °C, the reaction is exothermic, associated with the initial decomposition stage of the organic species involved in the gel.

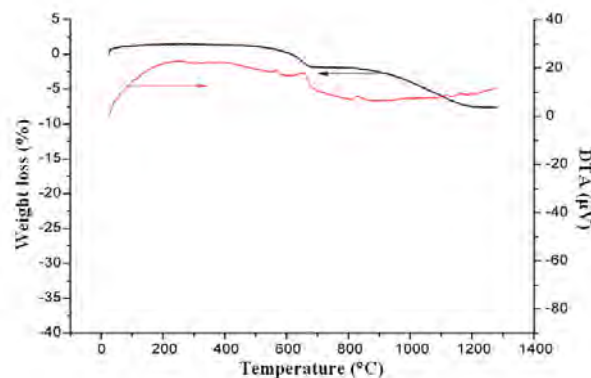


Fig. 2. – TG/DTA of the BCY 20 precursor synthesized with the agar method.

3.2 XRD Measurements

The X-ray diffraction patterns of BCY20, powder and pellet, obtained with the Agar synthesis are shown in figure 3.

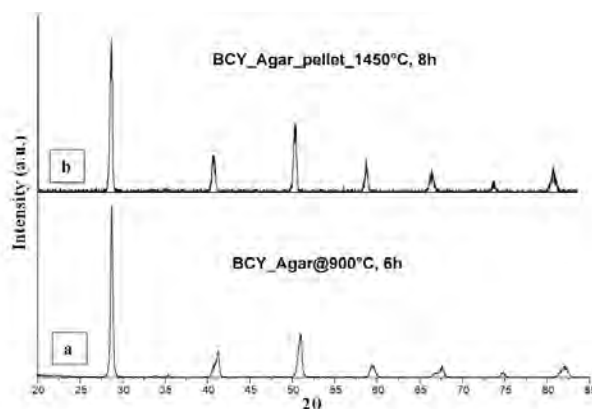


Fig. 3. - XRD patterns of the BCY20 obtained with the agar synthesis method, a) powder calcined at 900 °C for 6 h, and b) pellet sintered at 1450°C for 8 h.

The XRD reveals that, with this method, a pure perovskite phase is reached at 900 °C while, with the standard synthesis procedure, the phase was pure only when temperature approached 1100 °C.

Another relevant aspect is related to the sintered pellet: in fact, the BCY20 pellet (90% of the theoretical density) was obtained with a sintering treatment carried out at 1450 °C for 6 hours. The decrease of the sintering temperature (usually around 1600 °C) avoids the presence of secondary phases related to aggregation processes caused to barium evaporation.

3.3 Dilatometric measurements

To better understand the sintering behaviour of the BCY20 obtained with the described synthesis procedure, dilatometric measures have been performed on two BCY20 samples: one sample was prepared with the Agar synthesis method, and one sample was realized using a traditional ethylene glycol method.

Figure 4 reports the dilatometric behaviour of the two BCY20 samples. From the results it is possible to observe that in the sample prepared with the agar method the shrinkage starts between 900-1000 °C, while in the sample prepared with the EG method the shrinkage starts at 1200 °C. Another important difference in the sintering behaviour of the two samples is recorded in the temperature range between 1100-1200 °C. At that point, in fact, the sample prepared with the EG method expands and then the shrinkage starts. The different dilatometric behaviour between the two BCY20 samples has a macroscopic effect as reported in figure 5 which shows the samples after the dilatometric measurements. From that picture it is clear that both samples are cracked, but in the EG sample the cracks are more.

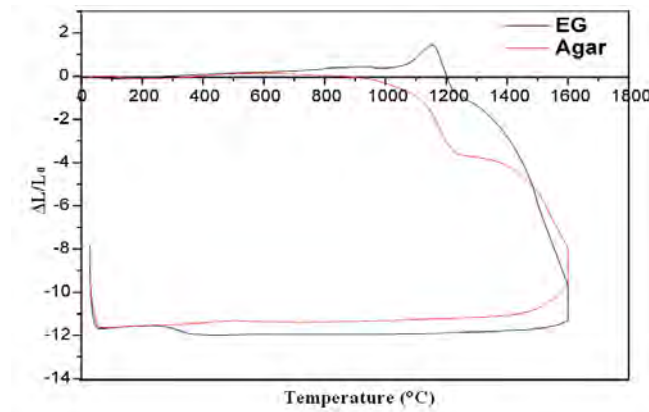


Fig. 4. - Dilatometric shrinkage of the two BCY20 samples obtained with the Agar synthesis (red line) and with the EG synthesis (black line).

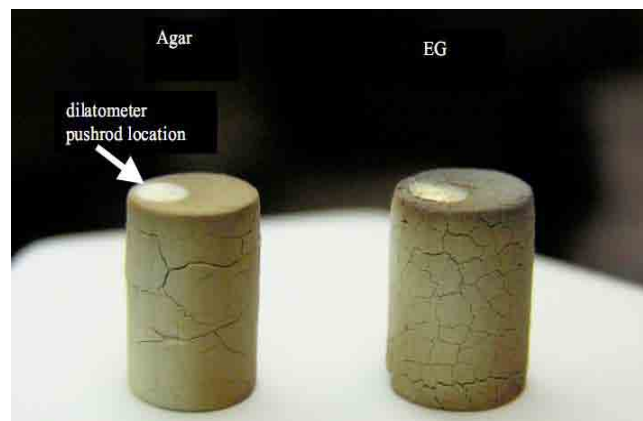


Fig. 5. - Picture of the two BCY20 samples after the dilatometric measurement.

3.4 SEM micrographs

The SEM micrographs reveal what the dilatometric measures have already shown. In fact, as figures 6 and 7 report, the BCY20 powders and pellets have a different microstructures according to the used synthesis procedures.

In particular figure 6 shows the SEM micrograph of the calcined BCY20 powder obtained with the agar method (a) and with the EG method (b), respectively. The main differences between the two BCY 20 powders are related to the dimension of the particles and to the different phases of the two powders. In fact, the particles obtained with the agar synthesis route are smaller than the other while the different shapes of the powders reveal different phases. In figure 7 the surface micrographs of the two BCY20 sintered pellet are reported. Even in this case, a difference in the particles size is observed. In fact, in the agar sample, the average grain size is around 100 nm, while in the EG sample, the average grain size is about 1-2 μm . Also the density of the two samples is different, in particular the BCY20 pellet obtained with the agar method, sintered at 1450 $^{\circ}\text{C}$, is more dense than the EG sample, sintered at 1600 $^{\circ}\text{C}$.

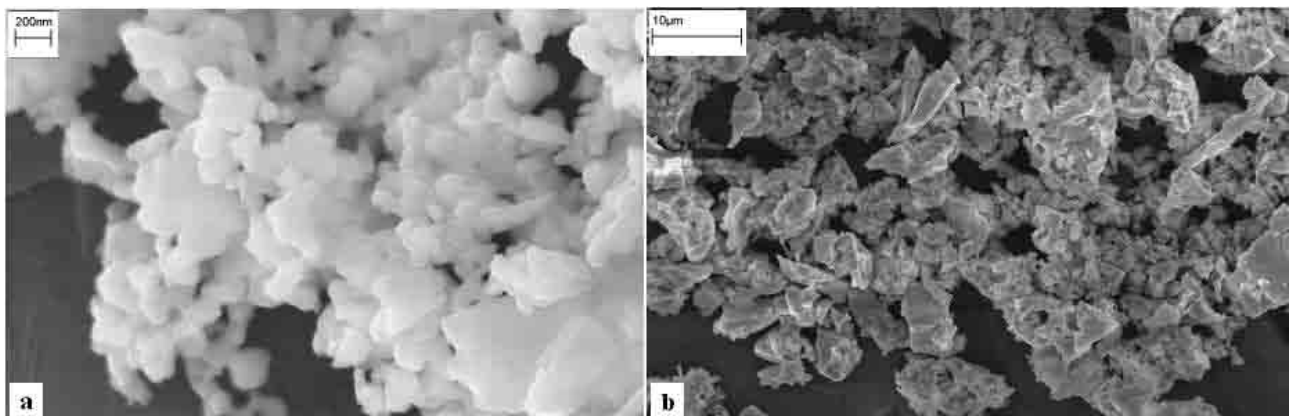


Fig. 6. - FE-SEM micrographs of the BCY20 powder, a) Agar method, b) EG method.

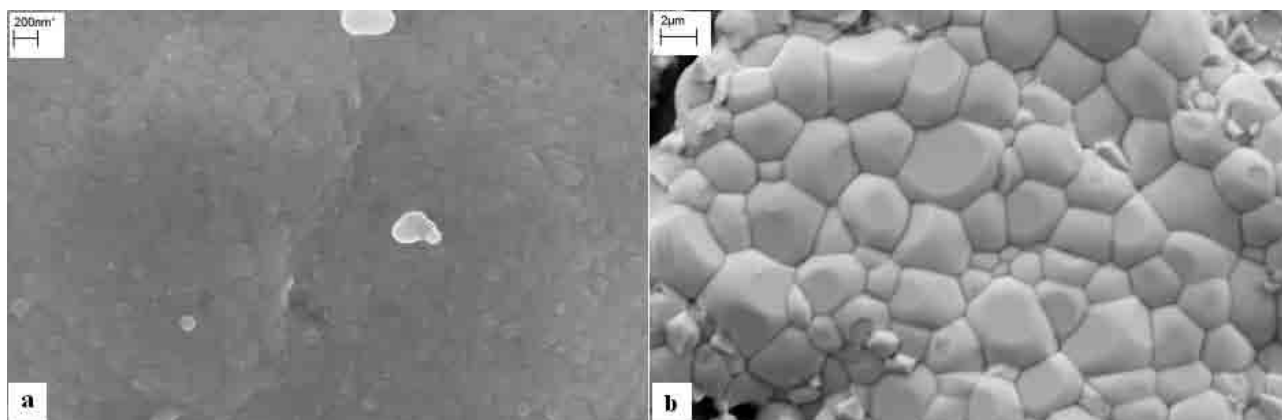


Fig. 7. - FE-SEM micrographs of the BCY20 pellet, a) Agar method, b) EG method.

3.5 Conductivity measurements

The electrolyte BCY20 pellet made with the agar method was placed into a single chamber reactor. The reactor was installed into a horizontal tube furnace and the cell was connected with a frequency response analyzer to measure the AC impedance spectra across the electrolyte. The conductivity of the perovskite sample with increasing temperature was measured and recorded in the range between 200-750 °C with steps of 25 °C intervals in air and wet hydrogen atmosphere. The activation energy of the proton conduction mechanism can be determined from an appropriate Arrhenius plot. In this way, the slope is equal to $-E/k$, where E is the activation energy and k is the Boltzmann constant. The Arrhenius plot for BCY20 is shown in figure 8. The activation energy for BCY20 is 0.40 eV, in agreement with the values reported in literature.

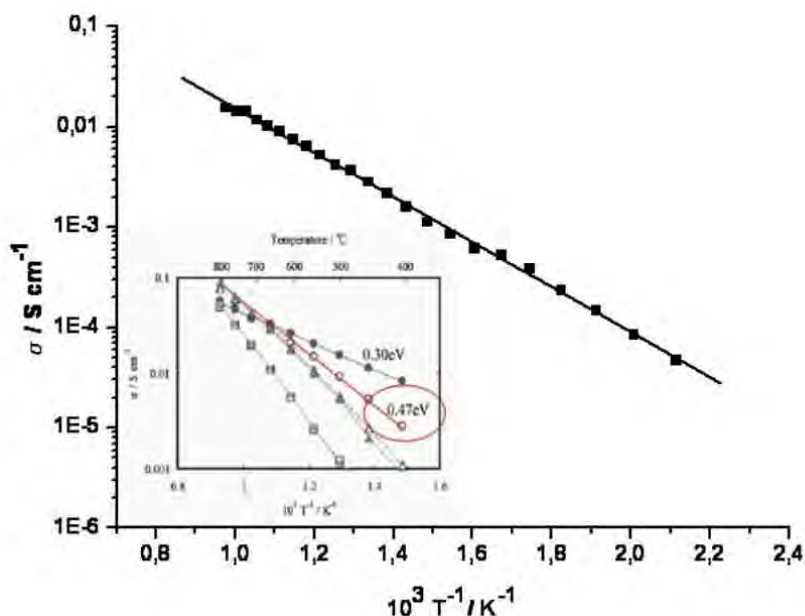


Fig. 8. - Arrhenius plot for BCY20 compared with literature data [9].

Acknowledgments

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Characterization of materials by means of laser-based techniques

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Abstract. Laser-based techniques are more and more used in the field of materials processing and analysis. In particular, laser spectroscopic techniques as the Laser Induced Breakdown Spectroscopy (LIBS) and Laser Induced Fluorescence (LIF) have been applied to investigate the chemical-physical properties and the morphological structure of several kinds of materials. Some results in different fields of application are reported.

1. Introduction

The application of laser-based techniques as analytical tools in materials science is widespread and very promising by now, also due to the continuous development of the laser technology. In this work, in particular, the attention will be focused on two spectroscopic laser techniques: Laser Induced Breakdown Spectroscopy (LIBS) and Laser Induced Fluorescence (LIF).

Laser induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopic technique. It is based on the spectral analysis of the radiation emitted by a plasma generated by the interaction of an intense laser radiation with a material sample. The elemental composition of the investigated sample can be determined from the analysis of the emission spectrum [1] and the element concentrations theoretically deduced [2]. LIBS is particularly suitable for rapid on-line analysis. Nowadays, LIBS has reached a mature stage for analytical applications on a wide range of materials in solid, liquid and gas phase [3]. Good results have been obtained by LIBS on surface and sublayers analysis.

The emission of radiation by luminescent materials is observed whenever an absorption of energy sufficient to activate allowed electronic transitions occurs. Laser induced fluorescence (LIF) is a molecular spectroscopy based on the interaction of the ultraviolet radiation emitted by a laser with the matter [4]. This technique, for a surface analysis, is fast, remote, non invasive and specific. Through the study of the fluorescence emission spectrum is possible to obtain information of analytical and qualitative interest [5]. Both techniques have been used in many fields of application.

2. Experimental

In the laboratory of laser applications of ENEA Frascati, LIBS and LIF experimental equipments have been developed.

2.1 LIBS apparatus

The LIBS apparatus has fully described in its general configuration elsewhere [6], here the main characteristics will be recalled. In 'Fig.1' a scheme is reported. The radiation source is a Nd:YAG laser (Handy Quanta System) working usually at the fundamental wavelength of 1064 nm and focalized by a lens on the surface of the studied sample. The plasma emissions were collected by suitable receiver optics and the optical signal was carried by an optical fiber to the entrance slit of monochromator (Jobin Yvon model TRIAX550) equipped with three different gratings.

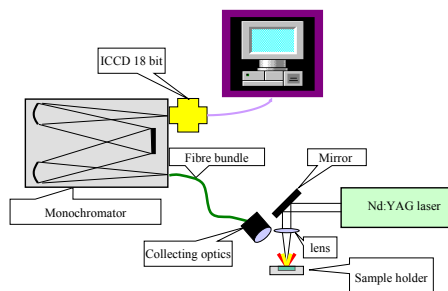


Fig. 1- Scheme of LIBS apparatus

The LIBS spectra were detected and recorded by a multichannel analyzer based on a gated ICCD, model Insta Spec IV. The experimental and acquisition parameters (energy laser, laser shots number, acquisition delay from the laser pulse, acquisition temporal gate) depend on the specific application. Stratigraphic analysis [7] with the identification of the chemical elements present at different depth is possible recording the LIBS spectra from the same point of the sample at increasing laser shots number.

Some advantages offered by LIBS make it very useful in many different applications: no sample pre-treatment is required, measurements can be performed directly in situ, in hostile environment too, on line data analysis is possible. Furthermore, LIBS is a fast spectroscopic method.

2.2 LIF apparatus

An innovative compact scanning LIF system has been developed at the ENEA of Frascati, based on a previous instrument's version [8]. The layout of the system is given in 'fig. 2'. The radiation source is a Thomson DIVA diode pulsed Nd:YAG laser, able to produce laser pulses both at 266 and 355 nm with a time duration of 10 ns at a fluence from 1 to 50 mJ/cm². The main advantages of this new version are its reduced size, all the mechanical and optical elements have been installed in an aluminum box of 58×43×36 cm³ for less than 15 kg, its small size and light weight that allow for an easy transfer of the system, and its operation from scaffoldings, in case of surfaces out of the current maximum range for remote operation (10 m). The spectrometer entrance is protected from the intense backscattered radiation by means of an appropriate dichroic filter. The digitized spectrum is transferred to a portable computer where a LabView program allows the user to set experimental parameters, to control data acquisition, and to perform a preliminary data analysis.

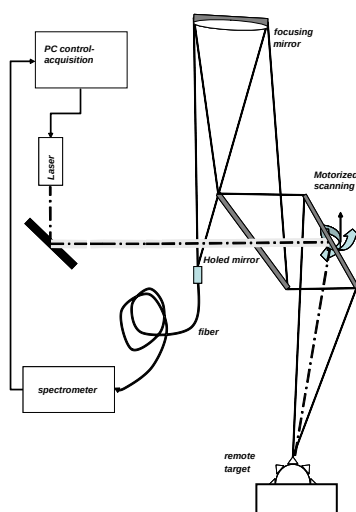


Fig. 2 – Scheme of LIF apparatus

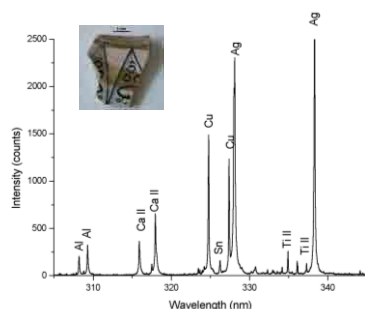


Fig. 3 - LIBS spectrum of ancient ceramic

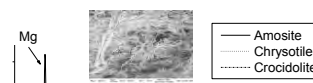


Fig. 4 - LIBS spectra of asbestos

The main advantages offered by this technique are the possibility to perform measurements in real time, in-situ without sample preparation, besides its minimum invasiveness.

3. Applications

Laser Induced Breakdown Spectroscopy and Laser Induced Fluorescence present several advantages with respect to other spectroscopic techniques and can be utilized for a variety of prompt analytical applications on different materials. Some applications will be reported on the following.

3.1 LIBS applications

LIBS has found in the Cultural Heritage preservation a fertile field of application due to its minimally invasive and only micro-destructive feature, the availability of portable instruments and the possibility of stratigraphy with on-line monitoring cleaning processes. These characteristics makes the technique suitable for qualitative and quantitative multi-elemental analyses on a large variety of samples surfaces in most different stages of preservation. Analysis of pigments [9] and different kinds of ancient materials as copper based alloys [10], ceramics [11,12] and marbles [13], for examples, has been performed by LIBS.

In 'Fig.3' a typical spectrum of gold lustre with silver and copper lines, emission line from Sn is coming from the underlying glaze, from a decorated Renaissance umbrian ceramic is shown.

LIBS has been successfully applied in laboratory analyses of soils and sediments, in order to trace the presence of heavy metals as pollutants [14] or to investigate sedimentation processes in natural ecosystems (Ross Sea, Antarctica) [15]. Among the environmental applications, the possibility of detecting and identifying asbestos by LIBS technique ('Fig.4') in samples of different kind, as for example building materials, has been demonstrated [16].

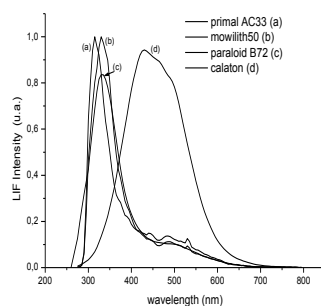


Fig. 5 - Fluorescence spectra at $\lambda_{exc}=266nm$ of acrylic resins

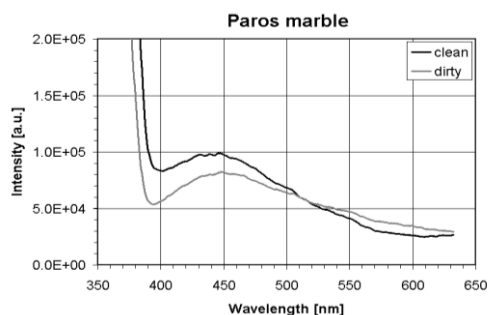


Fig. 6 – LIF spectra at $\lambda_{exc} = 355$ nm of Paros marbles clean and with crust

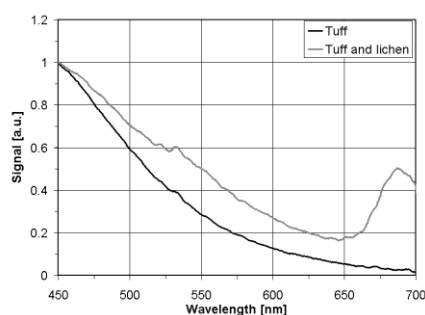


Fig. 7 – LIF spectra at $\lambda_{exc} = 355$ nm of tuff and deteriorated tuff.

The LIBS applicability in situ makes it one of the most interesting techniques to carry out remote measurements inside a tokamak vacuum chamber directly, without any removal of the internal coverings.

A recent study aimed to assess the diagnostic potentialities of the LIBS technique for the qualitative and quantitative determination of superficial contaminants deposited and/or adsorbed on the superficial coating of a tokamak reactor, has been led[17].

3.2 LIF applications

The performance of laser induced fluorescence (LIF) as a diagnostic tool for cultural heritage has been evaluated by exploiting the ENEA scanning LIF system to investigate different materials relevant in this field of application. The possibility to detect and discriminate different acrylic resins on fresco has been demonstrated both on laboratory samples and on original wall paintings by in situ measurements [18,19]. In 'Fig.5' the fluorescence spectra corresponding to four different resins are reported.

The effect of deteriorating agents on different materials has been investigated. The presence of a detrimental crust on a marble from Paros due to the external exposure has been well emphasized by the LIF signal, as can be seen in 'Fig.6'.

The detrimental effects on tuff surfaces of biodegrading agents, as fungi and lichens, has been detected by LIF allowing to observe characteristics invisible with the naked eye while avoiding to move sample from their original location. In 'Fig.7' the chlorophyll fluorescence emission at 680 nm from a deteriorated area respect to a clean one reveals the presence of a biodegradation process.

In conclusion, laser-based techniques can be used in the field of materials analysis with good results and many fields of application are possible. The experimental conditions need to be optimized according to the specific application.

Acknowledgments

All activities reported in this paper have been developed with my colleagues: F. Colao, R. Fantoni, L. Fiorani, V. Lazic, A. Palucci.

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Integrated approach for high resolution surface characterization: coupling focused ion beam with micro and nano mechanical tests.

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Abstract. In the present paper, we will give a brief overview about the synergic use of two high resolution techniques with focus on applications on thin coatings: Focused Ion Beam (coupled with electron beam) imaging, milling and deposition technique (briefly called FIB) and Nanoindentation. After a basic description of both techniques (architecture, probe-sample interaction basics and operation modes), we will demonstrate effectiveness of this approach for microstructural investigation on very small samples without any sample preparation or pre-processing by presenting two case studies:

(i) *Analysis of residual stresses of engineered surfaces by coupling focused ion beam controlled material removal and nanoindentation testing, and*
(ii) *Nano-mechanical characterization of sputtered niobium thin films for application in accelerating cavities.*

1. Introduction

At present, mechanical characterisation of engineered surfaces is gaining more and more interest for the growing industrial application of surface modification and coating techniques, which are usually applied to improve either surface mechanical or functional performances (i.e hardness, load bearing capacity, wear resistance, surface free energy and chemical reactivity, electrical resistivity, thermal conductivity) [1].

Furthermore, it has to be considered that the development of nanostructured materials and the growing use and application of nano-systems and nano-structures make the use of advanced procedures for nano-scale mechanical characterisation strictly necessary [2]; in other cases, mechanical behaviour can be strongly influenced by microstructural and size effects (grain size, defects, interfaces, porosity,...), so multi-scale characterisation procedures [3] are strongly needed for a determination of the correct correlation function among process parameters, surface properties and in-service performances.

It is therefore clear that a comprehensive, statistically reliable, economically sustainable procedure for the characterisation of engineered surfaces has not yet been developed in literature, especially when a strong microstructure and size dependent behaviour is observed.

In the present work, a new developed characterisation procedure for the mechanical characterisation of engineered surfaces is presented, based on the combined use of high resolution microscopy (FIB-SEM, TEM, AFM) and surface mechanical characterisation techniques (nanoindentation, scratch testing).

Mechanical characterization activities are essentially based on nanoindentation testing, which at present is the prime technique used in nanomechanics to investigate the mechanical properties of the materials on the sub-microscale. It has long been used to study the elastic, plastic and fracture properties on the surfaces of bulk samples, as well as for thin-films [4-6]. More recently, it became possible to perform controlled compression, shear, and bending tests on nanostructures smaller than a micron, such as nanospheres, nanowires and nanopillars [7-8].

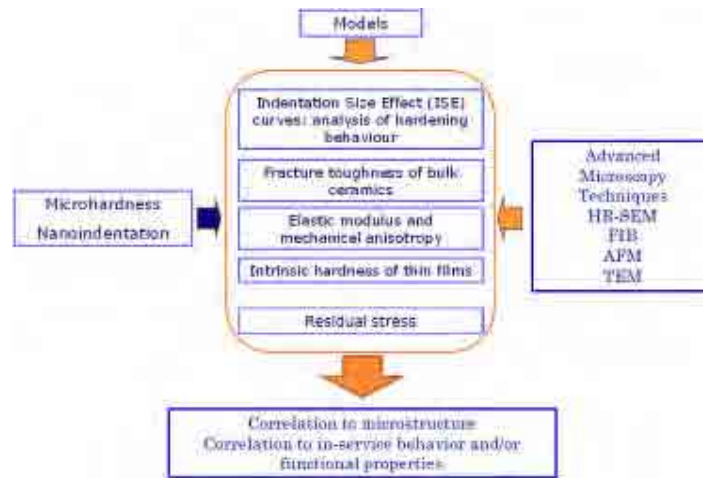


Fig. 1 – Concept scheme representing how the proposed integrated approach can be applied for improving the understanding of mechanical behavior of nano-structured systems and then give the correlation to microstructure and functional properties.

On the other hand, focused ion beam techniques are used for advanced sample preparation and microstructural characterization. FIB systems [9] utilize a finely focused beam of gallium ions (Ga⁺) operating at low beam currents for imaging and at high beam currents for site-specific milling. By controlling the location, beam size and current density of the ion beam, material can be selectively removed from sub-micron areas. Most apparatus nowadays available in the market also contains in situ scanning electron microscopy (SEM) capabilities for real time imaging of the ion milling site and even 3D tomography. The capability of high-resolution imaging using both secondary electron and secondary ion signals has made the FIB microscope a unique imaging tool. Stress-free cross sectioning using the primary gallium ion beam provides valuable microstructure information beneath the specimen surface. FIB techniques can be also used for TEM specimen preparation: a finished electron transparent portion of the sample (usually 5 μm x 20 μm) is obtained by FIB micro-milling and then placed by a micromanipulator on a sample holder to be inserted into the TEM microscope: this procedure at present represents the one site-specific and artefact-less outstanding TEM sample preparation techniques.

One of the present challenges in the field of material science and surface engineering is represented by the development of new integrate methodologies which are based on the combined use of nanoindentation techniques and high resolution microscopy, with the main aim of investigating the structural and microstructural evolution during nano-mechanical testing of nano-scale systems [7-8].

Following this approach (see figure 1), results arise from the application of integrated methodologies (see figure 1), which start from indentation experiments and finally come to the evaluation of mechanical properties of investigated materials, by the support of modelling (both analytical and numerical) and high resolution morphological and microstructural characterisation activities, such as Scanning and transmission electron microscopy (SEM, TEM), Focused Ion Beam microscopy (FIB) and Atomic Force Microscopy (AFM) techniques.

In this paper, two case studies are reported, explaining how the combined use of FIB and nano-mechanical testing can be crucial for the correct evaluation of mechanical and functional performances of nano-structured systems:

- Analysis of residual stresses of engineered surfaces by coupling focused ion beam controlled material removal and nanoindentation testing;
- Nano-mechanical characterisation of sputtered niobium thin films for application in accelerating cavities;

2. Case study 1: Analysis of residual stresses of engineered surfaces by coupling focused ion beam controlled material removal and nanoindentation testing

Residual stresses play a crucial role in determining the deformation behaviour and performance of engineering components and materials, from bulk alloys and composites used in construction and manufacturing industries down to micro-mechanical studies of stresses in individual grains within polycrystalline aggregates, thin films and coatings, and MEMS/NEMS systems [10].

At present, one of the main challenges in the field of residual stress measurement in nanostructured systems is represented by the development of site-specific micro-scale evaluation techniques, which should be also semi-destructive method that allow routine determination of residual stress in engineered components.

In a previous work some of the authors [10], a new optimised method for the determination of residual stress at the microscopic scale was presented, based on focused ion beam (FIB) controlled material removal and relaxation strain mapping by Digital Image Correlation (DIC) techniques [11].

The newly proposed approach (figure 1) involves incremental focused ion beam (FIB) milling of annular trenches (ring-drill) at material surface, combined with high resolution SEM imaging of the pattern of markers previously deposited at the sample surface.

An optimised procedure for FIB milling is presented, allowing a complete automation of the procedure, also reducing the artefacts due to the ion milling of the stubs. Digital image correlation (DIC) analysis of the relative displacements between markers with respect to the undisturbed state provides a measure of strain relaxation.

The comparison of these strain relief measurements with finite element modelling (FEM) allows the evaluation of the residual stress state, in a manner similar to that used in macroscopic incremental hole drilling. Furthermore, the assessment of complete biaxial residual stress state is possible in this configuration, by measuring the relaxation strains along three different directions, in contrast with earlier studies that involve the machining of linear slots.

Results were presented [10] for residual stress evaluation of a 3.8 μm TiN coating on WC-Co substrate obtained by cathodic arc evaporation physical vapour deposition (CAE-PVD) techniques, showing an average compressive stress state of -5.63 GPa. This result was in good agreement with the estimate obtained by XRD ($\sin^2\psi$ method) analysis of -5.84 GPa on the same sample, adopting the same elastic constants [10].

Nevertheless, further studies are still needed in the sense of exploring potentialities of the new proposed technique in terms of strain resolution and sensitivity, by testing soft metallic coatings, which are also expected to be in a low tensile residual field.

Here we present some original results on a 1.5 μm Au coating on silicon substrate deposited by DC sputtering PVD techniques (voltage 410 V, current 0.2 A). This coated system is particularly relevant for the fabrication of MEMS structure, where residual stress plays a significant role in determining the final shape of the structure. In this case, residual stress was measured both by the new FIB-DIC technique [10] and by curvature measurement and application of the Stoney equation [12].

On the basis of several repeated tests carried out in this study the value of residual stress in the coating was then found to be equal to $+270.64 \pm 88.62$ MPa for the DC sputtered Au coating. These results are in good agreement with the estimate obtained by curvature measurement $+280$ MPa for the Au coating.

These results also confirm that even low tensile residual stress states can be evaluated by the ring-drill technique, with a spatial resolution of the order of 1 μm , which is comparable with the resolution obtained by the use of synchrotron sources.

In addition, the combination of FIB milling and SEM imaging within a single experiment ensures the ease and efficiency of use of the present method, since it does not require the laborious and time-consuming transfer of samples between instruments. In fact, the current procedure can be successfully automated for systematic automatic residual stress mapping across significant areas.

This technique seems therefore to be absolutely relevant also in the case of stress analysis on MEMS structures, where an in-situ evaluation of residual stress should be strongly needed, and was not possible to be performed by the conventional XRD or curvature-based methods.

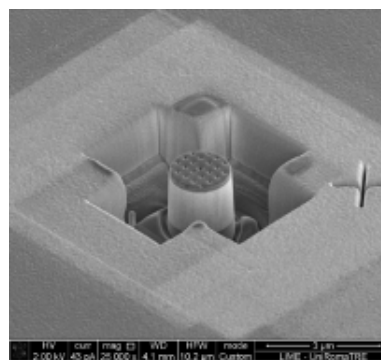
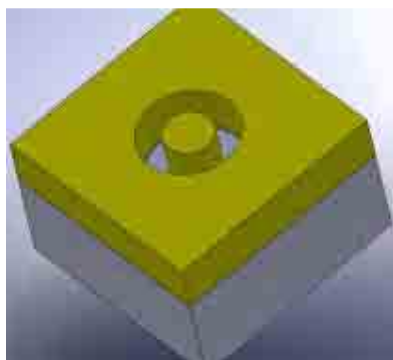


Fig. 2 – Illustration showing principle of ring-core milling, and the idealized geometry of the remaining “stub”

Fig. 3 – Example of one of the realized pillars on a PVD Au coating on Silicon substrate.

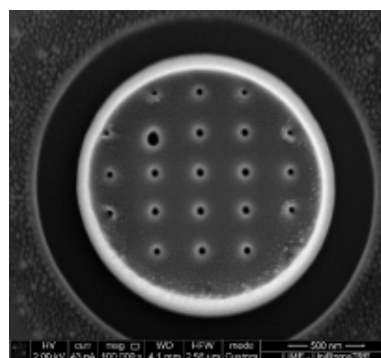
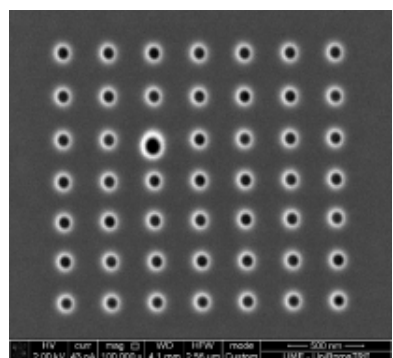


Fig. 4 – Example of the patterning realized over the surface before ring-drilling

Fig. 5 – Micrograph of the patterning after ring drilling. The measured displacements of the milled dots gives the relaxation strain related to the stress relief process.

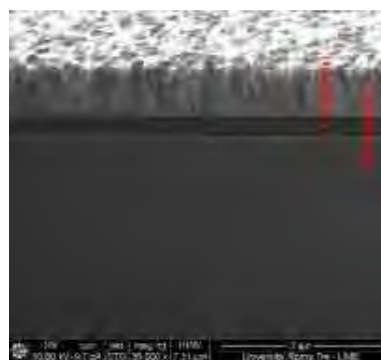
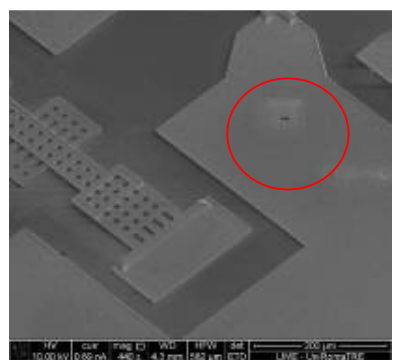


Fig. 6 – In-situ residual stress measurement in proximity of a MEMS structure (red circle) by the ring-drill method

Fig. 7 – FIB cross section (imaging by using the ion probe) of the PVD Au coating under investigation

5. Case study 2: Nano-mechanical characterization of sputtered niobium thin films for application in accelerating cavities

Niobium films obtained by Magnetron Sputtering PVD have been used for many years in superconducting and RF cavity applications [13-14].

Several experimental studies have underlined the strong influence of coating thickness, microstructure and density, coating/substrate interface and surface oxide layer on its Residual Resistance and superconducting properties [13-14].

For these reason, a comprehensive surface chemical, morphological and mechanical surface characterisation is required, in order to find out the appropriate correlation functions among process parameters\microstructure\surface properties\RF performances, and an exhaustive and statistically well-founded procedure has not yet been developed.

The objective of this work [15] was to determine the influence of applied bias Voltage on morphological and Mechanical surface properties of MS-PVD Nb thin films on OFHC Cu substrate, and its correlation with their superconducting properties.

The idea at the basis is that the use of the developed advanced methodologies for surface mechanical characterisation could be successfully used also for acquiring information on microstructural and even functional behaviour of coatings

Experimental activities were focused on the analysis of the influence of the applied BIAS voltage during PVD deposition on mechanical and microstructural properties and functional performances of coatings, with the main aim of proposing indentation techniques as a complementary quality control tool for the indirect evaluation of coating performances.

Two sets of coatings were then realized, characterised by different values of applied bias voltage (100 V and 0 V, respectively) ; process parameters are reported in [15].

Cross-section coating investigations were performed by using Focused Ion Beam (FIB) techniques: SEM microstructural investigations have been performed after FIB sectioning, while interfaces structure and microstructure and thickness of the surface oxide layer have been investigated by TEM after FIB sample preparation. Surface mechanical properties (intrinsic hardness, elastic modulus, surface oxide layer properties) were analysed by means of nano-indentation testing: 25 tests (Agilent G200 Nanoindenter equipped with Continuous Stiffness Measurement). Test parameters and calculation procedures are reported in [15].

All microstructural and surface mechanical obtained information were then correlated to superconducting properties, evaluated by Critical Temperature T_C and Residual Resistance (RRR) measurements of coatings on Quartz substrate.

In fact, results of nano-mechanical testing on the BIASED and UNBIASED PVD Nb coatings showed significant and often unexpected differences, between coating on different substrate and obtained with or without an applied Bias voltage during deposition.

As shown in table 1, which summarises results of mechanical characterisation activities, significant differences in hardness and modulus were measured for the same **Biased** coating on Copper or Quartz substrate.

In particular, a much lower hardness and higher scatter of experimental data were observed in case of Biased coating on Quartz, compared to the same on Copper substrate.

As a confirmation of this, contrasting microstructural characteristics were observed on biased and unbiased coatings on different substrates: biased Nb films on copper showed higher roughness and finer

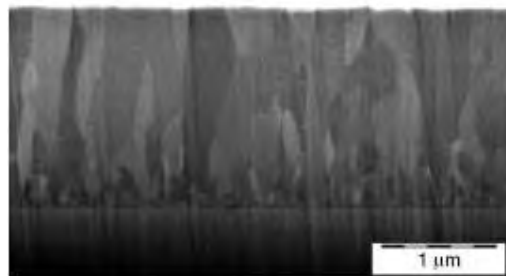
Table 1. Summary of mechanical characterization activities and comparison with T_C measurements

Sample code #	Description	Nanoindentation		Critical temperature measurement
		H (GPa)	E (GPa)	T_C (K)
796	Nb on Cu BIAS type	3,10 ± 0,58	101,5 ± 23,61	Not measured
797	Nb on Quartz BIAS type	1,63 ± 0,30	76,22 ± 48,99	9.45 ± 0.025
803	Nb on Cu CERN type (NO BIAS)	2,59 ± 0,35	108,68 ± 11,65	Not measured
804	Nb on Quartz CERN type (NO BIAS)	2,19 ± 0,31	95,95 ± 26,31	9.38 ± 0.05

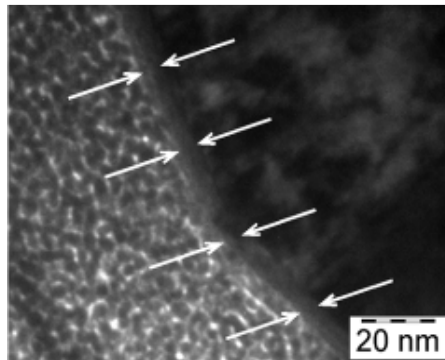
grain size, compared to the unbiased samples on the same substrate, while opposite results were obtained for coatings on quartz substrate. Such results suggest that attention should be paid to the use of RRR and T_C results (obtained for coatings on quartz substrate) for making conclusions on cavity performances. Focused ion beam (FIB) analysis confirms that biased films on copper have finer grain size than unbiased films, while the use of FIB techniques in sample preparation, coupled with TEM observation, gave a much deeper understanding of the coating microstructures at the nanoscale: in particular, the presence of the surface oxide layer was observed, and an estimation of its thickness was performed. It has to be



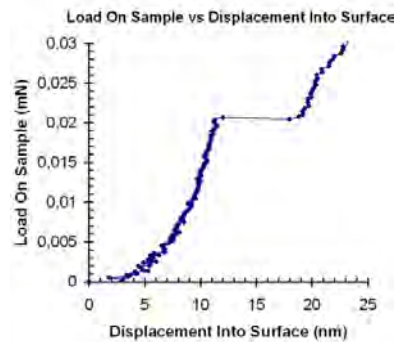
TEM lamella obtained by FIB milling and thinning. In-situ SEM-FEG observation (SE, 5 KV), 12000x



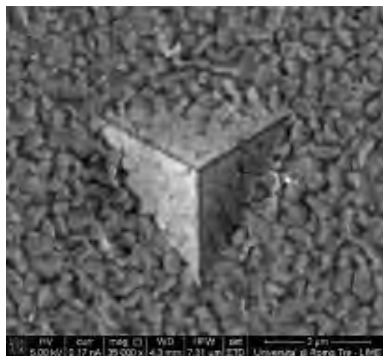
Microstructure of a Nb coating on Copper substrate. SEM-FEG (SE, 5 kV, 60000x) observation after FIB cross-section.



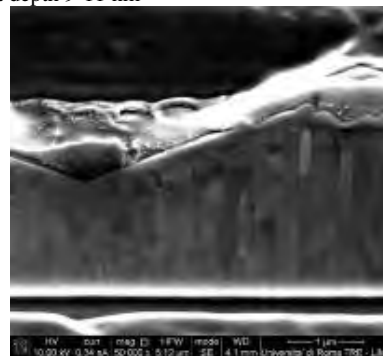
Detail of the surface oxide layer, Nb on Cu BIAS type (TEM BF 660000X after FIB lamella thinning)



Nanoindentation testing on Nb thin films: Detail of the L-d curve highlighting brittle failure of the surface oxide layer at depth 9-11 nm



SEM-FEG imaging of a Berkovich nanoindentation mark



FIB/SEM cross-section analysis of a Berkovich nanoindentation mark. Analysis of piling-up and deformation mechanisms of columnar grains during indentation

Fig. 8.

underlined that at present no other technique can give equivalent morphological and microstructural thin film characterization, including speed of analysis, site-specific morphology, and composition and crystal orientation.

In addition, nanoindentation testing also allowed an indirect (and cheaper compared to high resolution microscopy techniques) evaluation of the presence and thickness of this surface oxide layer (Figure 8), which has been already correlated to coating's superconducting performances.

All these considerations confirm how important and effective can be a comprehensive multiscale-multitechnique mechanical and microstructural characterisation procedure, also in case of functional coatings.

5. Conclusions

In this paper, the application of high resolution - multitechnique – multiscale procedures to the nano-mechanical characterisation of engineered surfaces is presented.

It is observed that only by the combination and synergic use of micro- and nano-hardness testing and SEM-TEM-FIB- AFM microscopy techniques a comprehensive characterisation of nanostructured coatings and complex structures can be achieved.

Two case studies are presented, both showing how nano-mechanical testing in combination with high resolution microscopy can be usefully applied to the characterization of coatings and nano-structured systems for functional (or non-mechanical) application.

In particular, (i) the use of FIB-DIC techniques for high resolution residual stress measurement on coatings for MEMS structures and (ii) the use of nano-mechanical testing for the investigation of microstructural effects of the functional performance MS-PVD Nb thin coatings are described and discussed.

These two applications gives an idea of how relevant can be the proposed procedure in many field of scientific and industrial interest, coming from coatings for applications in particle accelerators to thin films for wear resistant applications, up to in-situ microstructural and nano-mechanical characterization in MEMS structures.

Acknowledgments

Authors acknowledge Daniele De Felicis assistance during FIB characterization activities, carried out at the “Interdepartmental Laboratory of Electron Microscopy” (LIME), University ROMA TRE, Rome, Italy, <http://www.lime.uniroma3.it>.

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Multifunctional Ion Beam Installation “HELIS” as a new instrument for advanced LENR research

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Abstract. The ion beam installation HELIS (P.N. Lebedev Physics Institute, Moscow, Russia) represents an ion accelerator of light elements with atomic number in the range $Z=1-54$ with ion energies ranging from 0.5 to 50 keV operating at deuteron current densities up to 2 A/cm^2 and intended to perform a wide spectrum of physical experiments related to LENR.

1. Introduction

The ion beam installation HELIS (P.N. Lebedev Physics Institute, Moscow, Russia) represents an ion accelerator of light elements with atomic number in the range $Z=1-54$ with ion energies ranging from 0.5 to 50 keV operating at deuteron current densities up to 2 A/cm^2 and intended to perform a wide spectrum of physical experiments: study of interaction of ion beam with various materials; preparing of thin-films of various materials (including films of high-temperature superconductors) by ion beam sputtering method; study of elementary and collective processes in ion-beam plasma, formed at interaction of intensive ion beam with gas medium; study of collisions of light nuclei with low energies.

- We propose to extend HELIS ability to wide spectrum of future physical experiments related to LENR: study of collisions of light nuclei with solid target at very low energies; study of DD-reaction enhancement down to $E_d = 1 \text{ keV}$ and multi-body (3D) reactions in metal targets; study of elementary and collective processes in ion-beam plasma, formed at interaction of intensive ion beam with gas and/or solid targets; preparation of thin-film coatings of various materials (including oxide films) by ion beam sputtering method; possibility of direct calorimetric measurements of excess heat *in-situ* during ion bombardment of metal targets; He-4 measurements during D-bombardment with quadrupole mass-spectrometer; direct X-ray measurements during metal target ion bombardment; four probe resistivity measurements of D-loading in Pd targets

2. Experimental

HELIS (Fig.1) is an accelerator of ions of various gases ($Z=1-54$, $E \leq 50 \text{ keV}$, $I \leq 50 \text{ mA}$) and consist of ion source (actually the accelerator) with an ion source gas system, LV and HV system; ion beam focusing system; vacuum system; ion beam diagnostic equipment for measurement of a current and energy of an ion beam.

The basic ion source HELIS is duoplasmatron (see Fig.2). It can produce the ion beam with characteristics presented in Tabl.1.

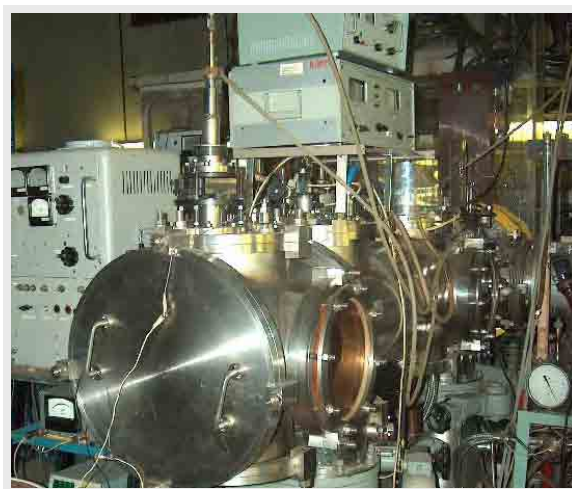


Fig.1 - General view of HELIS installation.

Table 1.

Total hydrogen beam current (at 50 keV)	≤ 50 mA
Energy range	1 -:- 50 keV
Energy spread	10 -:- 100 eV
Reduced emittance	$2 \cdot 10^{-5}$ -:- $5 \cdot 10^{-5}$ cm·rad

HELIS have two additional sources of ions: 1) high-frequency source with a current up to 1 mA and energy of ions ≤ 30 keV (emittance at 30 keV $\sim 1.5 \cdot 10^{-3}$ cm·rad); 2) high-frequency source with a current up to 8 mA and energy of ions 0,25-:-0,5 keV. For beam focusing the electromagnetic lens which provides focal length $f=11$ cm at $I=780$ A is used.

Fig.2. presents proposal of HELIS total experiment set up. Ion accelerator and detector holder need to fill up by different detecting systems. They include flow calorimeter, Q-mass-spectrometer, fast and slow neutron detectors (NE-213 and He-3), charged particle detectors (CR-39 track and dE/E SSB detectors), gamma and X-ray detectors (Ge and CdTe). Sample holder need to be add by four probe resistivity measurements of D-loading in targets and thermistor for target temperature control.

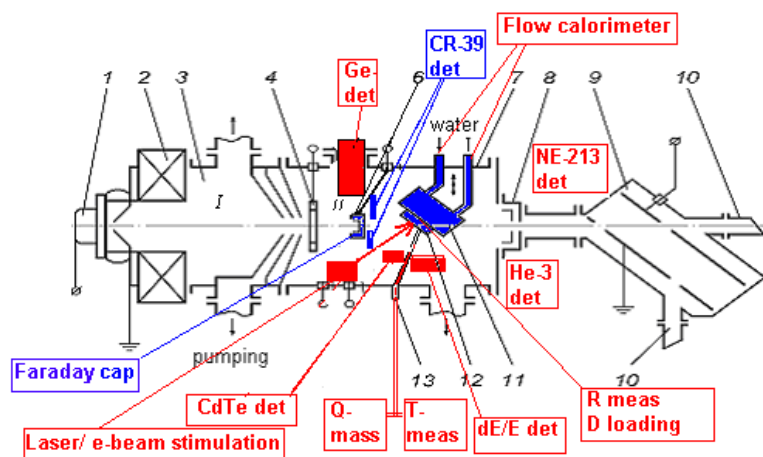


Fig. 2 - HELIS total experiment set up: 1 – ion source (duoplasmatron); 2 – electromagnetic lens; 3 – three-stage chamber of differential pumping; 4 – meter of a current of a transient-time type; 5 – auxiliary ion source; 6 - Faraday cap; 7 – chamber of targets; 8 – the device for calorimetric definition of a current of an ion beam; 9 – electrostatic analyzer; 10 – receivers of parsed fragments; 11 – water (or liquid gas)-cooled holder of the target; 12 - target; 13 – feeder of gas in an vacuum chamber. Detector blocks: ■ Blocks already existing. ■ Blocks needed to be add.

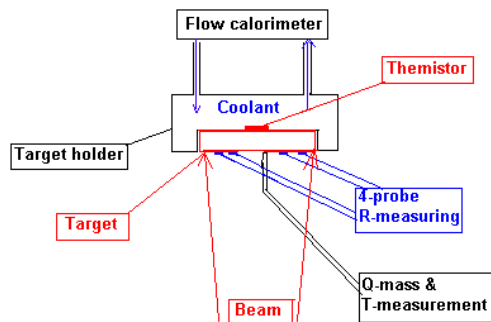


Fig. 3 - Target holders with water cooling.

3. Conclusion

The HELIS facility can be used for study of dd- and dT-reactions yields from various targets at low energy of deuterons and can be equipped by various nuclear detectors, including dE/E Surface Silicon Barrier detector pair, CR-39 plastic track, neutron and X-ray detectors. In general, the HELIS facility with additional installations mentioned above, will allow us to carry out full LENR experiment upon a deuterium implantation into metal targets, involving simultaneous measurements of excess heat, D-loading and He-4 emission, along with accompanying nuclear radiations.

Part II

About the nuclear origin



Charged Particle Emissions and Surface Morphology of Pd/PdO:D_x and TiD_x Targets Under Electron Beam Excitation

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Abstract. We report charged particle emission from metal deuterides upon e-beam excitation of their surface. Detection and identification was made using CR-39 plastic track detectors with Cu and Al absorbers. Protons with primary energy 3 MeV and α -particles with energies $E_\alpha > 10$ MeV are observed.

1. Introduction

First principles calculations of hydrogen desorption from metal hydrides with a high hydrogen solubility [1], show that excitation of the hydrogen subsystem in those deuterides produces plasmons that create strong electric fields ($F \sim 10^8$ V/cm) on a lattice parameter scale ($a \sim 0.3$ - 0.4 nm). As a result, the mean energy of desorbed protons/deuterons (E_d), escaping from the hydride surface, is increased from $kT(1/40$ eV) to several eV ($E_d = F \times a \sim 3$ - 4 eV) or two orders of magnitude larger, effectively producing “hot” deuterons. Such a deuteron acceleration mechanism, along with a large electron screening, could strongly enhance DD-reaction product yield, even at these extremely low excitation energies.

The purpose of this present study is:

- To verify the hypothesis that excitation of the hydrogen subsystem in metal deuterides enhances DD reaction yield.
- To check feasibility of energetic alpha-particle emission under e-beam irradiation.
- To test a new triple CR-39 detector design in vacuum experiments, allowing charged particle identification

2. Experimental

Three plastic track (noiseless) CR-39 detectors are exposed to deuterated samples being excited by an electron beam. The CR-39 detectors were covered by Al and Cu foils with known stopping ranges (this arrangement can be considered as the simplest dE-E detector without time converter), see Fig.1. The Foreground counts are read out from the CR-39 surface of the detectors facing the sample. The Background counts are read from the rear sides of these same detectors that face either the vacuum chamber or the stainless steel support. The sample-detector holder assembly is mounted in the SEM vacuum chamber ($p = 10^{-6}$ torr) and irradiated by a collimated electron beam ($J = 100$ - 300 nA, $E = 30$ keV). The desorbed deuterium and generated charged particles reach the detectors from the spot produced by e-beam, area $S = 8 \times 6$ mm². The effective distance between the center of the spot and the detectors 1 and 2 is about $\langle R_{eff} \rangle = 12$ mm.

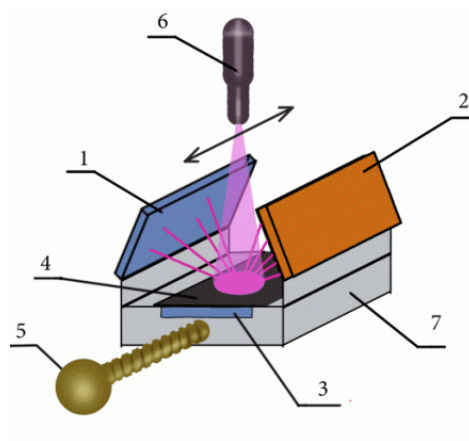


Fig.1. - 1,2 and 3 – are the CR-39 detectors covered with the 11 μm Al (1), 25 μm Cu (2) and 33 μm Al (3) foils, respectively, 4 –deuterated sample, 5-manipulator, 6-electron gun, 7- stainless support

The Landauer CR-39 detectors ($2 \times 1 \text{ cm}^2$) with initial total track density ($N \leq 20 \text{ cm}^{-2}$) were calibrated using a Van De Graaf accelerator (normal incidence protons beams with the energy ranging from 0.6 – 3.0 MeV), a cyclotron α -beam (11 – 30 MeV) and with alpha sources. Calibration functions, track diameter vs. particle energy, were obtained for various CR-39 etching times (Fig.2) or equivalently, depths. Special calibration of CR-39 detectors in a four detector experimental series has also been carried out using extended Pu-238 alpha source placed at the sample position. The calibration showed that overall efficiency of the detectors 1 and 2 is $\varepsilon = 2.6 \%$, while the efficiency of the detector #3 is of $\sim 8.0 \%$. Note in these experiments more than 80 % of alpha tracks detected by detectors 1 and 2 have normal incidence.

In reference experiments without e-beam stimulation two CR-39 detectors (no metal cover and one covered with 25 μm Cu) were used to obtain background levels in the SEM.

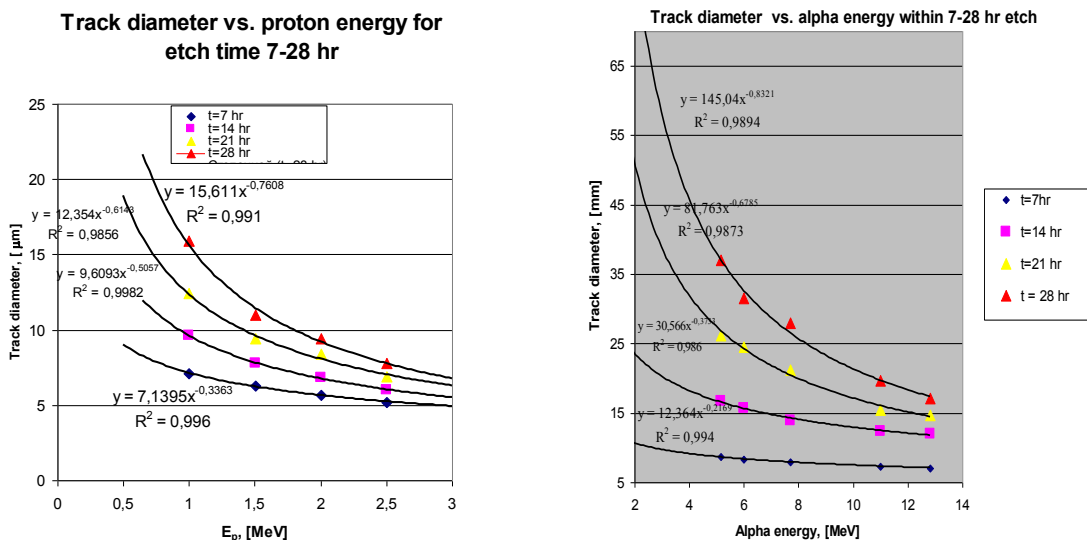


Fig.2. - Landauer CR-39 track diameter vs. charged particle energy (accelerator calibration data) for protons (left) and alphas (right) of normal incidence at various etching time (etching conditions: 6 N NaOH at $t = 70^\circ\text{C}$)

The PdO/Pd/PdO samples are prepared by thermal oxidation of Nilaco (Japan) Pd foil (99.95 % purity), 50 μm thick with area $S = 30 \times 10 \text{ mm}^2$. Electrochemical loading uses 0.3M-LiOD solution in D_2O with Pt anode; $j = 10 \text{ mA/cm}^2$ $T \sim 280 \text{ K}$ (below room temperature) in a special electrolytic cell with separated cathode and anodic spaces. ($x = \text{D}/\text{Pd} \sim 0.73$, about 40 min is required). The samples are rinsed in pure D_2O and then placed in liquid nitrogen in a Dewar flask to cool to $T = 77 \text{ K}$. The cooled samples are rapidly mounted (during 1 min) in the sample holder, Fig. 1, with a set of CR-39's and irradiated by the e-beam ($E = 30 \text{ kV}$, $J = 0.2\text{-}0.6 \mu\text{A/cm}^2$).

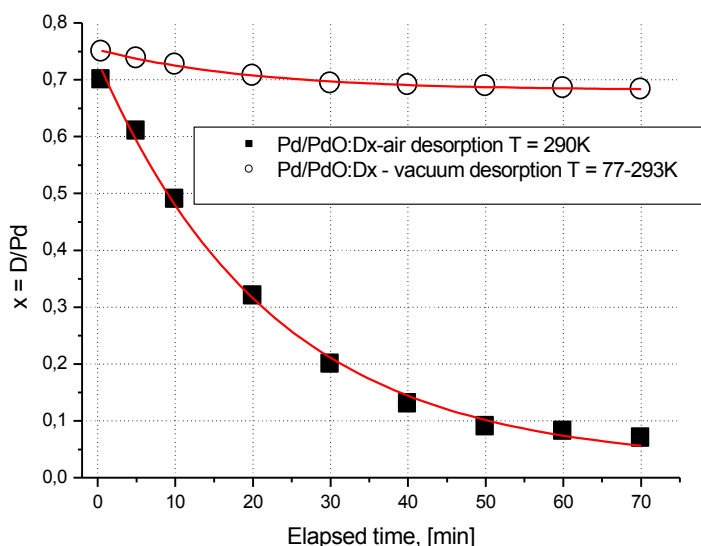


Fig.3. - D-desorption rate from the Pd/PdO:D_x samples in vacuum (electrolysis at $T=280 \text{ K}$ with cooling down to $T = 77\text{K}$ after electrolysis termination)) and in air at ambient conditions (electrolysis at $T=290\text{K}$). Notice very low D-desorption rate in vacuum

D-desorption from the Pd/PdO:D_x sample in vacuum without e-beam excitation and in air are shown in Fig. 3. Under e-beam excitation the desorption rate is $J_D \sim 3.3 \times 10^{15} \text{ D/s-cm}^2$. This desorption rate is consistent with the rate of D-desorption in air at ambient conditions ($\sim 2\text{-}3 \times 10^{15} \text{ D/s-cm}^2$). Results of Rutherford Back Scattering/Elastic Recoil Detection (alphas $E_\alpha = 2.2 \text{ MeV}$, depth $2 \mu\text{m}$) (RBS/ERD profiles) of samples are presented in Fig.4.

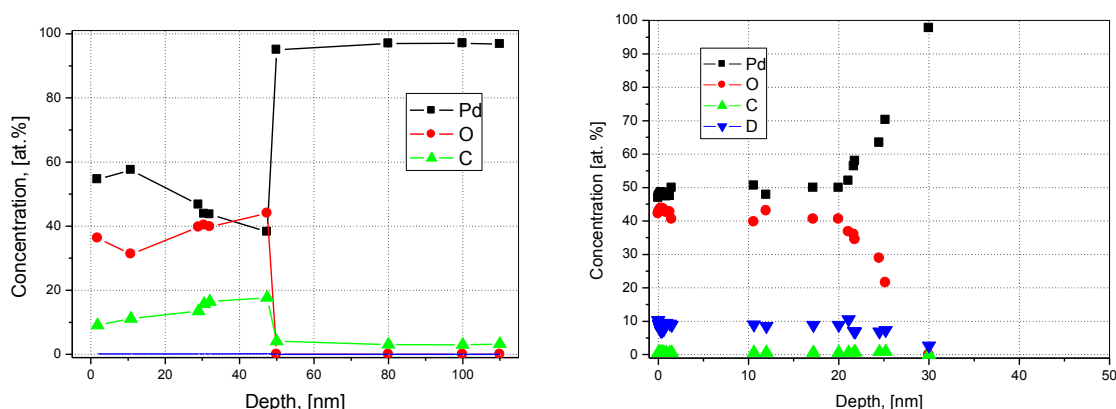


Fig.4. - RBS/ERD profiles of the Pd/PdO samples prior to D-loading –left; after electrochemical loading and D-desorption in vacuum during 50 min of e –beam ($J=0.6 \mu\text{A/cm}^2$ $U = 30 \text{ kV}$) treatment – right

After 50 min of e-beam bombardment some moderate reduction of PdO and carbon layers is observed (from 40 to 25 nm). The residual D is located within the PdO layer. SEM measurements show that e-beam bombardment

is accompanied by formation of numerous pores (from Pd through the PdO) with diameters in the range of 100 – 2000 nm (see Fig. 5). These larger diameter pores ($\varnothing > 350$ nm) have not been found in the “blank” Pd/PdO:H_x samples after e-beam. Large craters with the $\varnothing \sim 10,000$ -12,000 nm are also present at the Pd/PdO:D_x surface after e-beam treatment.

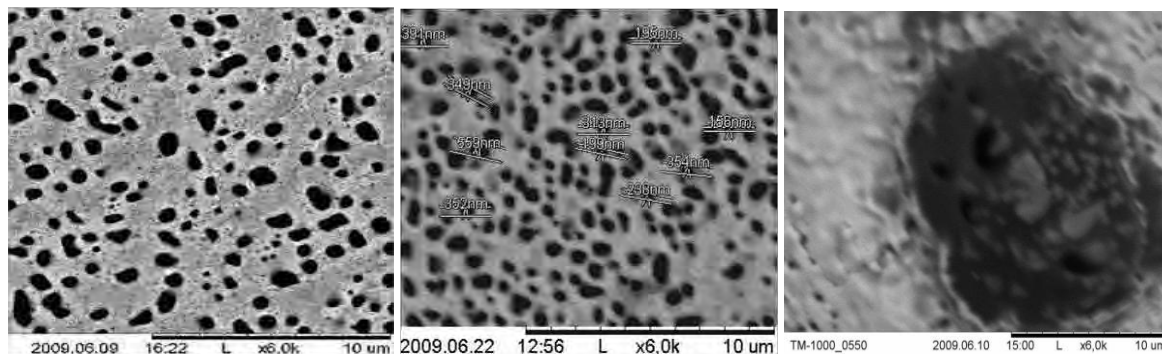


Fig.5. - SEM Pd/PdO:D_x-left and Pd/PdO:H_x-center images after electrolysis + e-beam. Notice larger diameter pore generation in Pd/PdO:D_x. Example of the $\sim 12,000$ nm diameter “crater” at the Pd/PdO:D_x surface after e-beam bombardment (right).

TiD_x samples were prepared as follows. The Ti foils, 30 and 300 μm thick, have been loaded in 1M solution of D₂SO₄ in D₂O during $t = 35$ hr at $J = 30$ mA/cm², in order to dissolve the TiO₂ oxide layer at the Ti-surface and to provide D-penetration. The average loading ($x = \text{D}/\text{Ti} = 0.1$ at depth of 2-3 μm) has been determined by weight balance. The D-desorption rate for TiD_{0.1}, from weighing before and after e-beam irradiation, is consistent with the $J_D \sim 2.0 \times 10^{14}$ D/s-cm². All desorbed deuterons in TiD are released by e-beam irradiation energy, since the chemical compound is absolutely stable at $T = 300$ K. RBS/ERD profiles of the TiD_x samples prior to e-beam bombardment –left; after D-desorption in vacuum during 60 min of e –beam are presented in Fig.6.

RBS data taken before e-beam treatment show the presence of a TiO₂ oxide layer at the surface down to 150 nm. After e-beam excitation the stoichiometry of the Ti oxide changes toward reduction of oxygen (TiO_{0.1}). The O-depth does not change. The X-ray spectrum shows almost complete oxide reduction. Estimates of D-desorption rate from TiD_x using RBS data before and after e-beam gives $v(\text{D}) = 1.5 \times 10^{14}$ D/s-cm², which is 20 times lower than $v(\text{D})$ in Pd/PdO:D_x. The pore size is very small. Some large diameter craters ($\varnothing > 10$ μm) appear at the TiD_x surface after both e-beam and X-ray irradiation.

2. Charged Particle Detection and Identification

Background measurements show that there are no proton and alpha emission effects without e-beam stimulation (see Fig's. 7 and 8).

Cumulative results with Background subtracted for 4 series of runs (total time of e-beam exposure = 3300 min) are presented in Fig. 9. Peak positions are shifted with increasing of shielding thickness. Left peak is accompanied with 3-MeV protons, other peaks – with alpha-particles with energies 10 – 20 MeV.

Reproducibility of results is illustrated by Fig.10: The number of counts in the 3 MeV peak is roughly proportional to the cumulative exposure time of detectors 1 and 2 to Pd/PdO:D_x samples under e-beam.

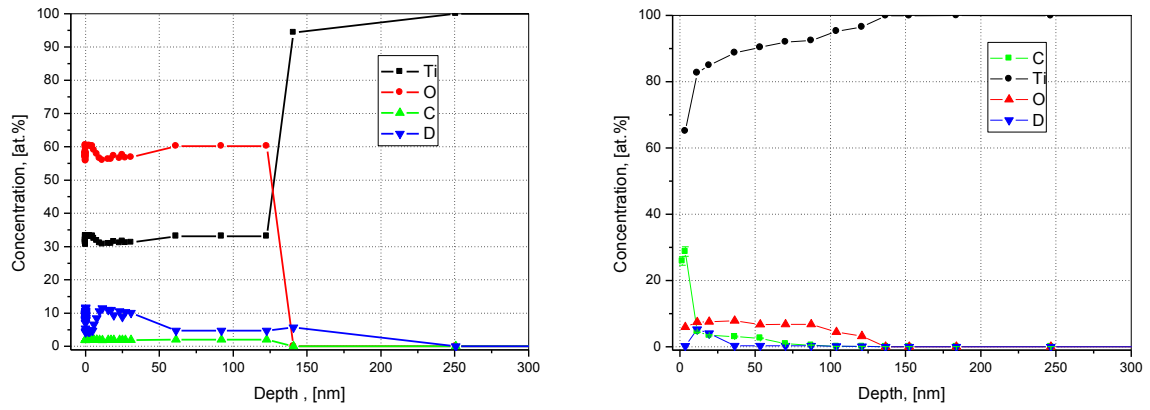


Fig.6. - RBS/ERD profiles of the TiD_x samples prior to e-beam bombardment –left; after D-desorption in vacuum during 60 min of e –beam ($J=0.6 \mu\text{A}/\text{cm}^2$ $U = 30 \text{ kV}$) treatment - right

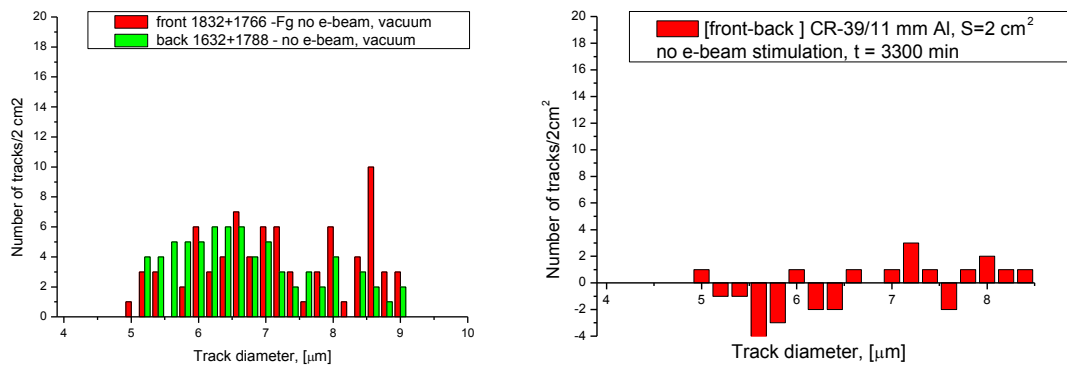


Fig.7. - Track diameter distributions for $\text{Pd}/\text{PdO}:\text{D}_x$ without e-beam stimulation: no proton and alpha effects: CR-39/11 μm Al filter (4 samples, $t = 3300 \text{ min}$). Front and back sides of detector (left). Difference of front and back sides of detector (right).

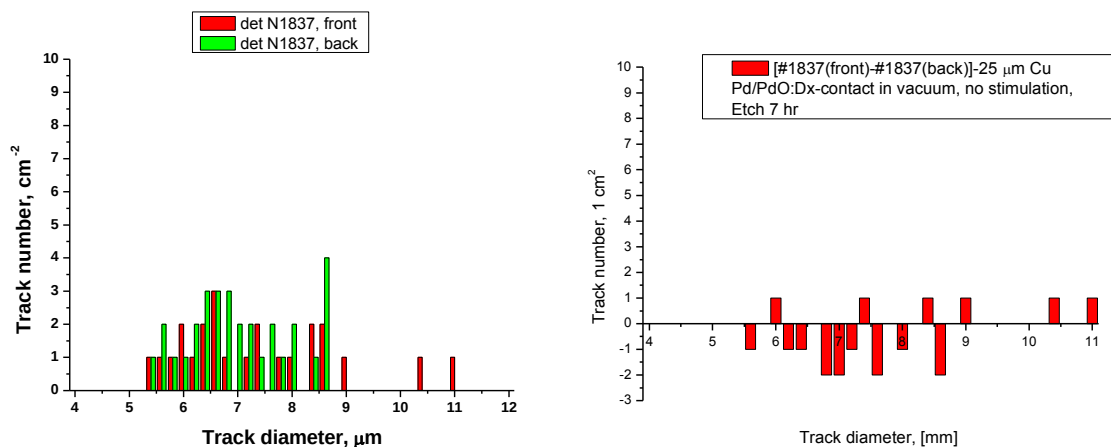


Fig.8. - Track diameter distributions for $\text{Pd}/\text{PdO}:\text{D}_x$ without e-beam stimulation: no proton and alpha effects: 25 μm Cu covered CR-39 (4 samples, $t = 3300 \text{ min}$). Front and back sides of detector (left). Difference of front and back sides of detector (right).

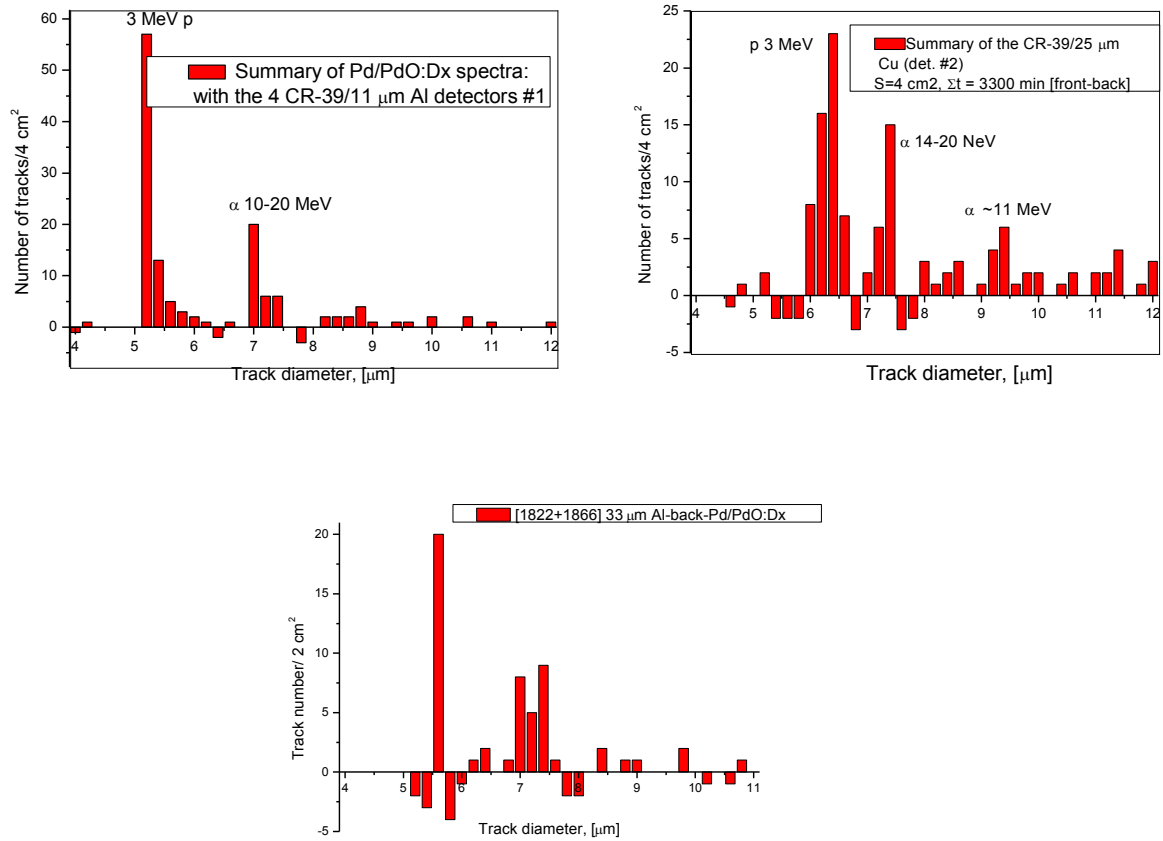


Fig. 9. - Total result with Background subtracted: Sums for 4 series of runs ($\Sigma t = 66 \times 50$ min, $S = 4$ cm² for #1 and #2): (11 μm Al)- left; (25 μm Cu)- right; the det. #3-below: $S = 2$ cm², $t = 1800$ min (33 μm Al). Notice shift of 3 MeV proton peak in these 3 detectors

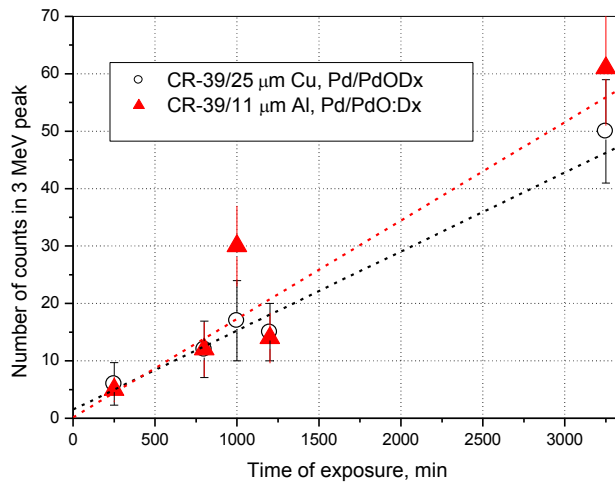


Fig. 10. - Reproducibility: The number of counts in 3 MeV peak is roughly proportional to the time of detectors 1 and 2 exposure with the Pd/PdO:D_x samples under e-beam

Additional proof of the correctness of the identification and energy of observed charged particles is obtained by successive etching of the CR-39 detectors (Fig.11) and comparing the diameters at various depths with the calibration curves (Fig.2).

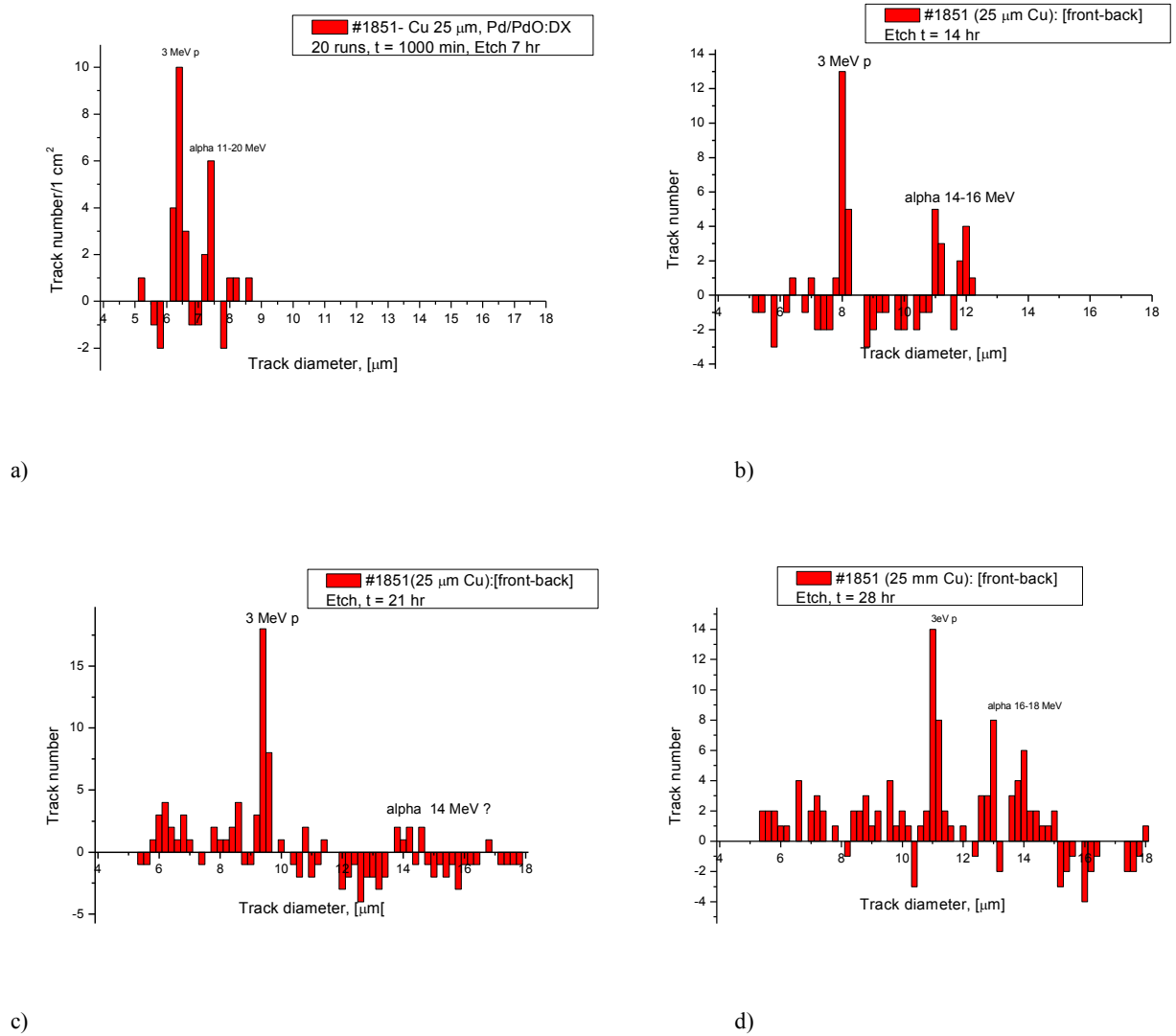


Fig. 11. - Differential spectra (with the subtracting of the rear face results) of #1851 CR-39/25 μm Cu filtered detector #2 after its etching during 7 (a), 14(b), 21(c) and 28(d) hr.

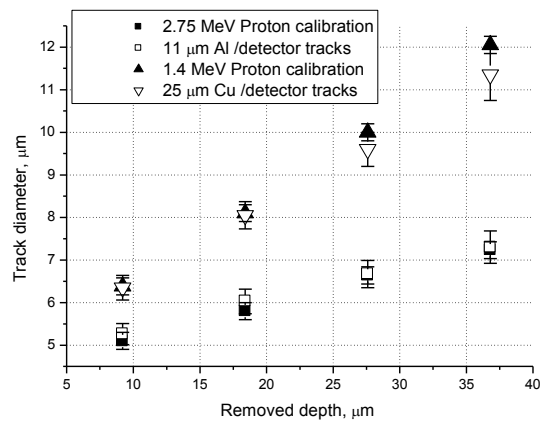


Fig. 12. - Track diameter vs. removed depth (d(h)) for “proton” tracks detected during sequential etching of the detectors 1 and 2, respectively.

Differential spectra (Foreground minus Background) of CR-39/25 μm Cu filtered detector #2 after etching during 7,14,21 and 28 h are presented in Fig.11. The same measurements were carried out for the 11 μm Al filtered detector (data not shown).

Fig. 12 presents the dependence of track diameters for proton-like tracks on removed depth. Note that in our etching conditions the bulk etch rate is $V_B = 1.3 \mu\text{m/h}$, and every 7 h we removed $\sim 9.1 \mu\text{m}$. The black squares and triangles represent the fit of experimental tracks from detectors 1 and 2 (empty squares and triangles, respectively) with $d(h)$ functions obtained using normal incidence accelerator CR-39 bombardment at proton energies 2.75 (consistent with 3 MeV proton after its passage through 11 μm thick Al foil) and 1.4 (consistent with 3 MeV proton after its passage through the 25 μm thick Cu foil) MeV, respectively. This provides additional evidence of stimulated emission of 3-MeV proton and energetic alpha particle emissions in Pd/PdO:D_x samples.

Particle emission rates are estimated by averaging results from absorber covered CR-39 detectors (11 μm Al and 25 μm Cu) with results:

- For 3 MeV protons: $N_p = (1.12 \pm 0.12) \times 10^{-3} \text{ p/s-cm}^2$ of the Pd/PdO:D_x sample (significance level, $L \sim 10.0 \sigma$). The yield of DD-reaction in the Pd/PdO:D_x target under e-beam bombardment, taken only for movable deuterons) is found to be $\lambda_{DD} \sim 6 \times 10^{-19} \text{ p/DD-pair}$ (4 orders of magnitude above the “Jones level”).
- For 10-20 MeV alphas $N_\alpha = (0.46 \pm 0.075) \times 10^{-3} \alpha/\text{s-cm}^2$ of the Pd/PdO:D_x sample, (significance level $L \sim 6.0 \sigma$).
- For the detector placed under the rare (non-irradiated by e-beam), position 3, side of the Pd/PdO:D_x sample: $N_p = (7.2 \pm 1.6) \times 10^{-4} \text{ p/s-cm}^2$ and $N_\alpha = (4.3 \pm 0.8) \times 10^{-4} \alpha/\text{s-cm}^2$ of the Pd/PdO:D_x sample.

Fig.13 presents the TiD_x e-beam stimulation results. Both statistically significant 3 MeV proton (5.2-5.4 μm track diameter) and 11-20 MeV alphas (7.0-7.6 μm track diameter) bands are found in the 11 μm Al covered detector (left); bands of 1.5 MeV protons (track diameter 6.0-6.6 μm , consistent with the 3 MeV proton losses in 25 μm Cu foil) and 14 MeV alphas (track diameter near 7.4 μm , consistent with $\sim 17 \text{ MeV}$ alpha losses in 25 μm Cu foil are detected (right). No statistically significant results have been found over all differential spectrum from the rare side of the TiD_x sample, position 3.

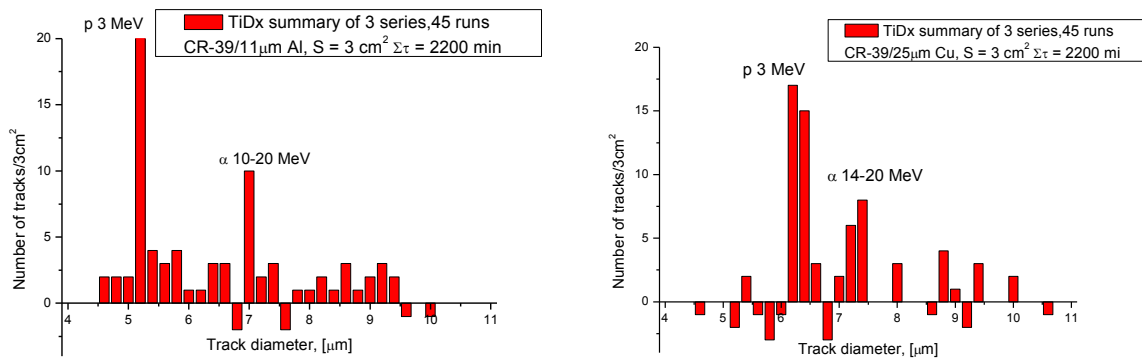


Fig.13. - TiD_x e-beam stimulation results: total 42 runs of 60 min each: two CR-39 detectors [11 μm Al (left) and 25 μm Cu (right)] with the Background (rear side) subtracting.

Average emission rates from foil covered CR-39 detectors (11 μm Al and 25 μm Cu) for 3 MeV protons and energetic alphas in TiD_x during 42 runs in 3 series ($t = 2200 \text{ min}$) are:

- For 3 MeV protons: $\langle N_p \rangle = (8.4 \pm 1.5) \times 10^{-4}$ p/s-cm² of TiD_x sample (the significance level $L = 5.6 \sigma$). The yield of DD-reaction in the TiD_x target under e-beam bombardment, taken only for movable deuterons) is found to be $\lambda_{DD} \sim 5 \times 10^{-18}$ p/DD-pair (6 orders of magnitude above the “Jones level”).

- For 10-20 MeV alphas $\langle N_\alpha \rangle = (4.7 \pm 1.0) \times 10^{-4}$ α/s-cm² of the TiD_x sample, (the significance level $L \sim 4.5 \sigma$). The soft component of α (E ~ 11 MeV) is not statistically significant from the non-irradiated by e-beam face of the TiD_x sample.

4. Discussions

DD-reaction rate in the Pd/PdO:D_x

A simple model of the experiment will be used to estimate the DD-reaction rate in the Pd/PdO:D_x target under electron bombardment. The e-beam stimulated D-desorption flux moving toward the Pd/PdO:D_x surface will be treated as a low energy projectile or “deuteron beam”. The deuterated surface of the Pd/PdO sample is treated as deuterium “target”. The deuteron (D⁺) “current”, is estimated from D-desorption rate, $J_d = 0.5$ mA/cm². The mean concentration of target is estimated from the mean D/Pd ratio during e-beam bombardment ($\langle x \rangle \sim 0.15$ or $N_d = 1.1 \times 10^{22}$ cm⁻³). The thick target yield I_{DD} is computed from:

$$I_{DD} = J_d N_{\text{eff}}(T) \times \int_0^{E_d} f(E) \sigma_{DD}(E) (dx/dE) dE$$

Here J_d – deuteron current density; $N_{\text{eff}}(T)$ – effective concentration of non-free D in metal at temperature T , captured at depth x : ($N_{\text{eff}}(T) = N_0 \exp(-\varepsilon_d \Delta T / k_B T T_0)$, where N_0 is the D concentration at $T_0 = 290$ K; $f(E)$ – enhancement factor [$f(E) = Y_{\text{exp}}(E)/Y_b(E) = \exp[\eta \pi(E) U_e/E]$]; σ_{DD} – is the bare DD- cross-section; dx/dE – is the stopping power in target calculated with Monte-Carlo code SRIM [4].

The deuteron screening potential U_e can be determine using the formula: $U_e = (T/T_0)^{-1/2} [a \ln(y) + b]$ [2] - an empirical equation obtained from the analysis of accelerator data for 70 elements of periodic Table (the data by Raiola et al [3]): where $a = 145.3$ and $b = 71.2$ – are numerical constants; $y = k y_0 (J_d/J_0)^{1/2}$, with $k = \exp(-\varepsilon_d \Delta T / k_B T T_0)$, $y_0 = \text{Pd/D ratio at } T_0 = 290 \text{ K}$, and $J_0 = 0.03 \text{ mA/cm}^2$. Substitution of $J_d = 0.5 \text{ mA/cm}^2$, $T = 290 \text{ K}$ and $\langle \text{Pd/D} \rangle = 6.7$ in eq. for U_e gives $U_e = 730 \pm 50 \text{ eV}$. This screening value falls roughly into the interval limited by Kasagi’s (600 eV for Pd/PdO [5]) and Raiola’s (800 eV for Pd [3])

The DD-reaction rate of ~ 0.001 p/s-cm² in 4π ster. could be reached in the Pd/PdO:D_x target (taking into account $U_e \sim 730 \text{ eV}$) only if the mean kinetic energy of the desorbing deuterons is of the order of $\langle E_d \rangle \sim 3-4 \text{ eV}$. In contrast, if the mean deuteron energy $\langle E_d \rangle \sim kT$, with the same U_e , the DD-reaction rate would be only $\sim 10^{-7}$ p/s-cm², or well below our detection limit. This result strongly supports the theoretical prediction [1] with regards to electron excitation of hydrogen subsystem in Pd deuteride (hot deuteron generation). The 3-4 eV deuteron flux claim serves as an evidence for the generation of a strong electric field ($\sim 10^8 \text{ V/cm}$) on a scale of the lattice parameter ($a_0 = 0.39 \text{ nm}$) due to plasmon formation in this experiment.

TiD_x DD-reaction rate

Taking $J_d = 0.03 \text{ mA/cm}^2$ and $y_0 \sim 2.0$ (the surface D-concentration is $x = \text{D/Ti} \sim 0.3$ during e-bombardment) one can obtain $U_e \sim 130 \text{ eV}$. At this small screening potential, in order to produce DD-reaction rate of the order of ~ 0.001 p/s-cm², the kinetic energy of deuteron flux (in laboratory system) has to be rather higher ($E_d \sim 500 \text{ eV}$). This high kinetic energy can be gained by D⁺ acceleration in a strong electric field created by electrostatic charging of the TiO₂ surface with e-beam. $(E_d)_{\text{eff}} = \varepsilon_0 + e E(\text{TiO}_2) x h(\text{TiO}_2)$. At $\varepsilon_0 \sim 3 \text{ eV}$ (the initial kinetic energy of D⁺ in Ti caused by plasmon generation), $E(\text{TiO}_2) \sim 3.5 \times 10^7 \text{ V/cm}$ (electrical strength of TiO₂) and $h(\text{TiO}_2) = 1.5 \times 10^{-5} \text{ cm}$, the $(E_d)_{\text{max}} \sim 500 \text{ eV}$ (!!!) suggesting D⁺ acceleration by a strong electric field during deuteron drift and diffusion through the Ti oxide.

5. Conclusions

- The vacuum experiments with and without e-beam irradiation, lead to the conclusion that an electron beam ($J \sim 100\text{-}300\text{ nA}$, $E = 30\text{ keV}$) stimulus of the Pd and Ti deuterided targets (cathodes) surface can enhance the intensity of the emissions of nuclear charged particles.
- Both products of DD-reaction (3 MeV) protons and high energy alphas (11-20 MeV) are clearly identifiable in e-beam stimulation experiment with the Pd/PdO:D_x and TiD_x targets.
- Signatures of 3 MeV protons and energetic alphas appear on the surface of all (2 or 3) independent detectors in the same experiment covered by metallic foil filters with different stopping ranges/powers.
- The data analysis on the Pd/PdO:D_x target supports reasonable estimates of DD-reaction cross sections and the enhancement factors to a very low deuteron energy ($E_d \sim 3.0\text{ eV}$). Extrapolation of DD-reaction cross section and the enhancement factor with a reasonable screening potential $U_e = 730\text{ eV}$, satisfactorily accounts for the detected DD-reaction rate in these experiments. This calculation and the underlying data strongly support the theoretical prediction [1] with regard to electron excitation of hydrogen subsystem in Pd deuteride.
- In order to enhance charged particle yield, we plan to vary target deuterides, as well as the current and energy of electron beam. These optimization studies will bring understanding of the possible technological value of e-beam and other excitation.
- More work also should be done with respect to the energy spectra characterization and the origin of the energetic alpha emission.

6. References

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Enhanced Electron Screening and Nuclear Mechanism of Cold Fusion

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Abstract: The enhanced electron screening effect observed in accelerator experiments for the ${}^2\text{H}(\text{d,p}){}^3\text{H}$ and ${}^2\text{H}(\text{d,n}){}^3\text{He}$ reaction in deuterized metallic targets may be a breakthrough in understanding the phenomenon of cold fusion. The dielectric function theory enables an extrapolation of experimental cross sections determined at higher energies down to room temperature, leading to an enhancement of the fusion reaction rates by a factor of 10^{40} compared to the value predicted for the deuterium molecule. An additional enhancement can be obtained due to a 0^+ resonance which should exist in the compound nucleus ${}^4\text{He}$ very close to the D-D reaction threshold. Combination of both processes offers a simple explanation of high penetration probability through the Coulomb barrier and the reaction branching ratio preferring the ${}^4\text{He}$ channel in heavy-water electrolysis experiments.

1. Introduction

Observation of a heat excess [1] and neutron emission [2] in the first heavy-water electrolysis experiments in 1989 seemed to be in contradiction to laws of nuclear physics. A simple calculation of the penetration factor through the Coulomb barrier at room temperature [3] gave reaction rates for the d+d fusion reactions being a factor of 10^{50} smaller than the rates needed for explanation the experimental results. On the other hand, the observed neutron emission should be about a factor of 10^7 weaker than a reaction channel responsible for the heat production and clearly correlated to the fusion of the ${}^4\text{He}$ nucleus [4]. Thus, the reaction branching ratios at room temperature completely contradict the experimental results obtained by means of the accelerator technique at deuteron energies of a few keV for which the mirror stripping reactions ${}^2\text{H}(\text{d,p}){}^3\text{H}$ and ${}^2\text{H}(\text{d,n}){}^3\text{He}$, being equally probable, dominate by a factor $>10^6$ the electromagnetic transition ${}^2\text{H}(\text{d},\gamma){}^4\text{He}$. Reproducibility of the cold fusion experiments has been highly increased in the last decade [5,6] and some important experimental conditions, under which the heat production takes place, has been found [7,8]. Nevertheless, a lack of reliable nuclear theory explaining at least some of the room temperature effects leads to an ongoing scepticism in the scientific community. Therefore, finding of the enhanced electron screening effect in metallic targets for the d+d stripping reactions [9], and similar observations of other groups [10-13] can play a key role in understanding of the cold fusion phenomenon. Screening of charges of the reacting nuclei by surrounding electrons in metallic environments increases the Coulomb barrier penetrability and results in an exponential-like enhancement of the cross sections compared to those measured for a gas target. That effect cannot explain, however, the change of branching ratios for the d+d reaction at room temperature and domination of the ${}^4\text{He}$ reaction channel. A simple mechanism of a single particle resonance located very close to the D+D reaction threshold in the compound nucleus ${}^4\text{He}$ will be presented here. Combination of the electron screening effect and the resonant process can explain most of the observed phenomena usually connected to the cold fusion and the heat excess production in heavy-water electrolysis experiments.

2. Enhanced electron screening effect

Electron screening effect can be described by a screening length a that corresponds to a distance from which the nuclear charges (ions) embedded in an electron gas can be treated as neutral. For strongly coupled plasmas where the average Coulomb potential energy between ions is larger than their kinetic energy, the screening length does not depend on the temperature and is of order of the Wigner-Seitz radius

$$a_{\text{ws}} = \left(\frac{3Z}{4\pi n_e} \right)^{1/3} \quad (1)$$

where Z and n_e are the ion charge and the density of free electrons, respectively. Dense astrophysical plasmas of White and Brown Dwarfs or of Giant Planets [14] are very good examples for strongly coupled plasmas.

Similarly, deuterons moving in metallic environments can also be considered using plasma physics methods. For the simple Bohr screening, the screened Coulomb potential energy between two reacting deuterons can be presented as follows

$$V(r) = \frac{e^2}{r} \exp\left(-\frac{r}{a}\right) \approx \frac{e^2}{r} - \frac{e^2}{a} \quad (2)$$

Now the screening length a is of order of the Bohr radius. For projectile energies used in accelerator experiments where $r \ll a$, the deuteron-deuteron potential can be simply described as the Coulomb potential reduced by a constant, the screening energy $U_e = e^2/a$. Thus, the “screened” cross section dependent on the penetration factor through the Coulomb barrier P corrected for the electron screening, can be expressed by the only weakly on energy dependent astrophysical S -factor

$$\begin{aligned} \sigma_{scr}(E_{cm}) &= \frac{1}{\sqrt{E_{cm}(E_{cm} + U_e)}} S(E_{cm}) \exp\left(-\sqrt{\frac{E_G}{E_{cm} + U_e}}\right) \\ &= \frac{1}{\sqrt{E_{cm} E_G}} S(E_{cm}) P(E_{cm} + U_e) \end{aligned} \quad (3)$$

Here E_{cm} denotes the energy in the center of mass system and E_G is the Gamow energy defined as follows:

$$E_G = 2\mu\pi^2 \frac{(Z_1 Z_2)^2 e^2}{\hbar^2}$$

where Z_1 and Z_2 are the charges of reacting nuclei and μ stays for the reduced mass. The screening energy U_e corresponds to a reduction of the Coulomb barrier height in the expression for the penetration factor. In comparison to the bare nuclei, the cross section for reactions in metallic environments exponentially increases for decreasing projectile energies, whereby U_e can be taken from fits to the experimental data. The U_e values determined in our experiments for C, Al, Zr, Pd and Ta targets are depicted in Fig. 1. For heavier metals the screening energy amounts to about 300 eV that is one order of magnitude larger than the value 25 ± 5 eV obtained in the gas target experiment [15].

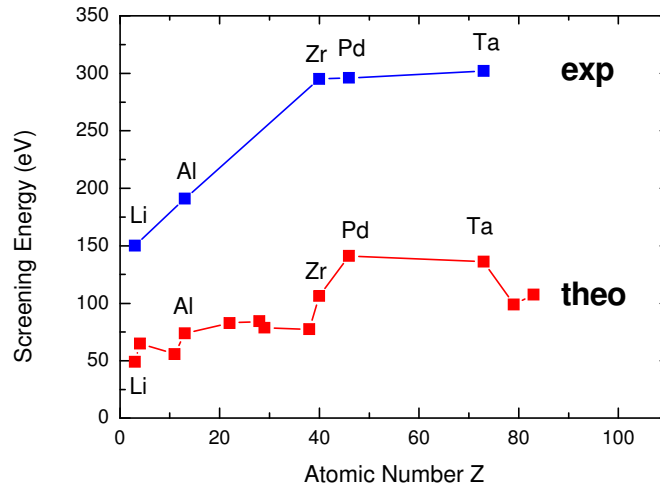


Fig. 1. - Experimental and theoretical electron screening energies obtained for C, Al, Zr, Pd and Ta targets.

The screening effect in metals can be described within the self-consistent dielectric function theory [9]. It enables to treat the electron screening as a static polarization of the metallic medium induced by the positively charged deuterons. The screened Coulomb potential $V(r)$ is a solution of the Poisson equation and can be expressed as a Fourier transform

$$V(r) = \frac{e^2}{r} \Phi(r) = \frac{1}{(2\pi)^3} \int \frac{4\pi e \varphi_1(q) e \varphi_2(q)}{\epsilon_v(q) \epsilon_c(q) q^2} \exp(i\vec{q}\vec{r}) d^3q \quad (4)$$

The wave-number dependent dielectric functions ϵ_v and ϵ_c describe polarization of valence and core electrons of host atoms induced by a charged impurity. $\Phi(r)$ and $\varphi_i(q)$ functions are the screening function and electronic charge-form factors of reacting nuclei, respectively (for details see [9,18]). Additionally, the cohesion screening contribution arising from the difference in binding energies between two reacting deuterons and the compound nucleus ^4He in the crystal lattice has to be included [9]. The theoretical calculations describe the observed material dependence of the screening energy qualitatively correctly (see Fig. 1). The main contribution to the theoretical values is provided by polarization of the free valence electrons, although the contribution of bound electrons (core polarization) and the cohesion screening cannot be neglected. However, the absolute values of the theoretically calculated U_e fail by a factor of about two. No reason for such a large discrepancy between theoretical and experimental values has been found so far. Recent experiments carried out under ultra high vacuum conditions [16,17] show that this discrepancy can be even larger. On the other hand, since the experimental screening energies obtained for insulating materials are rather small (<50eV) [12,13] we can conclude that the large screening energies should result from conduction electrons.

An independent test of the enhanced screening effect can be obtained by study alpha radioactive decays in different insulating and metallic environments. Higher screening energies for metallic environments result in a slight decrease of life times of alpha decays [17,20].

3. Nuclear reactions at room temperature

Since the astrophysical S-factors for fusion reactions are usually known down to lowest projectile energies the only uncertainty of nuclear reaction rates at room temperature results from the screening energy U_e . However, the screening energy as defined in Eq.(2) loses its physical sense for the closest approach distances comparable with the screening length a . That corresponds to projectile energies comparable or smaller than the value e^2/a . Thus, in order to apply Eq.(3) for calculation of the reaction cross section at room temperature, we have to replace U_e by an energy-dependent effective screening energy U_{eff} . Similar to U_e , the effective screening energy can be still interpreted as an appropriate reduction of the bare Coulomb barrier which should match to the penetration through the screened Coulomb potential. Therefore, U_{eff} has to be calculated from a condition setting equal the penetration factors as applied in Eq.(2) and that obtained within the WKB approximation with the screened potential $V(r)$:

$$\sqrt{\frac{E_G}{E_{cm} + U_{eff}}} \exp\left(-\sqrt{\frac{E_G}{E_{cm} + U_{eff}}}\right) = \exp\left(-\frac{2\sqrt{M}}{\hbar} \int_{R_1}^{R_2} \sqrt{V(r) - E_{cm}} dr\right) \quad (5)$$

Here R_1 and R_2 are the classical turning points in the WKB expression, and M is the deuteron mass. The results of calculations for Pd are presented in Fig.2. There are two well defined limits: at the high energy ($E_{cm} > 1$ keV) and at the low energy ($E_{cm} < 10$ eV). The ratio between the low-energy and the high-energy U_{eff} value amounts to about 0.58, being nearly independent of the actual deuteron-deuteron potential. Additionally, the cohesion screening energy has to be added leading to the total screening energy at the zero projectile energy U_0 that is equal to about 0.78 of the high-energy limit U_e [9].

At deuteron energies below 10 eV, the effective screening energy remains almost constant, hence the expression for the cross section takes a very simple form. Starting from Eq.(3) we obtain

$$\sigma_{scr}(E_{cm}) \cong \frac{1}{\sqrt{U_0 E_{cm}}} S_0 \exp\left(-\sqrt{\frac{E_G}{U_0}}\right) \propto \frac{1}{\sqrt{E_{cm}}} \quad \text{for} \quad E_{cm} \rightarrow 0 \quad (6)$$

where U_0 and S_0 are the screening energy and the S-factor taken at the projectile energy zero, respectively. Surprisingly, the cross section increases at low energies as the barrier-penetration factor stays constant and the wave-length dependence dominates [9]. The same expression is also valid for other nuclear reactions at room

temperature. Taking into account that the U_e for the deuteron stripping reaction ${}^2\text{H}(\text{d},\text{p}){}^3\text{H}$ amounts to about 500 eV [17] ($U_0=360\text{eV}$), the reaction cross section at room temperature reaches value $\sigma_{scr}=10^{-15}$ b which is comparable with the cross sections for nuclear transitions induced by the weak interactions. It means that the fusion reaction at room temperature should be measurable by use a suitable experimental set-up.

For the electrolysis experiments, a very useful quantity that can experimentally be determined is the nuclear reaction rate defined here without number densities of involved nuclei as follows

$$R_{scr}(E_{cm}) = \sigma_{scr}(E_{cm})v_{rel} = \sigma_{scr}(E_{cm})\sqrt{\frac{2E_{cm}}{\mu}} \cong \frac{\sqrt{2}S_0}{\sqrt{\mu U_0}} \exp\left(-\sqrt{\frac{E_G}{U_0}}\right) \quad (7)$$

Here v_{rel} is the relative velocity between the reacting nuclei and μ denotes the reduced mass. Due to the energy dependence of the cross section at very low energies (see Eq.(6)), the reaction rate depends only on U_0 and not on E_{cm} . Therefore, no assumption about the distribution of the deuteron velocity at room temperature is necessary.

Nuclear reaction rates at room temperature very strongly depend on both the Gamow and screening energies. In order to illustrate it we compare the nuclear reaction rates of three fusion reactions between hydrogen isotopes for which the screening energy should be the same: ${}^2\text{H}(\text{d},\text{p}){}^3\text{H}$, ${}^2\text{H}(\text{p},\gamma){}^3\text{He}$ and ${}^3\text{H}(\text{p},\gamma){}^4\text{He}$. Without any electron screening contribution, the first reaction induced by nuclear forces ought to be much more probable than the others mediated by electromagnetic interaction, which is confirmed by large differences between the values of the astrophysical S-factors (see Table 1). However, as it was argued in the work of Koonin and Nauerberg [3], the small reduced masses in the channels p+d and p+t result in small Gamow energies, which consequently leads to an increase of reaction rates at very small projectile energies (see Fig. 2). Correspondingly, for small screening energies below 200 eV, the ${}^2\text{H}(\text{p},\gamma){}^3\text{He}$ reaction is the most probable reaction at room temperature. However, if the screening energies would be higher the ${}^2\text{H}(\text{d},\text{p}){}^3\text{H}$ reaction dominates. Its reaction rate will be for $U_0=360$ eV by a factor of about 10^3 larger than the values for the other reactions. On the other hand, this relatively large screening energy can provide the neutron production rate in the ${}^2\text{H}(\text{d},\text{n}){}^3\text{He}$ reaction of about 10^{-15} neutrons per deuteron pair and second. This is above the neutron production rate estimated in the experiment of Jones et al. [2] but significantly below the nuclear reaction rates necessary for explanation of the heat excess observed in the experiment of Fleischmann and Pones [1].

4. D-D threshold resonance

The observation of the excess heat production is probably connected to the fusion of ${}^4\text{He}$ [4] with the rate by about a factor of 10^7 larger than the neutron emission. Thus, beside the screening effect an additional phenomenon changing the branching ratios and increasing the reaction rates at room temperature should obviously exist. Alteration of the branching ratio by a factor of 10^7 might be achieved within the classical nuclear physics without any exceptional mechanisms. An example for such an approach could be a narrow resonance in the ${}^4\text{He}$ nucleus lying close to the d+d reaction threshold. Supposing a nearly single-particle width of this resonance for the deuteron channel and simultaneous quenching of the nucleon decay channels, one can explain major experimental results concerning the cold fusion. The deuteron width of the resonance can be expressed by the R-Matrix formula

Table 1. Astrophysical S-factors, Gamow energies and reduced masses for three different fusion reactions between hydrogen isotopes.

Reaction	d + d $\rightarrow$ t + p	p + d $\rightarrow$ ${}^3\text{He}$ + γ	p + t $\rightarrow$ ${}^4\text{He}$ + γ
S_0 (keV barn)	55.5	$2.5 \cdot 10^{-4}$	$2.6 \cdot 10^{-3}$
E_G (keV)	986.3	657.7	739.7
μ (amu)	1.00728	0.67141	0.75506

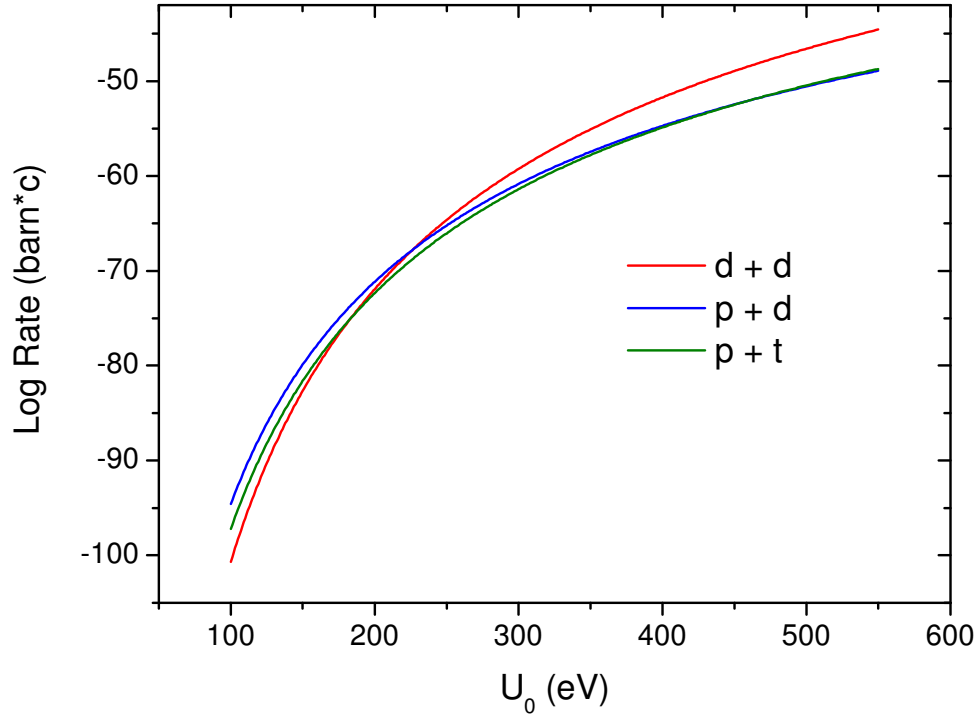


Fig. 2. - Nuclear reaction rates for three different fusion reactions in dependence of the electron screening energy U_0 (presented in log scale).

$$\Gamma_d = 2P_d \frac{3\hbar^2}{2\mu a_d} |\theta_d|^2 \quad (8)$$

where P_d , μ and a_d are the penetration factor, the reduced mass and the channel radius for the d+d channel, respectively, and $|\theta_d|^2$ denotes the dimensionless reduced resonance width. Since the total resonance width Γ is assumed to be dominated by the deuteron width ($\Gamma \approx \Gamma_d$), its value will drop for low sub-Coulomb deuteron energies very rapidly with decreasing penetration factor. On the other hand, the resonance strength, observed for instance for the proton decay channel, is given by the ratio $\Gamma_d \Gamma_p / \Gamma$ and should be independent of the resonance energy if we take into account that the proton width Γ_p remains nearly constant. Thus, the height of the single particle resonance ($\sim \Gamma_d \Gamma_p / \Gamma^2 \approx 1/\Gamma_d$) strongly increases as the resonance energy decreases – we speak about so-called narrowing of the single particle resonance. For the resonance energy of about 10 eV, the resonance width would be of a few eV and its height would raise by a factor larger than 10^6 . Furthermore, the hypothetical resonance could change the reaction branching ratios within the resonance width in favour of those supposed for the cold fusion. The 0^+ assessment of spin and parity of this resonance makes forbidden its gamma decay to the ground state being also 0^+ in agreement with heavy-water electrolysis experiments where no gamma emission has been observed. Due to the single particle nature of this resonance, the neutron and proton decay channels should be negligible compared to the d+d partial width. Therefore, the decay of the resonance can only take place by non-radiative electromagnetic channels as the internal pair creation, the electron conversion or in the process we call the deuteron conversion where the energy excess of the compound nucleus ${}^4\text{He}$ of about 24 MeV will be transferred to a neighbouring deuteron. Decay probabilities of non-radiative channels leading to a direct fusion of ${}^4\text{He}$ in metallic environments will be discussed in a separated paper [19].

The small width of the supposed resonance would also explain the problems connected to the reproducibility of cold fusion experiments. Small local changes of the lattice structure can vary the resonance energy by a few eV due to alteration of the screening energy as already determined for alpha decays [17]. Thus, dependently on local crystal defects, the deuteron density and other target material parameters that are not usually controlled in the experiments, the ^4He fusion cross section can be resonant or not and consequently we could observe an enhanced production of helium by many orders of magnitude only at special material conditions.

5. Conclusions

We have shown that the electron screening effect plays a crucial role for room temperature nuclear reactions. The enhancement factor of the nuclear reactions due to electron screening is material dependent and reaches at room temperature for heavy metals a factor of about 10^{40} compared to the cross sections calculated for the gaseous deuterium [3]. The electron screening effect makes possible to observe experimentally also other reactions between hydrogen isotopes using an appropriate set-up (see Table 1). Contradictory to previous calculations, the $^2\text{H(d,n)}^3\text{He}$ and $^2\text{H(d,p)}^3\text{H}$ reactions should still have the largest cross sections at room temperature. The corresponding reaction rates are in agreement with small amounts of ^3H and ^3He found in the heavy-water electrolysis experiments.

Domination of the ^4He channel by a factor of about 10^7 over other open channels in experiments where a heat excess has been measured can be explained by a 0^+ single particle resonance placed in the compound nucleus very close to the reaction threshold. De-excitation of this resonance state should only take place by non-radiative electromagnetic channels that are very difficult to detect experimentally. Furthermore, an interplay between the electron screening effect that strength depends on local crystal structure of the target material and the resonance reaction mechanisms is able to clarify difficulties with regard to a bad reproducibility of the cold fusion experiments. Crystal defects or changes of local deuteron density can shift the resonance energy even by a few eV resulting in the non-resonant reaction mechanism and suppression of the ^4He fusion channel. Thus, controlling of the microscopic structure of target materials in future cold fusion experiments ought to be very important.

On the other hand, a material enabling large fusion rates at room temperature should also ensure a high deuteron density and a relatively low deuteron binding energy in the lattice. The latter condition is necessary in order to reach large deuteron mobility, which further increases the reaction probability by many orders of magnitude. Therefore, Pd still seems to be an ideal material for study nuclear reactions at room temperature.

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Investigation of Anomalous Densities of High-energy Alpha-Particles Tracks in CR-39 Detectors during Electrolysis of Heavy Water on Palladium Cathodes.

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Abstract. Recently, several researchers claim the finding of anomalous alpha-particles generation during very simple electrolysis experiments with heavy water and palladium cathodes. The phenomenon seems to improve if deuterium formation on the cathode is associated with deposition of palladium nanostructures coming from chlorides of the same metal present in the electrolytic solution. Due to the relevance of the claims and considered the simplicity of the experimental apparatus, several tests have been performed in order to confirm the claimed results. The results of these tests will be the object of this scientific report.

1. Introduction

Palladium is an element of Group X which has the peculiar characteristic to be extremely permeable to hydrogen; indeed, it is able to adsorb this gas up to 900 times its volume at room temperature. When adsorbed, the gas redistributes itself in the metal lattice, but it is not clear if this behavior is due to the formation of hydride or is only a temporary binding. The very high permeability to hydrogen (and its isotopes) is used in the industry to purify this gas with systems forcing it to flow through palladium membranes, which stop the impurities.

In 1989 M. Fleischmann and S. Pons reported the “strange” result of anomalous temperature rising measurements on an electrolytic cell with a palladium cathode. The electrolyte was LiOH in heavy water D₂O. The sensational impact of their claim was due to the fact that the entity of extra heat generated was not compatible with a chemical origin and consequently its source should be a nuclear reaction.

The concentration of H-D in palladium depends from the thermodynamic parameters; in the cathode, by effect of applied potential, concentration rises up prominently. This mechanism, named “loading”, is used to achieve the wanted thermodynamic non equilibrium in order to increase the deuterium concentration in the cathode, the necessary condition to have excess heat production. According to Fleischmann and Pons claim, the temperature raise, which were observed at high “loading” maintaining constant the applied power, would be explained invoking a nuclear mechanism in the metal lattice: D atoms reduce their relative distance, overcoming the electrostatic repulsion of the Coulomb barrier getting to nuclear fusion events. Palladium matrix should act as a sort of catalyst for the reaction. From 1989 many researchers, working both in civil and military field, began an experimental activity on these phenomena, indicated with the acronym LENR (low energy nuclear reactions). In particular, researchers tried to set up excess heat experiments, also varying the experimental embodiment; moreover, theoretical studies were developed to explain the mechanism of low temperature nuclear fusion. The attention was especially dedicated to the production of energetic particles and gamma radiation. In fact, their detection should be a clear clue that nuclear reactions were involved. Concerning particle emission, according the classical theory, during fusion a flux of them (alpha, neutron, gamma) has to be generated to carry almost a part of the energy produced. Unfortunately, many trials to detect them were unsuccessful. The prevalent opinion is that LENR does not produce the neutrons flux as for the standard model of this kind of reactions, even if it is hard to explain why. By the way, several scientists continued to look for neutron emission, but the results are not representative. Another research line was the detection of other corpuscular emission, based on the use of well known plastic detectors. Precise protocols are implemented for alpha particles in order to distinguish between the particles generated during the electrolysis and those normally present in the environment as by-product of Radon decay. Radon is a radioactive gas present in particular rocks. Many experiments were performed in the past and are going on to check for alpha emission during palladium loading using a plastic detector, called CR39 (Fig. 2). When a particle hits the detector, it breaks the polymer chains and the damage becomes visible by a chemical etch in NaOH solution. The etch rate depends on the

temperature of the bath. After etch, a small conical hole appears in correspondence of the incidence path of the particle having the geometrical axis direction depending from the incidence angle.



Fig. 1 - Experimental embodiment.



Fig. 2 – CR39 detector

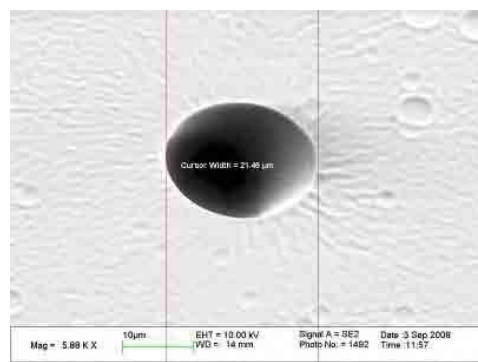


Fig. 3 - SEM photo of an alpha particle track after etch

2. Experimental Details

Two kinds of experiments were performed:

- Electrolysis of LiCl electrolyte in D2O;
- Codeposition of Pd on the cathode adding PdCl₂ in the solution. Effects of high and low electrolysis current densities were also tested;
- Comparison of all the test results with CR39 detectors placed in the same embodiment, but without electrolysis.

In the very simple embodiment (Fig. X) the electrolytic cell was a glass tube with an internal diameter of 9 mm having a flange to accommodate an O ring for sealing. Another identical glass tube, empty, was connected to the one with the electrolyte with interposed the CR39 plastic detector having a size 23mm x 35mm x 1.39 mm, produced by INTERCAST EUROPE. CR39 for nuclear measurement is very pure and without defects. The cathode was formed by a palladium wire (diameter 50 µm) fixed on sensible side of detector and between the cathode and CR39 a 11 µm Mylar foil was interposed to prevent the contact of the electrolyte with the detector; all the embodiment parts were fixed together by a metallic clamp. The cell was filled with 8 ml of 0.5 M LiCl/D2O solution. D2O used was undertaken at double distillation to assure its purity. Power supply was a current generator able to generate up to 3 A; voltage and current were continuously monitored by a digital multimeter. The current was incremented in step of 1 mA till 10 mA every 8 hours; at 10 mA the electrolysis went on from 3 to 10 days. To evaluate the counts two reference samples were prepared like experiment 1, 10 mA constant for three days, using only light water for electrolysis.

3. Etch

After any experiment, the detector development process to count the high energy tracks was performed in a NaOH 6.25 M solution, at a temperature of 70°C; the solution was contained in a beaker heated by an hot plate electronically controlled at ± 0.2 °C. The etching time was 6 hours. After the etch the detectors were rinsed in D.I. water, then neutralized in HCl diluted for 10 minutes and finally rinsed again in D. I. water and dried in a flux of filtered nitrogen gas.

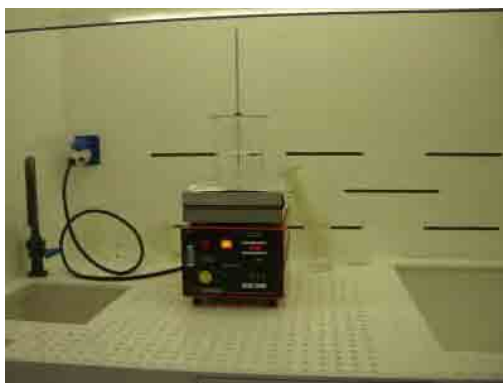


Fig. 4 - Heated etch bath (NaOH)

4. Track Analysis

The count track was performed using a system formed by a Leica binocular microscope in transmission configuration with a webcam and a PC running dedicated software for image acquisition. CR39 detectors were put on a plate with a hole 12 mm wide just to analyze detector area faced to the inner part of the cell during the electrolysis. To analyze the exposed area of 1.186 cm² 125 photos with 10x objective were taken.

The experiments using CR39 have the aim to demonstrate the existence of nuclear reaction inside the palladium cathode; because the “mark” of these reactions are particles emission, it is necessary that the number/density of them detected on CR39 after deuterium electrolysis are SIGNIFICANTLY higher than the same figures related, for instance, in absence of current flow or using light water. Moreover, because of the direct contact between the cathode and the detector, it is expected to detect a higher density over all in the detector area close to palladium cathode.

The results do not show a significant difference with respect to the detectors used as reference (light water). The Mylar film interposed between cathode and detector acts like a shield for particles with energy less than a specified value which depends on the film thickness. To evaluate the penetration thickness of the particle in Mylar the freeware software SRIM was used. This code calculates stopping power, projected range and other parameters for proton and alpha particles with energy up to 10 MeV. For Mylar 11 μ m thick used in the experiments the minimum energy for alpha particle to go across the film is 2.5 MeV. All particles less than 2.5 MeV are stopped. The absence of a significant increase of trace number on detector excludes particles emission with more than 2.5 MeV.



Fig. 5 - System for tracks count

Table 1. Track Density (cm⁻²)

Blank		Electrolysis	
# 1	189	# 1	222
2	154	# 2	296
		# 3	136
		# 4	112
		# 5	74

5. Experiment without MYLAR

In the specific literature, the first experiments based on the electrochemical loading and CR39 detectors were performed without any protection film between the detector and the electrolyte. The solution used was D2O with a small addition of palladium chloride salt (LiCl or LiSO₄); the possibility that during electrolysis a surface damage of the detector happened was not evidently taken into account.

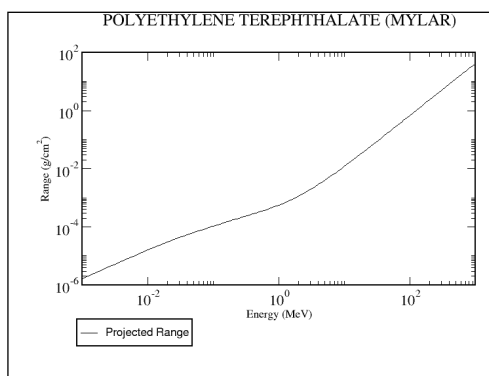


Fig. 6 - Stopping power curve for Mylar

Some researchers reported positive results in terms of high count of traces identified as particle emission from cathode just with experimental arrangements which did not use any interposed film. Comparing images of the reported traces with similar relative at radioactive emission from americium or uranium the difference is very evident. To investigate this point some experiments without Mylar were performed. After electrolysis, just to a naked eye detectors showed some milky and rough appearance; moreover, the area just in contact with palladium wire showed a marked white line. Optical microscope analysis highlighted the presence of many “balls” in coalescence each other; similar structures did not resemble at all with traces from nuclear particle. SEM analysis on some detectors confirmed this strong difference. The surface damage can be so caused from chemical etch of liquid on plastic surface.



Fig. 7 - Example of CR39 area count



Fig. 8 - Artifact on CR39 surface, without Mylar



Fig. 9 - Artifacts in CR39 area faced cathode, without Mylar protection

6. Codeposition Pd/D

Szpac and Mosier-Boss performed some experiments in which palladium, coming from palladium salt present in the solution, was codeposited on cathode together with deuterium gas generation with the purpose to have nanostructure of palladium on the cathode were the “loading” could reach an atomic D/Pd ratio close to 1. The same authors reported positive result concerning particle emission during electrolysis. To verify this claim, two trials of codeposition were performed, using as palladium source palladium chloride PdCl₂, added in the solution at 0.05 M, concentration. During these experiments two different procedures in increasing the electrolysis current were used. In trial A the starting current was 10 mA up to complete Pd deposition, then raised to 20 mA and maintained at this level for three days; in trial B the electrolysis started at low current – 0.6 mA – then maintained at this level until the palladium deposit on cathode was complete. In both cases it was possible to determine the end of palladium deposition by the solution color change from orange to transparent. So, for the experiment B the current was gradually raised up to 50 mA and the reaction went on for 7 – 10 days. The maximum current density was 0.5 A/cm² for experiment 1 and 5 A/cm² for experiment 2. At the end cell was disassembled and the detector etched in the chemical bath. In both experiments the Mylar foil was interposed.

Table 2. Codeposition Parameters

Exp. -A-		Exp. -B-	
10 mA	Pd dep.	0.6 mA	Pd dep.
20 mA	3 days	2 mA	1 day
		5 mA	1 day
		20 mA	3 days
		50 mA	2 days

7. Results

In the case of trial A after few hours a non uniform sponge-like palladium deposit was formed on the cathode; in trial B the deposit instead was very uniform and compact. Cathode of trial B, analyzed in a SEM, showed a globular structure (cauliflower type) plus palladium dendrites present over the entire active surface. Same results are reported from Szpac and Mosier Boss with a cell put in a strong electric field. Concerning trace count, no difference was found with respect to reference sample using light water.

For both the experiments an 11 microns thick Mylar foil was interposed between the cathode and the CR39 detector. At the end of the experiments the detectors have been treated as previously described and the cathode submitted to SEM analysis.

In Fig 10 it is shown a SEM image of the cathode surface where it is possible to observe the dendritic and globular structure of the deposited Pd. Similar structures are reported in [2]; moreover it is useful to notice that the dendritic structure, as reported in [2], should be present only in experiment where the cell is placed inside a strong electric field: no electric field was present in our experiments. The track count reported in Tab. 3, does not show significant differences compared with “blank” samples, neither with electrolysis experiments without Pd codeposition.

Table 3. Track Density (Codepos.)

Exp. -A-	113 tr./cm ²
Exp. -B-	146 tr./cm ²

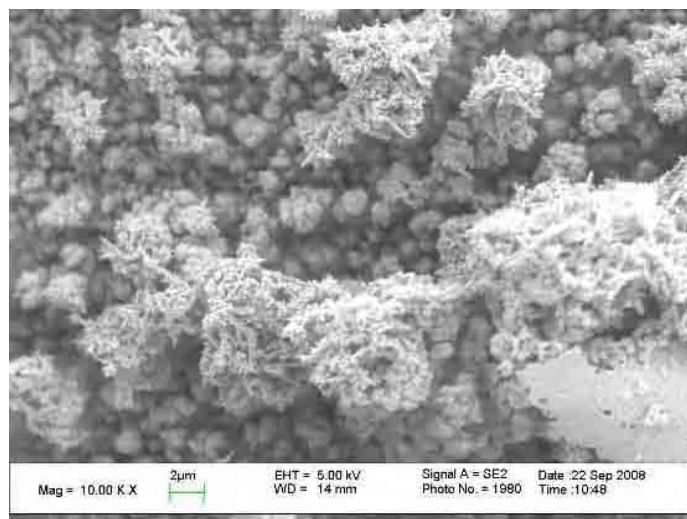


Fig. 10 - SEM photo of dendritic structures on the Pd cathode

8. Conclusions and acknowledgments

The experiments described above did not highlight a meaningful increase of Alfa particles nuclear tracks with energy greater than 2.5 MeV respect to the background of blank experiments, during electrolysis in heavy water with palladium cathodes. Same results came out also in experiments where palladium chloride salts were added to the electrolyte, in order to have nanostructures of Pd deposited on the cathode and increase deuterium loading in the Pd lattice. So, the outcomes of the experiments seem to confirm what is also reported in references [3] and [4].

A new series of test with simple electrolysis and codeposition is planned in the first part of the year 2010 using a different supplier for the CR39 detectors in order to reduce the background tracks level.

We are particularly grateful to Dr. P. Neri of INTERCAST EUROPE for the supply of CR39 detectors and Dr. F. Celani for the supply of heavy water and Pd cell cathode wires.

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Neutron Detection: Principles, Methods, Issues (and Tips)

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Abstract. The production and detection of neutrons in the so called “cold fusion” phenomena is claimed since the first announcement by Fleischmann and Pons in 1989. In the last twenty years the same claim has been made by other authors despite they were operating under different experimental conditions. However, most of the scientific community is yet sceptic about the actual emission of neutrons from events that in a more general statement are known as “low energy nuclear reactions in condensed matter” (CMNS) and the methods adopted by the various authors are often subjected to several criticisms. Indeed CMNS phenomena are rather complex and relate with several different subjects so synergy among various experts is necessary. Among these subjects, neutron detections requires a particular care and expertise because the measurements are carried out with a very low signal to noise ratio. In this paper a very brief review of the main physical laws and basic detection principles for neutrons are addressed. It is not in the author’s intention to investigate whether or not neutrons are actually emitted in CMNS phenomena, however, some tips that could allow to unambiguous measurement of neutrons from a CMNS type experiment will be addressed too.

1 Introduction

Since the first announcement by Fleischmann and Pons [1] and just after by Jones [2] and Scaramuzzi [3] who claimed the production and detection of 2.5 MeV neutrons from DD nuclear reactions produced by “*Electrochemically Induced Nuclear Fusion of Deuterium*”, the actual emission of neutrons from the so called “cold fusion” phenomena is a matter of discussion among the scientists.

In the last twenty years a great debate has arisen to establish whether or not neutrons are actually emitted and at which energy. Many authors attempted the neutron detection under experimental conditions often far different [4,5] from these discussed in [1-3]. The results were often contradictory and in some cases claim for detecting neutrons of higher energy were made [6,7]. On the other hands, some authors considering the “strange” and not reproducible results, suggested that from the so called “*low energy nuclear reactions in condensed matter*” (CMNS) phenomena, neutrons are not produced. Following these authors, the observed “anomalous” heat production is to be ascribed to nuclear reactions which led to the production of charged particles. However, recently in a attempt to measure such charged products some authors claimed they found 14 MeV neutrons [8].

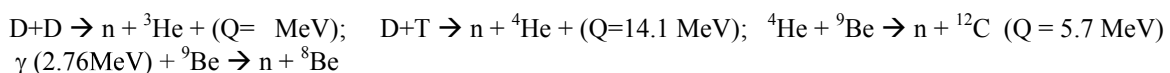
The above short story of “cold fusion” phenomena is far to be complete, but clearly points out that the question of whether neutrons are actually produced and at which energy is still open. More debating is the question “how” neutrons are produced. Even within the community working on CMNS there are different ideas. Indeed CMNS phenomena are rather complex and relate with several different subjects so synergy among them is necessary. Among these subjects, neutron detections requires a particular care and expertise because the measurements are carried out with a very low signal to noise ratio. It is not in the scope of this paper to review the various experiments nor to put specific questions or criticism to any of the papers available in the literature and reporting about neutron measurements from CMNS experiments. The present paper represents an attempt to clarify some basic aspects about the neutron physics and detection.

Last, but not least, in the author’s opinion time has come to try to measure neutrons in a CMNS experiment (if any) in unambiguous manner. This can be attained in a series of experiments where the detection of neutrons is detailed designed, carefully performed and repeated.

2 Neutron Sources

The neutron was discovered in 1932 by Chadwick and since the early days of its discovery the “strange and intriguing” properties of the neutron were studied with great interest by the physicists.

Neutrons can be produced by nuclear reactions. There are a number of reactions routinely used for producing neutrons, among them typical sources of neutrons are :



Since neutrons are neutral they are not sensitive to the coulomb barrier of the nucleus and thus can easily interact with them. The type and probability of interaction can be foreseen if the initial state of the nucleus and the energy of the neutron is known. Neutrons cannot be accelerate since they are neutral, but always they loose energy as soon as they interact with matter. This means that if *monoenergetic* neutrons of energy E_0 are produced, after moving in the surrounding material the neutrons will have a continuous spectrum ranging from the initial energy E_0 down to the thermal one (E_{th}).

3 Neutron Interactions

The neutron-matter interaction is depending upon the so-called cross-sections. The latter, for a given nucleus in a known initial state, depends upon the energy of the incoming neutron. The concept of “cross section” is familiar in the nuclear and atomic physics and relates with the “probability of occurrence of a certain process when a particle is interacting with another particle or nucleus. Strictly speaking the cross-section is not a probability but an area since it is measured in barn ($1 \text{ barn} = 10^{-24} \text{ cm}^2$). Physically the cross-section can be regarded as the area seen by the projectile when approaching the nucleus and to which “actually” it interact. The larger the area the larger the “probability” (cross section, σ) of a certain interaction. This concept can easily be explained by quantum physics if the incoming particle (the neutron in our case) is assumed to be a wave of probability [9,10]. As a consequence of the neutron-nucleus interaction there are many different “final” states, each one characterized by some “typical” reaction products. The j -th final state will have cross section σ_j , so we can define the total cross-section as the sum of the above different “final” states : $\sigma_{Tot} = \sum_j \sigma_j$. In this sense, if we consider the ratio $f_j = \sigma_j / \sigma_{Tot}$, f_j is the probability of having the reaction of type j .

σ_{Tot} is the so-called *microscopic* total cross-section which must not be confused with the *macroscopic* cross-section for a given material defined as $\Sigma = \sigma_{Tot} * N$ where N is the number of nuclei per unit volume. Σ is measured in cm^{-1} and $L = 1/\Sigma$ (cm) is the *mean free path* and gives the mean distance travelled in a medium by a neutron of a energy E before to produce an interaction.

The total cross-section can be divided into two broad families, the *elastic scattering* and the *NON-elastic* scattering cross sections, respectively. The latter comprises several different types of cross sections (Inelastic scattering, compound nucleus reactions or radiative capture, fission, charged product reactions, spallation, stripping etc.), each representing a specific type of n-nucleus interaction. The basic difference between these two broad families is in the neutron energy. Roughly speaking for energy lower than a 0.1 MeV the n-nucleus interaction is an elastic scattering. As soon as the neutron energy increases and reaches at least that of the first excited level of the target nucleus, inelastic scattering (that is one of the above mentioned reactions) can occur, each one with a probability defined by f_j .

The cross sections of the various nuclides as function of the neutron energy are available in a number of nuclear data libraries (e.g.[11]). From the analysis of some typical neutron cross-sections versus the neutron energy (Fig. 1), it can be seen that they behave in a rather standard mode but for a fixed neutron energy E_n the cross section value can be very different, depending upon the nucleus. Three different energy regions can be observed:

- 1) the $1/\sqrt{E_n}$ or $1/v$ region (v being the neutron velocity), in the very low energy part and up to 1-2 eV;
- 2) the *resonance region* from the eV region and up to ~ 10 keV;
- 3) the *high energy region* (>0.1 MeV).

The cross sections values at the thermal energy E_{th} (σ_{th} , where $E_{th} = 0.025 \text{ eV}$ at $T=300^\circ\text{K}$) depends upon the isotopes and can change of many order of magnitude. The σ_{th} values varies from 10^{-3} b for D and O up to 10^6 b for ^{135}Xe . At low (thermal) energy, the neutrons move slowly so, compared to “fast” neutrons they need a longer time to cross a nucleus so the probability to be captured is higher for thermal neutrons than for the fast ones. On the other hands, the scattering cross-section at the thermal energy results of the same order of magnitude for all the nuclides. The latter fact can be intuitively explained considering the scattering between the neutron and the nucleus similar to that occurring between two rigid spheres. In this case the scattering cross section σ_s is proportional to the nucleus cross section area πR^2 , R being the nucleus radius which in turn is given by $R = r_0 A^{1/3}$ where A is the atomic mass and $r_0 \approx 1.5 \cdot 10^{-13} \text{ cm}$. Indeed, the elastic scattering cross section is slightly varying with the neutron energy for most of the nuclei.

The neutron cross section behaviour can be explained in a rigorous mode by quantum mechanics (e.g. [9]).

3.1 Prompt and delayed Gamma-Rays

A peculiar aspect of the neutron-matter interaction is the production of the so called “*mixed n- γ field*” in which the neutrons and gammas are simultaneously present. The measurement of this mixed field represents a possible approach to demonstrate the neutron production in physical phenomena. Since gammas are *always* produced by

neutrons, if neutrons are measured but no gammas are observed (both during and after the neutron emission), caution is mandatory before to claim that a neutron emission was actually observed.

It is fundamental to distinguish between two classes of gammas emitted from a medium interacting with neutrons: *a)* prompt gamma-rays; *b)* delayed (or activation) gamma rays.

The *prompt gamma-rays* are those emitted in “real-time” whilst the neutrons are moving and producing n-nucleus interaction (e.g. inelastic scattering). The n-interactions excite the nuclei which decay by emitting gammas in a very short time (10^{-14} sec, so the name *prompt*). The prompt gamma-rays energy spectrum range from a few hundred of keV up to 15 MeV and even more, depending upon the nucleus.

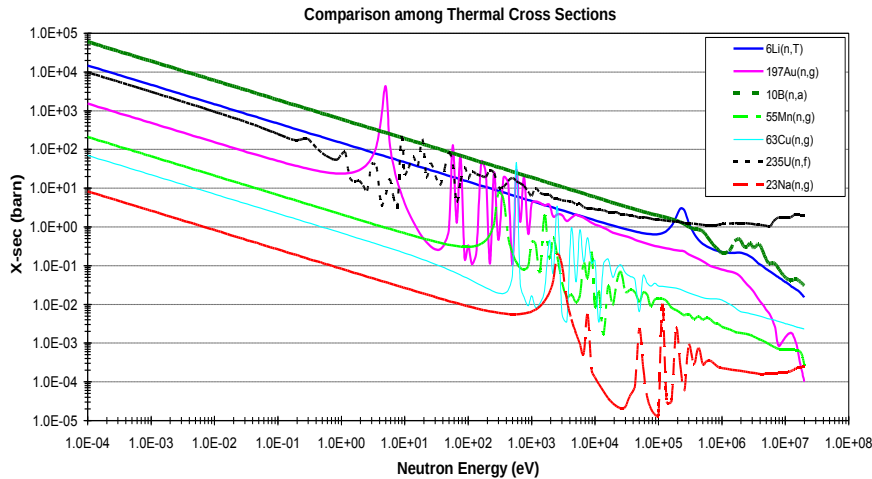


Fig. 1. - Cross-section versus neutron energy for some materials.

It is important to stress that the prompt gamma-ray emission is observed at any neutron energy and the energy of the emitted gammas can be neutron energy dependent. The latter property is used for performing elemental analysis by prompt gamma ray neutron activation analysis (PGNAA). PGNAA can also be used to measure the intensity and the energy (by analyzing the gamma-ray lines) of the neutron source.

The *delayed gamma-rays* are emitted by the excited states of the neutron activated materials which in turn are produced by the (n,x) nuclear reactions (here x means, n', p, d, α etc.). These excited states decay by alphas and/or betas (some time directly by gammas, this is the *isomeric transition*) but the daughter nuclei are still excited and usually decay by emitting one or more gammas of energy ranging from a few tens of keV up to 3 (or more) MeV. The delay time also known as decay time, can be very variable. Again from the produced gamma-ray lines it is possible to know the energy of the neutron source and also its intensity. The detection of the “activation” products is the most direct and safe method to demonstrate that neutrons have been actually produced.

The prompt as well as the delayed gamma-ray emission can be foreseen for each nuclide provided that the energy of the neutron is known. Libraries of nuclear data are available for this purpose (e.g.[11]).

4 Neutron Detection

The detection of neutrons can be attained by considering their interactions with matter. As already explained the n-matter interaction depends upon the neutron energy so we must expect that there are different type of detectors at different neutron energies. Always a neutron is detected using an in-direct method, that is thanks to the conversion of a neutron into something else, so we will detect gammas or charged particles. The conversion process is produced inside the “detecting” medium which not necessarily is the detector.

Among the many detectors developed so far to measure the neutrons (see e.g. [12]), we can distinguish two broad families: *a)* active detectors, *b)* passive detector.

Are considered active the detectors that need an external bias for operating (e.g. fission chambers, scintillators, ionization chambers, Geiger-Muller etc.). It is also important to distinguish between detectors operating in pulse or in current mode. The first type is recommended for sources emitting burst of neutrons. The current mode is suggested for long lasting neutron emissions but also for high (and some time low) intensity sources. When close to the neutron source and or to the detector are present sources of EM radiation caution is necessary and shielding is strongly suggested. Proper shielding is also requested for the cables that can act as antenna. Screened or super-screened cable are recommended.

The passive detectors instead, do not need any external biasing (e.g. thermoluminescent detectors, activation foils, CR-39 etc.) even if internal junctions are possible. The use of passive detectors require other type of cautions specific for each detector. For example, thermoluminescent dosimeters usually do not withstand high temperature

and require an accurate background dose measurement with long lasting exposure. CR-39 must not be exposed to sun or heated as well and must be handled with care since any surface damaging can result in a wrong track. Their response can also be enhanced by using a thin layer of plastic to produce recoil protons or other charged particles. The most simple detectors to be used are the activation foils for which a few recommendation are mandatory the main being to avoid contamination (to be cleaned before the experiment) or exposition to neutron sources before the experiment.

Basing upon the claimed results, the detection of neutrons in a CMNS experiments consists basically in a short-lasting neutron emission that typically starts suddenly, as a burst. The claimed level of the neutron emission is very variable from a few counts up to many hundreds so pulse detectors seem appropriate although the count rate can be very low. Assuming, as working hypothesis, the neutrons to be emitted from a DD reactions, neutrons will have an energy of about 2.5 MeV so almost all the detectors above mentioned can be used to detect them.

A problem is represented by the need to separate the background from the “true” signal especially if the counts are just a few. Under these circumstances it seems also difficult to perform the spectrometry since the statistics is an important aspect of the latter measurements. The measurement of the background prior the experiment is mandatory, but the background must be also measured after the end of the experiment to verify that no changes in the environments have happened in the meantime. Whether possible the spectrometry of the background radiation must be performed. Both n and γ background must be measured.

Due the many problems envisaged in the past in the CMNS experiments and also accounting for the many criticisms it is suggest to use a redundant array of different type of detectors rather than to use a single detector. The simultaneous signature of the various detectors will guarantee about the neutron (and gamma) emission.

Active detectors such as fission chambers or scintillators of large sensitive volume, seem more appropriate since allow also for the measurement of the time dependent neutron emission that can help in the analysis of the physical problem. To enhance the response of the detectors (e.g. fission chambers, H₃-tube, Li-6 covered or coated detectors) the neutrons can be slowed down by using a few centimetres of moderators (e.g. polyethylene) located in front of the detector or all around the neutron source.

Another important point is the simultaneous detection of neutrons and prompt gammas by coupling the neutron detectors with some gamma detectors (in this case γ -spectrometry is also feasible). Some materials such as H, emits typical prompt gamma-rays (2.2 MeV for H) so their detection can be a further and independent proof of the neutron emission.

It ought to be stressed that instrumentation borrowed from the health physicist usually is not recommended for this type of measurements since most of this instrumentation have low sensitivity (and high sensitivity for both type of radiation is needed), are not very fast since usually measure the “level” of radiation and also cover a very large energy and sensitivity range but their response can be too slow.

Another measurement that is always possible is that of the “activation” products due to neutrons emission. In this case some activation foils (e.g. Au, In) can be used. To increase the sensitivity large surfaces and several grams of materials must be used and the foils must wrapped inside a moderator (polyethylene) or can also be introduced in the aqueous solution. To increase the signal to noise ratio the measurements should be carried out in a “low background” laboratory.

If Pd or Ti plates are used as electrodes in a CMNS experiment, it is expected that some (low) activation is also present in these materials. Ti reacts both with fast and thermal neutrons while Pd only with thermal neutrons. Both natural Ti and Pd are a mixture of several isotopes and almost all of them react with neutrons. The characteristic gamma-ray lines can be detected by a spectroscopic apparatus (e.g. using a Germanium detector). A calibration before the experiment is suggested using plates made with the same material and irradiated in a reference neutron flux, in order to study both the γ -ray spectra for a comparison and in case to get a quantitative analysis of the neutron production in the CMNS experiment.

5 Monte Carlo simulation of a CMNS experiment

To better understand the issues to be faced in a CMNS experiment when attempting to measure the neutron emission a simulation of a “typical” experiment was performed by using the Monte Carlo code MCNP.

The model is reported in Fig.2. A glass cylinder (2 mm thick) is filled with water and it is containing a neutron source. The detector is at a fixed distance from the source and the system is housed in a concrete box with walls and roof having the same thickness (15 cm) while the floor is more thick (30 cm). The neutron source is at 1m from the floor while the dimensions of the concrete box are 4x4x6 m³.

By changing the dimensions (radius) of the glass cylinder (and thus the quantity of water contained in it) as well as the energy of the neutron source (DD and DT neutrons), the neutron and gamma spectra in a region simulating the detector and located next to the cylinder (see picture) are calculated. The detector is a cylinder of air and its distance from the centre of the neutron source is kept constant as the cylinder radius changes.

5.1 Results of the simulation

The calculation was performed using two neutron source energies: $E_{DD} = 2.5$ MeV and $E_{DT} = 14$ MeV. A second calculation was run enveloping the water cylinder in a second cylinder made of stainless steel (SS) 1 cm thick. The SS cylinder in some papers was used as “electromagnetic” shield but the use of shields made of Al or μ -metal, is suggested when using (variable) magnetic fields. This shield will have an impact also on the neutron and gamma emission and must be accounted for.

In Fig. 3 the neutron spectra calculated at the detector position are shown. The calculations were performed for three different radii of the glass cylinder: $R = 1.0$; 2.5 and 5.0 cm respectively. Fig. 3 shows the effect of the increasing radius on the calculated neutron spectrum at the detector location. As the water thickness increases the neutron spectrum enlarges. For $R = 5$ cm, the typical tail at the low energy part of the spectrum is visible as well as the thermal peak. It is interesting to note that the neutron background spectrum and intensity do not change very much. For comparison the neutron spectrum due to DT neutrons is also reported.

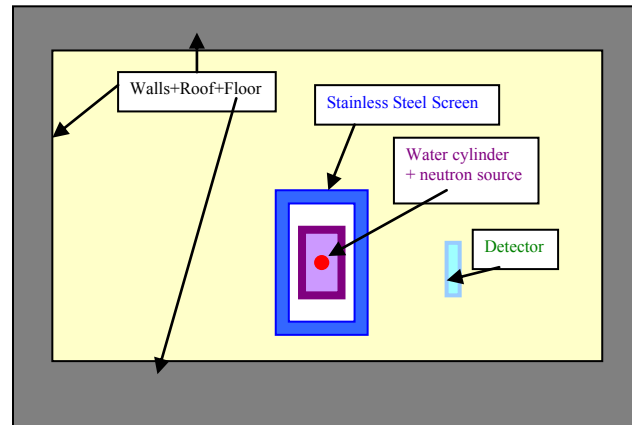


Fig. 2. - MCNP Model of a CMNS experiment

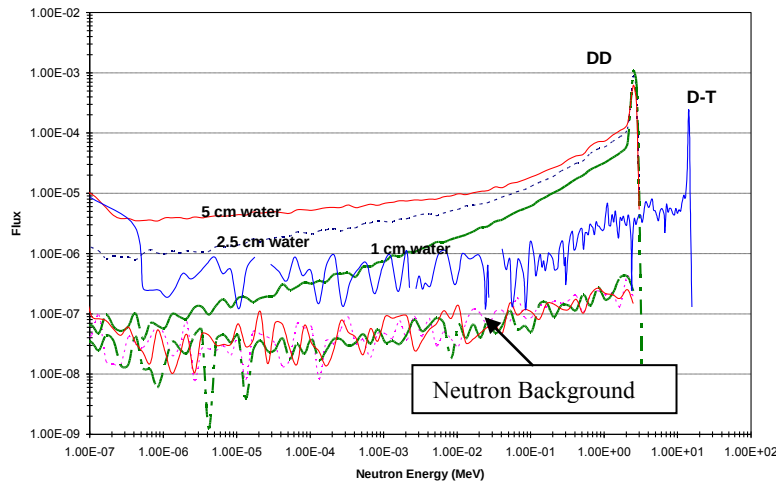


Fig. 3. - Calculated neutron spectra as a function of the Radius R at the detector's position

In Fig. 4 the prompt gamma-ray spectra calculated for the DD source are reported together with the spectrum calculated for the case of the SS cylinder enveloping the neutron source. The effect of higher neutron energy (DT source) on the “prompt” gamma-ray spectrum is shown too. The above results point out several important facts:

- The neutron spectrum depends upon the neutron source energy and the amount and type of material surrounding it. The background, due to wall return effects, depends mainly on the geometry of the system (source-walls distance).
- Any material interposed between the neutron source and the detector can affect the “shape” of the neutron spectra as well as will modify the spectrum of the prompt gammas.
- The “prompt” gamma-ray spectrum depends upon the neutron energy.

d) Walls, roof and floor always contribute to the total response via scattered neutrons (and gammas). A more general statement is that any material and structure surrounding the source affects the detector's response.

6 Tips for unambiguous neutron detection in a CMNS experiment

The above discussion, together with the short notes reported on the neutron detection, allows us to summarize the discussion and to give a few suggestions and tips for unambiguous detection of neutrons that indeed, is what is still requested to a CMNS experiment.

To be unambiguous neutron detection must provide a clear and not questionable signature of the event. For this reason a simple but affordable system is suggested. The detectors should have a large volume to increase the detection efficiency (but also the background is increased), operate in pulse mode and over all be based upon different principia. So fission chambers can be coupled with scintillators as well as with activation foils. Scintillator can simultaneously measure and discriminate neutrons and gammas provided that a proper discriminating electronics is set-up. Calibration is also needed for all the detectors both with respect the energy and whether possible efficiency. The "neutron source" can be enveloped by a moderator in order to slow-down neutrons and enhance the response of the used detectors (some scintillators, e.g. NE-422, are sensible to slow neutrons, while NE-213 is sensible to high energy neutrons (> 1 MeV)). Since the neutron emission is expected in the range of some MeV a few centimetres (3-5) of polyethylene can be sufficient. Activation of ^{197}Au , ^{109}Ag or ^{113}In which are sensible to thermal neutrons and have a relative short activation time is possible. The use of short life nuclides is suggested for activation since the expected neutron fluences are not too high.

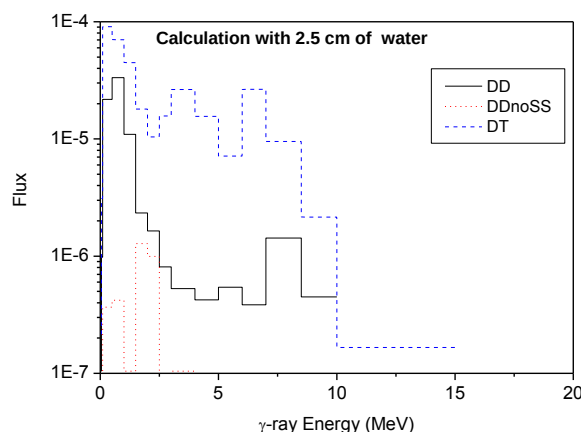


Fig. 4. - Prompt gamma-ray spectra calculated for a DD neutron source also enveloped in a SS shield. The prompt gamma-ray spectrum obtained with DT neutrons is also reported for comparison.

A detector based on ^{109}Ag can be particularly suited for a CMNS experiment since it allows for neutron activation to be detected, its short half-life (about 24 sec) β -decay can be efficiently measured by a beta counter (e.g. a simple Geiger-Muller tube) so following the decay curve. This instrument will give a double, independent and unambiguous signature of a neutron activation. The advantage is that the activation is not influenced by any possible external EM noise or field while the measured activation will follow a well known decay curve. Last, but not least, the measurements must be repeated and the results reproducible.

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Search for Nuclear Reaction Products in Gas Phase Experiments – Deuterium Permeation and Absorption –

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Abstract. Employing both *in situ* and *ex situ* accelerator analyses, we have attempted to replicate the Iwamura-type nuclear transmutation of Sr to Mo under deuterium permeation through a variety of multilayered CaO/Sr/Pd samples. Apparently positive results have been obtained in 8 of 14 runs, although the identification of Mo peaks in the PIXE analysis is not definite. It is implied that sputtering loss of the atoms could be responsible for the observed tendency that the areal density of Sr decreases in most cases, while there are modest increases in Mo. In addition to the accelerator analyses, γ -ray detection has been tried for samples implanted with W atoms in expectation of transmutation from ¹⁸³W to radioactive ¹⁹¹Pt.

In another series of experiments, we examined heat and ⁴He generation by deuterium absorption in nano-sized Pd powders, as reported by Arata and Zhang. In order to determine the cause of the large isotope effects observed, nuclear ash including charged particles, neutrons and gamma rays was examined.

1. Introduction

Iwamura *et al.* claimed [1] that nuclear transmutation occurs during forced permeation of deuterium (D) through multi-layered films of X/CaO/Pd, with X being the element to be transmuted, *e.g.*, ¹³³Cs transmuted to ¹⁴¹Pr, ⁸⁸Sr to ⁹⁶Mo, etc. We have attempted to replicate the transmutation using a modified exposure system to enable *in situ* characterization of the sample, which was installed at the end of a beam line of a tandem electrostatic accelerator 5SDH2. In addition to this system with a reversed flow direction, a stand-alone D permeation system was used to examine the phenomenon by *ex situ* PIXE analysis. The results have been presented in ref. [2], and are briefly summarized in the present paper.

Arata and Zhang recently reported [3] that highly pure D₂ gas charging of Pd nano-powders in the form of Pd-ZrO₂ nano-composite induced significantly higher temperatures inside the reactor vessel than on the outside wall for more than 50 hours, while runs with H₂ gas showed almost no temperature difference. To verify that the excess heat originated in a nuclear process, a QMS was employed to show the existence of ⁴He as nuclear ash in the vessel and in the powder after the charging. The charging system is a sophisticated, yet simplified, version of the previous-generation DS reactor [4]. Replication experiments using systems similar to the DS reactor with Pd-black seem to be successful [5,6].

However, few reports on replication experiments producing heat and ⁴He with the new configuration have been published in spite of the extreme importance of the phenomenon. It is crucial to confirm the phenomenon of heat and ⁴He generation with fully quantitative reliability.

We have initiated our own replication experiments to confirm the phenomenon and to investigate the underlying physics. We have reported the first results of deuterium/hydrogen absorption and accompanying heat generation in ref. [7-11], where an anomalously large absorption energy and isotope effects were found. In the latter half of the present paper, a description of our efforts to detect possible nuclear reaction products is given.

2. Deuterium permeation experiments

2.1 Summary of PIXE analysis

We have tried to replicate the nuclear transmutation of Sr ($2 - 50 \times 10^{15} \text{ cm}^{-2}$) to Mo under deuterium permeation through a variety of multilayered samples; (v)/M_n/CaO/Sr/Pd/(D₂), (v)/Pd/M_n/CaO/Sr/Pd/(D₂), (v)/Sr/Pd/CaO/Pd/(D₂), and (v)/Pd/CaO/Sr/Pd/(D₂), where (v) stands for vacuum and “M” for a layer of CaO(18nm)/Sr/Pd(22nm). The D flow rate was 0.03 – 0.6 sccm, and the fluence was $0.1 - 2 \times 10^{23} \text{ cm}^{-2}$. The deuterium loading reached 0.86 for the sample (v)/Pd/M₉/CaO/Sr/Pd/(D₂), and the areal densities of Mo were $0 - 4.7 \times 10^{15} \text{ cm}^{-2}$. Apparently positive results were obtained in 8 of 14 runs, although the identification of Mo peaks in the PIXE analysis was not definite.

A tendency has been observed, however, for the areal density of Sr to decrease in most cases, while there are modest increases in that of Mo. Figure 1 shows the areal densities of Sr and Mo atoms as a function of time, or equivalently the deuterium fluence. In the former the density values are normalized to the initial values to show that almost all samples have decreasing density of Sr, while the absolute values are plotted in the latter. Although some samples have contaminant Mo atoms inherently, most samples show increasing density of Mo.

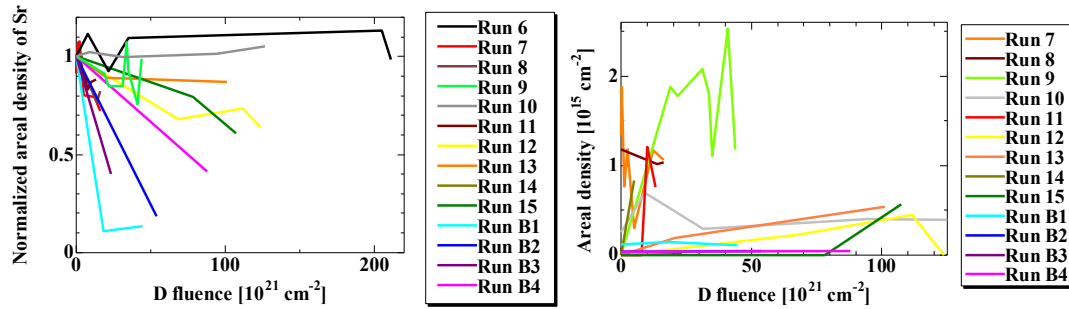


Fig. 1. - Temporal variation of areal densities of Sr (left) and Mo (right).

These results imply that sputtering loss of the atoms by 3-MeV protons and/or 4-MeV ⁴He used for PIXE and ERDA analyses could be responsible for these changes. Although a simulation program ACAT has shown that the contribution of sputtering to the decrease would be 2 orders of magnitude smaller than the decrease observed, the sputtering yield for deposited atoms weakly bonded to the bulk atoms should be much larger than the bulk atoms. This could account for the decrease in areal densities of Sr and Mo, which could result in the apparently smaller transmutation yield.

2.2 Radioactivity measurement

If the transmutation product is a radioisotope, detection will be much easier. If we assume the regularity of transformation that the atomic number and the mass number increase by 4 and 8, respectively, we can expect, for example, a production of ¹⁹¹Pt (emitting 0.538-MeV γ rays with a half life of 2.86 d) from ¹⁸³W. We prepared samples with a structure (V)/Pd/CaO/W/Pd/(D₂). The thickness of the first Pd layer and the second CaO layer were 38 nm and 2 nm, respectively. The tungsten atoms were introduced into the samples by implantation with 380-keV W⁺⁺ ions accelerated by the tandem Pelletron 5SDH2, and were expected to be distributed at a depth of 40 nm with a range straggling of 16 nm.

Gamma ray measurements were performed with an NaI(Tl) scintillation probe during permeation, and an HPGe detector after finishing the permeation. Unfortunately, we were statistically unable to find the 0.538-MeV γ ray peak in the spectra. This means that the areal density of ¹⁹¹Pt was below 10^7 cm^{-2} .

3. Absorption experiments

3.1 Experimental apparatus

Among possible nuclear reaction products, neutrons and γ rays are detectable outside the gas absorption chamber. During the absorption runs using the A₁-A₂ system, these were simultaneously monitored with a BF₃ neutron dose rate meter and a scintillation probe, respectively [7-9]. The radioactivity of some samples after the absorption runs was also measured using an imaging plate. However, we have not succeeded in finding meaningful signals in these measurements.

X rays and charged particles have a mean free path or a range too small to allow measurements outside the chamber wall. An experimental system shown schematically in Fig. 2 was prepared for charged particle measurements independently of the A₁-A₂ heat measurement system. A solid state detector, a Si surface barrier detector (SSBD) or an ion implanted Si detector (IISD), is located inside the reaction chamber containing a sample holder on which several tens of milligrams of the Pd-Zr oxide complex samples are mounted. A sheath heater is wound around the holder for sample baking, and the holder temperature is measured with an alumel-chromel thermocouple attached on the side of the holder. During the sample baking a retractable shield plate is inserted between the sample and the SSBD/IISD to avoid its deterioration by heating. Energy calibration of the SSBD/IISD is done with use of an ²⁴¹Am checking source placed on the retractable shield. During the calibration and before deuterium absorption runs, the chamber is evacuated with a TMP-diaphragm pumping kit. The deuterium gas is introduced into the reaction chamber through a liquid nitrogen cold trap and a “SuperNEEDLE” valve which enables precise control of the gas flow rate mechanically.

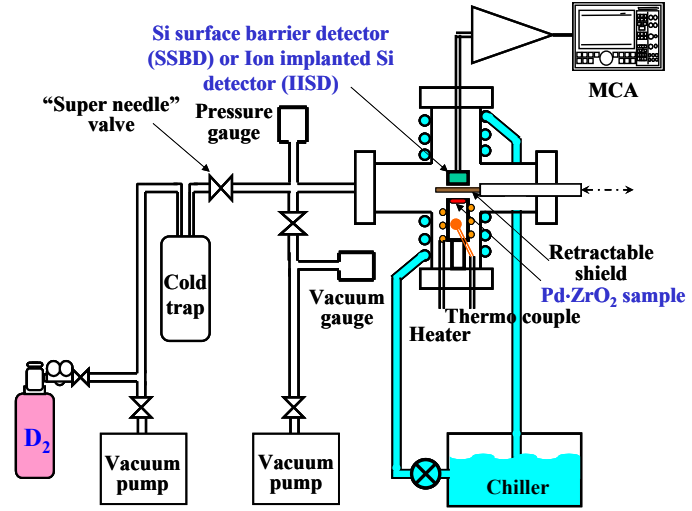


Fig. 2. - Schematic of the system B for particle measurement.

3.2 Examples of the measurement

In the initial stage of this study, we used an SSBD with a depletion layer thickness of 200 μm and the used sample PZ1. The energy spectra recorded during a 5-day run D-PZ1#3B through D-PZ1#4B and evolution of the counting are shown in Fig. 3(a) and (b), respectively. Here, the run number following “#” is advanced for every run after each gasfill-evacuation cycle, while the number preceding “#” is advanced for every new piece of the sample PZ (Pd-ZrO₂).

We see several counts in the energy range from 2 to 4 MeV and a few counts at 7 - 9 MeV. Although these could be caused by charged particles, we cannot rule out the possibility that these are due to electronic noise induced by mechanical shock or oscillation. It is shown in Fig.3(b) that these counting increased during phases of pressure change. Although it is fascinating to imagine that some nuclear events are occurring when

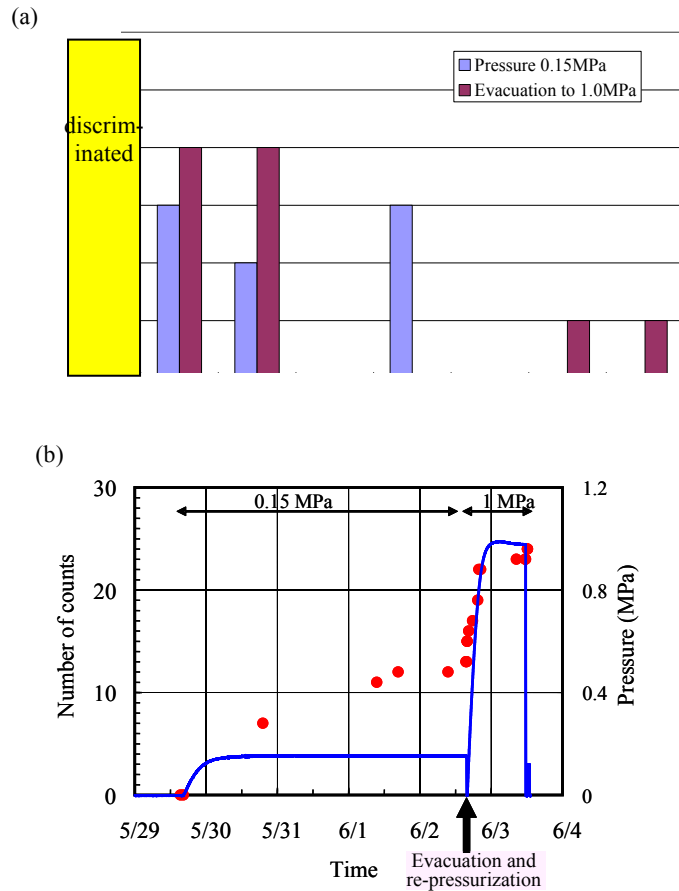


Fig. 3. - (a) Spectra recorded by SSBD with a 200- μm -thick depletion layer, and (b) Evolution of counting in the “1-12 MeV” range of the spectra measured by the SSBD during the run D-PZ1#3B through D-PZ1#4B.

deuterium atoms flow into/out of the Pd lattice, we cannot draw such a conclusion at present.

It is known that any SSBD suffers from deterioration or breakdown when it is used in a hydrogen atmosphere. The output pulse height from the SSBD used in the run D-PZ1#3B through D-PZ1#4B was reduced by a factor of about 30% and the FWHM increased by a factor of about 5. Although the deteriorated characteristics was stabilized after the initial use for several hundred hours, it was better to abandon it in the succeeding runs using virgin samples. We used an IISD with a depletion layer thickness of 500 μm which is known to endure use in a hydrogen atmosphere.

Figure 4(a) and (b) show the energy spectra and evolution of pressure and counting of the IISD and other radiations monitored outside the reaction chamber during the runs D-PZ14#1B (blue), D-PZ15#1B through D-PZ15#2B (red). The broken line in (a) shows the spectrum of ^{241}Am - α particles used for energy calibration of the detectors. We observe several tens of counts in the energy range 2 - 5 MeV in these runs. In (b) the IISD countings are integrated over the runs D-PZ14#1B, D-PZ15#1B-2B, and the baking period. They are reset between the operations.

The integrated IISD counting increased during the baking period between D-PZ14#1B and D-PZ15#1B, which is due largely (85%) to signals lying in the energy range 4.7 - 5.6 MeV. This indicates that the upper surface of the retractable shield plate has a contamination of ^{241}Am . It was found that the active surface of the IISD could see the contamination spot in case of insufficient retraction of the shield plate during the runs. This can account for the increase in the counting also during the runs D-PZ14#1B and D-PZ15#1B-2B.

As shown in Fig. 4(a), the spectra during these runs are a little different from that of the ^{241}Am - α particles, which is also implied by the difference between the counting in the energy range 1 - 8 MeV and that in the range 4.7 - 5.6 MeV. The energy shift of the ^{241}Am - α particles by about 0.8 MeV is consistent with the energy loss of 5.486-MeV α -particles in a 5 mm-MPa hydrogen gas. We see again, however, a tendency that the counting increases during the phase of pressure change. It could be possible that the signals lying in the energy range 2.0 - 4.5 MeV originate in charged particles emitted through some nuclear phenomenon in the sample.

Finally, it is noted that we observed no increases in the signals of neutrons and gamma rays.

3.3 Summary of charged particle measurements in gas charging system

We have observed several to several tens of counts in the 1 - 10 MeV range, which appeared to be emitted coincidentally with pressure change. However, we cannot rule out the possibility that they are due to electronic noise or contamination of ^{241}Am . Up to now, we have obtained no firm evidence of charged particle emission. We are planning detection of X-rays as another candidate for the reaction products.

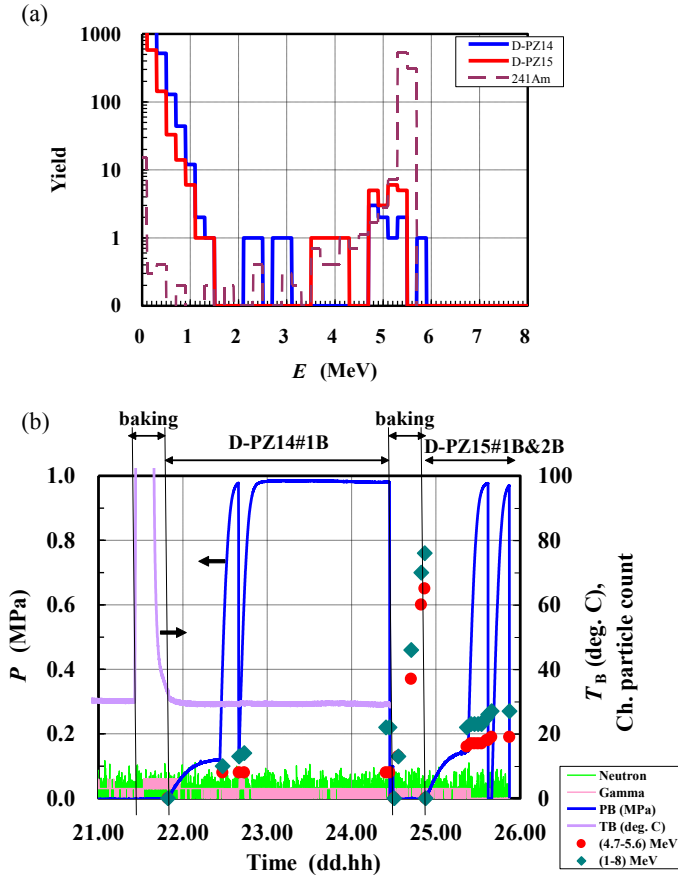


Fig. 4. - (a) Spectra recorded by the IISD with a 500- μm -thick depletion layer, (b) Evolution of pressure and IISD counting and other radiations during the runs D-PZ14#1B through D-PZ15#2B.

4. Concluding Remarks

Employing both *in situ* and *ex situ* accelerator analyses, we have attempted to replicate the Iwamura-type nuclear transmutation of Sr to Mo under deuterium permeation through a variety of multilayered CaO/Sr/Pd samples. Apparently positive results have been obtained in 8 of 14 runs, although the identification of Mo peaks in the PIXE analysis is not definite. It is implied that sputtering loss of the atoms could be responsible for the observed tendency that the areal density of Sr decreases in most cases, while there are modest increases in Mo. Gamma ray measurement for samples implanted with W atoms has also been performed in expectation of transmutation from ^{183}W to radioactive ^{191}Pt , but we have not yet obtained positive results.

In deuterium absorption experiments of Pd-Zr oxide nanopowders, detection of possible nuclear ash including charged particles in addition to neutrons and gamma rays has been examined. We have observed several to several tens of counts in the 1 - 10 MeV range, which appeared to be emitted coincidentally with pressure change. However, we cannot rule out the possibility that they are due to electronic noise or contamination of ^{241}Am . Up to now, we have obtained no firm evidence of charged particle emission.

In both of the above measurements, one of the problems is that the signal-to-noise ratio is rather small. If any nuclear reaction is occurring in the former experiments, it is necessary to find a way to increase the reaction rate not only from a detection point of view but also from a practical application point of view. In the latter, if any nuclear reaction emitting charged particles is responsible for the anomalous heat evolution, it should be possible to detect millions of charged particles. We need further study to look for the conditions suitable for such a reaction and its detection techniques.

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Impurity Measurements by Instrumental Neutron Activation Analysis on Palladium, Nickel and Copper Thin Films

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Abstract. Nowadays, the main cold fusion experiments are performed during electrolysis processes onto palladium, nickel and copper thin films. In studies devoted to verify the nuclei formation during these tests, a specific research activity has been developed at ENEA Research Centers: different experiments were set up for verifying and testing the data present in literature. Each step of the procedure has been analyzed and deeply investigated: the materials such as electrolysis equipments, electrolytic solutions, electrodes, etc. were preliminarily analyzed by Instrumental Neutron Activation Analysis (INAA) for identifying and reducing all the pollution sources.

Successively, different experiments were performed using films of palladium, nickel and copper as electrodes. At the end of each test, all the materials and the electrolytic solutions used and the blank as well, were analyzed by INAA for checking and measuring the presence of nuclei originating from nuclear transmutations.

1. Introduction

Some abnormal electrochemical facts have long been known to the scientific community, not related to the chemical phenomena occurring during the electrolysis: unexpected excess of heat and X-ray emission. The possibility of obtaining more heat than that generated by electrochemical reactions, was shown by Fleischmann and Pons in 1989 [1]. After, Jones [2] considered the possibility of cold fusion reaction p/D taking place in the lattice of a metal at temperature slightly above ambient temperature, cold compared to peak thermonuclear fusion temperatures (10^8 K) [3].

While there are clear evidences [4-7] on excess heat not justified through electrochemical reactions, there is less clearness, but still high uncertainty about the other related phenomena such as neutron production [3,8], ^4He production [5,7,9], tritium production [10-12], nuclear ash formation [13-16].

Because these possibilities are just random, sporadic, of low intensity and not related to each other, it should be considered the X-ray emission and the production of new species from nuclear transmutation reactions occurring during the experiments. Our attention is addressed to this second task for understanding what may actually happen in condensed matter.

Some authors [13,14] stated that after electrolysis experiments on mono- or multi-layered thin films of Pd and Ni, performed using both light and heavy water and various electrolytes (e.g., Na_2CO_3 or LiOH), new atomic species may be observed in condensed matter. According to these authors, some of the observed species are present at low levels and cannot be regarded as impurities, but real nuclear transmutation products. Some other authors reported the observations of new atomic species hypothesizing their production by nuclear transmutations in condensed matter during electrolysis experiments on mono- and multi-layered thin-films [16].

The main critical point of this approach is the contamination levels of the single components used during the electrolysis process. For these reason we set up some experiments analyzing the electrodes with relative blanks and the electrolytic solutions with relative standards by the Instrumental Neutron Activation Analysis (INAA). Preliminarily, some candidate materials have been undergone to INAA, discarding those without minimum impurities content; after, the blanks (i.e., electrodes and electrolytes) and the electrodes and operated electrolytes exhausted, were analyzed.

From the analytical point of view, the INAA was chosen because it is a non destructive analytical method (i.e., all samples can be stored and analyzed again) and highly sensitive (very low limit of detection, LOD, high sensitivity and high precision) (table 1), is a bulk method (INAA is an analytical technique that allows to analyze the entire mass of the sample) [17], permits the determination in the same sample up to 50-60 elements with no chemical sample manipulations (no errors due to excess contamination, positive artifacts, or down due to loss of material, negative artifacts).

Table 1. Nuclear data (radioisotope, cross section, half-life, peak energy and limit of detection) of the elements investigated in this study (a: calculated according to ref. 18; h: hour; m: minute, d: day; y: year).

Element	Product nuclide	Cross Section [19] (barn)	Half life		γ -Ray used (keV)	LOD ^a (ng)
Ag	¹⁰⁸ Ag	35	2.41	m	632.9	0.1
Ag	^{110m} Ag	37.2	250.4	d	657.7	
Al	²⁸ Al	0.232	2.246	m	1778.8	30
As	⁷⁶ As	4.3	26.3	h	559.2	0.001
Au	¹⁹⁸ Au	98.8	2.70	d	411.8	6×10 ⁻⁵
Br	⁸⁰ Br	8.5	17.4	m	617.0	0.002
Br	⁸² Br	2.69	1.47	d	776.5	
Cl	³⁸ Cl	0.428	37.2	m	1642.4	2
Co	⁶⁰ Co	37.2	5.272	y	1332.5	0.06
Cr	⁵¹ Cr	15.9	27.7	d	320.0	0.1
Cu	⁶⁴ Cu	4.5	12.74	h	1345.8	
Cu	⁶⁶ Cu	2.17	5.1	m	1039.0	0.4
Eu	¹⁵² Eu	5900	12.7	y	1408.0	2
Fe	⁵⁹ Fe	1.15	45.1	d	1099.2	20
Ga	⁷² Ga	4.71	14.1	h	834.0	0.002
Hf	¹⁸¹ Hf	12.6	42.4	d	482.2	0.02
Mg	²⁷ Mg	0.038	9.45	m	1014.4	20
Mn	⁵⁶ Mn	13.3	2.58	h	846.6	8×10 ⁻⁵
Mo	⁹⁹ Mo	0.45	2.75	d	141.0	0.03
Na	²⁴ Na	0.53	15.02	h	1368.6	0.004
Ni	⁵⁸ Co	0.113	70.78	d	810.7	6
Pd	¹⁰⁹ Pd	12	13.46	h	88.1	
Pd	^{109m} Pd	0.2	4.69	m	188.9	
Sb	¹²² Sb	6.25	2.70	d	564.0	0.001
Se	⁷⁵ Se	51.8	120.4	d	264.6	0.1
Sm	¹⁵³ Sm	206	1.948	d	103.1	5
Ta	¹⁸² Ta	21	115	d	1221.3	0.01
V	⁵² V	4.88	3.75	m	1434.2	0.9
W	¹⁸⁷ W	37.8	24.0	h	685.7	0.001
Zn	⁶⁵ Zn	0.78	243.8	d	1115.5	0.1

In this study we analyzed the following elements: Ag, Al, As, Au, Br, Cl, Co, Cr, Cu, Eu, Fe, Ga, Hf, Mg, Mn, Mo, Na, Ni, Pd, Sb, Se, Sm, Ta, V, W, Zn.

2. Experimental Part

2.1 Electrolysis process

2.1.1 Apparatus and Conditions. The experimental cell (Fig. 1), 15 mL polyethylene vessels, have been constructed using pure polyethylene (PET) (Kartell S.p.A., Milan, Italy) containers at very low impurity levels. The anode is a Pt wire (99.98% pure Pt) wrapped in the shape of a planar spiral. The cathode is a metallic thin film containing Cu, or Ni, or Pd, deposited onto a polyethylene disk (12 mm diameter and 1 mm thickness) made of the same ultrapure material of the cell; after the etching treatment of the supports the films were prepared by sputtering contemporaneously over two adjacent polyethylene targets to obtain a blank film electrode with the same deposition of the working one. The cathode contact is made with a "C" shape platinum wire inserted into a polyethylene support to prevent the electrolysis between anode and cathode connections. The electrolysis conditions were: time 1-5 hours, solution LiSO₄ 10⁻⁴, 10⁻³ and 1M, current 5-190 mA and voltage: 3-7 V.

Before the process, all the equipments were cleaned. The cleaning procedure is the following: washing

with $18 \text{ M}\Omega\text{cm}^{-1}$ ultrapure distilled deionized water; washing with HNO_3 65% (Merck Specpure, Darmstadt, Germany) for 1 minute; rinsing with $18 \text{ M}\Omega\text{cm}^{-1}$ ultrapure distilled deionized water; rinsing with KOH 20% in ethanol (ultrapure reagent) (Carlo Erba, Milan, Italy); rinsing with ethanol (ultrapure reagent) (Carlo Erba); rinsing several times with $18 \text{ M}\Omega\text{cm}^{-1}$ ultrapure distilled deionized water; drying at room temperature. The Pt wire is cleaned by acetone and ethylene in a previous supplementary step. The handling occurs with acrylic gloves. The film preparation, cleaning procedure, cell assembly and all the experiments were performed in a class 100 clean room using dust-free gloves. The tools used to assemble the cell components has been selected to avoid the presence of contaminants.

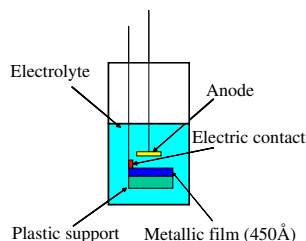


Fig. 1 - Electrolytic cell

2.1.2 Electrolysis Experiments. Two series of experiments were performed [20]: 1) mono layer, double layer (Cu/Ni) and multi layer thin-films (Cu/Ni/Pd/Ni/Pd) electrodes (450, 250/450, and 250/450/450/450/450 Å thicknesses, respectively) either electrolyzing Li_2SO_4 10^{-4} and 1M solutions (ultrapure compounds dissolved in $18 \text{ M}\Omega\text{cm}^{-1}$ ultrapure distilled deionized water); 2) mono and double layer electrodes (Cu; Ni; Cu/Ni and Cu/Pd) and Li_2SO_4 10^{-3} and 1 M.

2.2 INAA analysis

2.2.1 Sample and Standard Preparation. After electrolysis the thin-film cathodes were removed in a clean room: the spent cathodes and relative blanks, put directly into the irradiation vessels, were irradiated and analyzed; 1 or 2 mL of spent solutions and relative blanks were put into the irradiation vessel, gently dried in stove at 40°C , and then irradiated. All the other samples (PET supports, Pt wire, lab gloves and lab papers) were undergone to the same treatment. The standards were prepared starting from calibrated solutions $1000 \mu\text{g mL}^{-1}$ of each pure element (Carlo Erba). Known quantities of each solution were exactly dosed by mean of a micropipette (Eppendorf) into the irradiation vessel, gently dried in stove at 40°C , and irradiated.

2.2.2 Irradiation. The samples are undergone to two different neutron irradiations: 1) in the pneumatic channel position (Rabbit) of the TRIGA MARK II reactor at the R.C. ENEA-Casaccia for 1 minute at neutron flux of $1.25 \times 10^{13} \text{ n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ (fluence $7.5 \times 10^{14} \text{ n}\cdot\text{cm}^{-2}$); 2) in the rotating rack (Lazy Susan) of the TRIGA MARK II reactor for 30 hours at neutron flux of $2.6 \times 10^{12} \text{ n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$ (fluence $2.8 \times 10^{17} \text{ n}\cdot\text{cm}^{-2}$). The rack is maintained in constant rotation to make consistent and uniform flow and energy spectrum of neutrons incident.

2.2.3 Measurements. The γ measurements were carried out by mean of a counting system constituted by a HPGe detector (EG&G Ortec, Oak Ridge, TN, USA) (resolution 1.70 keV at 1332.50 keV, relative efficiency 23%, peak to Compton ratio 58:3), an ORTEC 672 amplifier and a multichannel buffer ORTEC 918A connected to 8k channel analyzer through data acquiring system ADCAM MAESTRO II. The energy and efficiency calibrations were performed by ^{137}Cs - ^{60}Co (furnished by Laboratorio Metrologia delle Radiazioni Ionizzanti, ENEA-Casaccia) and ^{152}Eu (furnished by Centre Energie Atomique, France) sources, respectively.

3. Results and Discussion

3.1 Preliminary tests on electrodes, solutions and equipment

Preliminary some tests are performed on materials used in the experiments: in particular, we analyzed blank electrodes, electrolytic solutions, PET support, Pt wire, lab gloves and lab paper.

Table 2 shows the element levels, expressed as Bq, in blanks (mono-, double- and multi-layer electrodes and Li₂SO₄ 1 M electrolyte).

Table 2. Activities of some elements determined in blank electrodes (Bq) and electrolytic solution (Bq mL⁻¹) after Rabbit irradiation.

Element	Mono Cu	Mono Ni	Mono Pd	Double Cu/Ni	Multi Cu/Ni/Pd/Ni/Pd	Li ₂ SO ₄ 1 M
Ag	<5840	<1500	<2200	<2790	<1660	<114
Al	<62	209±1	468±8	2223±12	558±14	3954±50
As	<41	<2	<5	<13	<12	<123
Au	<13	2±1	<3	<5	<3	
Br	<391	<29	145±30	404±111	<133	8920±662
Cl	<32	<30	111±16	168±18	78±15	<81
Cu	298000±2490	2330±105	<166	259140±1308	163560±1742	
Mg	<89	<21	<26	<51	<39	<252
Mn	56±17	66±4	109±5	118±8	143±10	<94
Na	<8	<3	<4	<3	<7	1217±80
Ni	46±16	322±8	<13	318±26	698±36	
Pd	1093±348	7±1	27869±178	337±6	43933±421	
V	<19	<13	205±7	609±10	130±13	<520

It can be noted that typical environmental contaminants such as Al, Br, Cl and Na, are at levels around or below the Minimum Detectable Activity (MDA). The electrodes are clean: the only interesting issue regards a significant activity of Cu and Pd and of Ni and Pd in mono-layer Ni and Cu electrodes, respectively. This is most likely due to a memory effect despite an accurate cleaning of the sputtering system. For the electrolyte, the only relevant fact concerns the activities of Al, Br and Na: the levels depend on the impurities composition of the lithium sulfate.

Table 3 shows the levels of the elements investigated in materials used in the experiments such as PET support, Pt wire, laboratory gloves, laboratory paper and the two solutions (Li₂SO₄, 10⁻³M and 1M).

Table 3. Activities of some elements determined in PET support after etching, lab gloves, lab paper (Bq), Pt wire (Bq g⁻¹) and electrolytic solution (Bq mL⁻¹) after Lazy Susan irradiation.

Element	PET support	Lab gloves	Lab paper	Pt wire	Li ₂ SO ₄ 10 ⁻³ M	Li ₂ SO ₄ 1M
Ag	6.19±0.12	<238	<0.75	1986±46	<0.05	<0.2
Co	0.27±0.07	52±21	18.1±0.6	<33	0.26±0.03	<0.2
Cr	9.43±0.35	<4430	115±6	<15000	4.8±0.2	<10
Eu	<0.08	<224	<1.6	<503	<0.05	<1.6
Fe	<0.35	<500	7.8±1.6	<229	0.79±0.07	<0.7
Hf	4.42±0.05	<407	37±1	<239	<0.11	<0.7
Ir	0.16±0.03	<239	<1.1	3020100±18138	<0.05	<0.4
Ni	<0.13	<410	<2	<44	<0.07	<0.4
Sb	<0.06	<185	46±1	<553	0.16±0.03	1.7±0.2
Se	<0.1	<213	<2	<249	<0.07	1.1±0.4
Ta	0.59±0.11	<374	629±8	1510±61	0.64±0.10	0.98±0.29
Zn	1.14±0.11	3919700±47784	820±12	148±52	0.59±0.10	1.76±0.29

The main considerations regard the levels of Zn in lab gloves, Ta and Zn in lab paper and Ag, Ir, Ta and Zn in Pt wire. The highest level of Zn in laboratory gloves is due to the ZnO or ZnSO₄ present inside the gloves as lubricant. This level should be not significant for our experience because, being inside the gloves, Zn can not be transported in the experiment. Maybe, other contamination source of Cr, Hf and Zn is the mould during the etching process. Finally, the values of such elements can justify a possible contamination from Pt wire.

Table 4 shows the results of the elements investigated after the first series of experiments using Li₂SO₄ as electrolytic solution on mono- (Cu, Pd and Ni), double- (Cu/Ni) and multi-layers, obtained subtracting the blank level. Among elements the Au levels are due to a contamination from the platinum anode because of the erosion occurring during the electrolysis process. Other considerations can be applied to Zn, and Mo, W, Cr which belong to the same chemical group and have the same chemical behavior. Further, they participate both to the preparation of the thin-film during the etching process and during the deposition of the thin-film. For these reasons, they can derive from a contamination occurring before the experiments. The most interesting result is the V level: in the various electrodes V amount is reproducible and ranges between 204 and 228 ng except for the mono Pd-layer (25 ng). Finally, levels of other elements are around or below MDA (e.g. As) and index of minimum contamination (e.g. Na)

Table 4. Activities (Bq) of some elements determined in spent electrodes and V amount (ng) after the first series of experiments. The second column reports the irradiation position (IP): R as Rabbit and LS as Lazy Susan. n.d.: not determined.

Element	IP	Mono Cu	Mono Ni	Mono Pd	Double Cu/Ni	Multi Cu/Ni/Pd/Ni/Pd
Activities						
Ag	R	<4150	n.d.	n.d.	<3750	<3430
Ag	LS	n.d.	42±1	<0.5	<0.6	<0.6
Al	R	446±8	<137	<39	<167	<145
As	R	<27	<5.2	<2.4	<16	<8.8
Au	R	<9	38±4	<3.4	15±7	16±7
Au	LS	n.d.	8490±33	1423±8	592±3	1481±11
Br	R	<200	<98	<70	390±138	<156
Br	LS	n.d.	66±1	<8	27.3±0.6	<8
Cl	R	<7	<28	<34	<29	<35
Co	LS	n.d.	2.5±0.5	<0.4	<0.6	2.3±0.4
Cr	LS	n.d.	129±4	<7.4	64±3	<11
Fe	LS	n.d.	<1.3	<1.2	4.5±0.4	<1.6
Mg	R	<57	<37	<16	<55	<49
Mn	R	94±13	99±7	<13	113±11	29±10
Mo	LS	n.d.	9.3±0.5	<0.8	1.4±0.2	32.4±0.4
Na	R	<9	18±7	<6	<12	<10
Sb	LS	n.d.	34±1	5.7±0.4	8.4±0.6	21.2±0.9
V	R	12766±81	12733±81	1507±29	13795±102	17424±425
W	LS	n.d.	578±2	<42	<50	112±3
Zn	LS	n.d.	82±2	71±1	11.8±1.4	92±4
Amount						
V		212	210	25	228	204

Table 5 shows the levels of the elements investigated in this study during the second series of experiments. For Cu/Ni double layers we are set up two different tests. Although it is already considered the subtraction of the blank, there are measurable levels of Ag, Cr, Fe, Se, Ta and Zn. This may be due to minimal presence of contaminants (detectable only by INAA). These contaminants are deposited on the cathode during the electrolysis process: even if they are measurable, this is really an apparent enrichment and, according to us, this is not due to transmutation phenomena in condensed matter. Furthermore, the levels of some elements, expressed as ng, show that ultra-trace levels of contamination should always be considered.

Table 5. Activities (Bq) and amount (ng) of some elements determined in spent electrodes after the second series of experiments (Lazy Susan irradiation position).

Element	Mono Cu	Mono Ni	Double Cu/Ni	Double Cu/Ni	Double Cu/Pd
Activities					
Ag	3.6±0.3	144±2	8.89±0.24	39.1±0.63	6.03±0.30
Co	<0.37	<0.39	<0.50	1.33±0.39	8.9±0.3
Cr	598±3	341±2	69±2	733±3	475±3
Eu	1.85±0.83	<1.07	<0.81	<1.46	<1.24
Hf	<0.94	<1.2	<1.1	<1.3	<1.2
Ir	76±6	451±3	156±1	407±3	154±1
Ni	<1.2	<1.34	<1.67	<1.70	2.08±0.20
Sb	<0.82	<0.82	<0.73	<1.04	<1.34
Se	5.88±0.32	4.15±0.32	<0.59	2.36±0.33	<0.88
Ta	9.75±0.44	6.46±0.48	<2.1	6.75±0.61	21.3±1.3
Amount					
Ag	27±2	1083±28	67±2	294±8	45±3
Co	<0.66	<0.70	<0.89	2.4±0.7	15.9±0.6
Cr	1020±9	582±3	117±3	1250±9	810±7
Fe	3410±160	2500±180	3060±270	3990±270	4790±25
Zn	1509±78	825±3	354±24	567±33	920±50

4. Conclusion

INAA was useful to investigate the possible formation of new species attributable to the transmutation phenomena. For this purpose we studied each system component and, after the experiments, the electrodes and electrolytes. Resuming the results it can be evidenced: a) the Ag, Au, Ir, Ta and Zn levels are due to contamination problem from platinum anode (mainly because of the erosion occurring during the electrolysis process); b) the presence of Cr, Hf, Mo, W and Zn can be attributed to mould during the etching process and to their participation to the thin-film preparation; c) the contamination of Ag, Co, Cr, Fe and Zn at very low levels (detectable only by INAA) can be attributed to cathode deposition during electrolysis. Actually, this is an “apparent” enrichment and not due to transmutation phenomena in the condensed matter

The only anomaly which is difficult to give some explanations regards the V levels (ranging between 25-280 ng) found in the first experiment. The proportionality with the applied current and the evidence on all kind substrates is pointing in the direction of an eventual contamination.

Finally, our consideration regards the future researches: a good strategy is to use suitable markers (e.g. radiotracers).

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Mass Spectrometry: Critical Aspects of Particles Detection related to Condensed Matter Nuclear Science

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Abstract. The detection of transmutations in Fleischmann and Pons experiments is a critical issue in order to assess the nuclear origin of the excess heat production. A very accurate study in this field has been carried out in ENEA, aimed to investigate the possible occurrence of nuclear transmutation in nickel hydride thin films. The research work, which took several years and involved an international collaboration between many research laboratories, came to the conclusion that the experiments didn't produce any evidence of transmutation experiments, pointing out the importance of using state of the art instrumentation in performing such a kind of study.

1. Introduction

In the last decades some scientific papers have been published on the study of nuclear transmutation reactions in condensed matter, in which the formation of new nuclear products as a consequence of eventual nuclear reactions was investigated. In this contest, a specific research activity based on electrolysis experiments has been developed at ENEA, by using Instrumental Nuclear Activation Analysis (INAA) [1] and Secondary Ions Mass Spectrometry (SIMS) [2, 3]. SIMS is a very powerful technique to approach this problem, since it is able to measure the atomic composition of a material with very high sensitivity, but also the isotopic abundance of each atomic specie, that, if different from the natural distribution, is a solid evidence of the occurrence of a nuclear reaction. Actually, the "appearing" of new elements which were not detected before, in Fleischmann and Pons (F&P) experiments, can be likely caused by contaminations, which are very critical to be ruled out due to the extremely low signals involved in the transmutation investigation.

In this communication, we review some previous results [2,3] concerning the study of nuclear ashes in nickel hydride thin films undergone to electrochemical experiments and report new experimental data which allow to get a definite and coherent interpretation of the complete research work.

2. Experimental methods

The electrochemical cells used in the F&P experiments were made of pure polyethylene. The anode was made of 99.98% Pt wire wound in the form of a flat spiral and the cathode was a thin film of Ni deposited by ion beam sputtering on a polymeric substrate made of the same pure polyethylene material of the cell. During the sputtering process, two identical films were deposited, one to serve as a control while the other was used for electrochemical loading with hydrogen to form nickel hydride. The electrolyte was 1M Li_2SO_4 in pure H_2O (distilled at 18 M Ω). Electrolysis was performed for time periods varying from 4 min to 20 hours. Additional details of the all the experimental setup can be found in previous publications [2, 3].

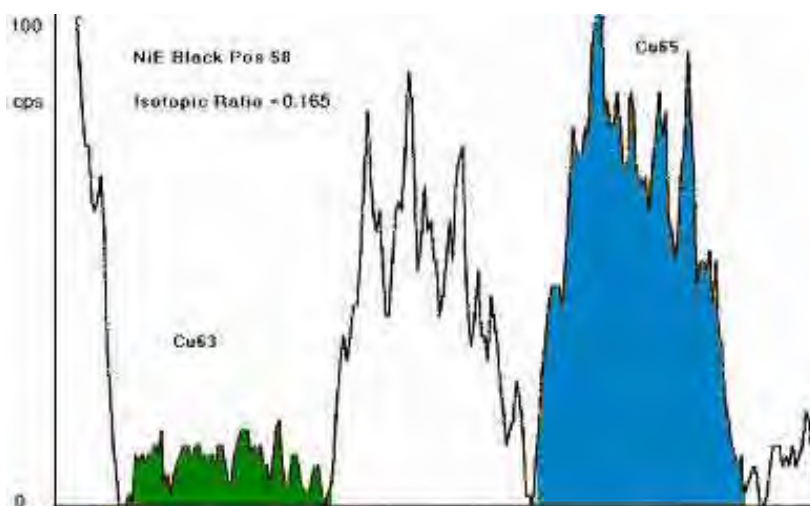


Fig. 1 - SIMS spectrum of the active film in the range of 63-65 nominal masses.

3. Results and discussion

Copper was selected as a marker for the experiment, because it is the most likely product of the reaction between protons and Ni and, in addition, Cu has only two stable isotopes having nominal masses of 63 a.u. and 65 a.u., respectively.

SIMS analysis was performed on the surface of the thin-film cathodes, both on the electrolyzed sample and its relative control one. The used facility was a Quadrupole Analyzer SIMS, which had 0.5 a.u. mass resolution and allowed to analyze both the samples in the same measurements run. Preliminary results showed, “apparently”, a quite big shift of the Cu isotopic ratio (see Fig. 1), being the $^{63}\text{Cu}/^{65}\text{Cu}$ mass ratio equal to 0.165 instead of the natural value of 2.2; in addition, by repeating the analysis in different zones of the sample, the observed discrepancy with the natural value was more significant into the center of the electrode than on the border [2].

In order to confirm the results, the measurements were repeated by a Super SIMS facility, the access to which was granted thanks to the scientific collaboration with the National Research Laboratory (NRL, Washington D.C., USA) [4]. Super-SIMS (also called Accelerator-SIMS) is the combination of Secondary Ion Mass Spectrometry with Accelerator Mass Spectrometry (AMS). The main advantage of this technique compared to conventional SIMS is the virtually complete suppression of molecular background and dark-counts. Detection limits for trace elements can therefore be improved by orders of magnitude and are only limited by contamination and count rates, achieving levels as low as ppb to ppt. The new measurements did not confirm the old ones, reporting a value of the Cu isotopic ratio equal to the natural one, within the measurement accuracy, in both the electrolyzed and the reference samples [3]. Speculations on the possible explanation of the discrepancy between the previous and the new results and on the presence of possible artifacts in both measurements were presented in ref. [3].

The possibility to repeat the measurement with a high resolution Time Of Flight (TOF) SIMS allowed the story to come to a conclusion. The employed instrument was the TOF MiniSIMS manufactured by SAI (Scientific Analysis Instruments), whose used was granted thanks to the collaboration with Assing S.p.A. (Italy). The TOF MiniSIMS has superior mass resolution ($m/\Delta m$ higher than 600 in the mass range of interest), that makes it able to distinguish between single elements and organic compounds. The new analysis revealed that the peak at the nominal mass 65 was constituted by two contributions, the more intense of which was assigned to an organic compound (C_5H_5^+), while the other at 64.93 a.u. well fit $^{65}\text{Cu}^+$ (see Fig. 2, bottom graph). The peak at 63 a.u. was also made by two sub-bands, one at higher mass assigned to C_5H_3^+ and the other at 62.93 a. u. to $^{63}\text{Cu}^+$ (see Fig. 2, top graph). Based on the above identification of the peaks, the mass ratio of the copper isotopes resulted to be 2.0, which well match to the natural value (2.2).

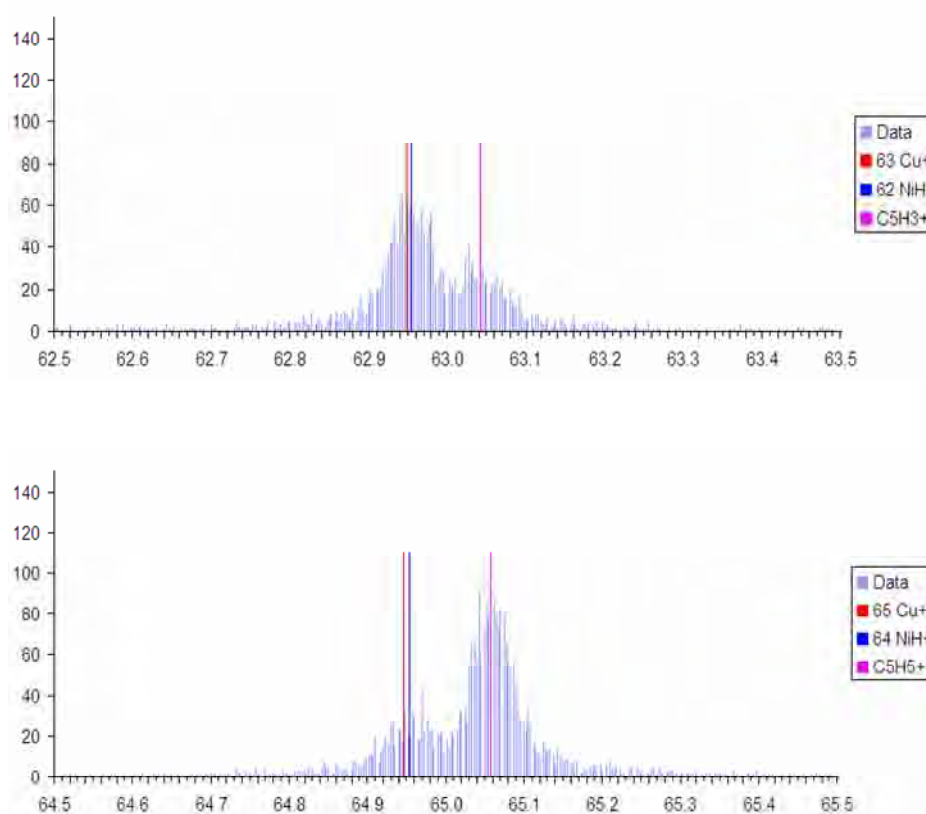


Fig. 2 - TOF-SIMS high resolution spectrum of the active film, in the range of 63 nominal mass (top) and 65 nominal mass (bottom).

The organic compounds detected by the TOF MiniSIMS were probably produced during the SIMS beam bombardment of the sample, emerging from the zones of the polyethylene substrate where the nickel film was more damaged. The higher the exposed area of the polymeric substrate (in the middle of the sample, because of the film micro-cracks) the larger the “apparent” shift.

The reason why the measurement performed by using SUPER-SIMS did not revealed the organic compound, although the instrument had a very high mass resolution, is that the high energy of the impinging ions destroys any organic compounds which may be produced. This did not happen in the case of TOF MiniSIMS and Quadrupole SIMS used in the first analysis, which both have the energy of the primary ions in the range of a few keV.

4. Conclusions

In conclusion, after the first experimental campaign we repeated two times the isotopic composition measurements, on the same samples, by using two high performance SIMS. The new analysis revealed that the Cu isotopic ratio was the natural one and that the apparent shift was due to the organic compound C₅H₅. Then, the apparent isotopic shift was an artifact produced by the not enough resolution of the SIMS used in the first measurement performed in 2003. Then the experiments didn't produce any evidence of transmutations.

The work highlighted the importance of using status of the art instrumentation in performing transmutations studies.

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Evidence for Fast Neutron Emission During SRI's SPARWAR/GALILEO Type Electrolysis Experiments #7 and #5, Based on CR39 Track Detector Record

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Abstract. We have reported [1] the detailed analysis of the CR-39 detector (Landauer) from SRI's #BE013-7 (#7) Pd deposition experiment where the detector was separated from the cathode wire by a 6 μm Mylar[®] film. The Mylar[®] protected the CR-39 surface from chemical, mechanical, and electrostatic (spark discharge) damage during electrolysis. In this report we compared those results with that of the CR-39 detector, installed as in #7, in an identically operated cell using light water and with the background detector placed 2 m from the electrolytic cell.

1. Introduction

For the last 3 years claims have been made that during Pd electroplating onto Ag-wire cathodes (or other metal wires) from Pd/D₂O solution, high intensity emissions of charged particles were observed [2]. The emissions have been detected using CR-39 track detectors. The typical pit densities observed in these experiments is 10^7 - 10^8 pit/cm² and the pits are primarily located on surface of the CR-39 nearest where the cathode wire was pressing directly onto the CR-39.

The purpose of this present study is:

- To search for reality of nuclear emissions reported using Pd electrodeposition technique and CR-39 detectors. To separate pits caused by mechanical defects (electric discharge) from that of nuclear origin.
- To test applicability of our track identification technique (see A. Roussetski et al, ICCF-12, Yokohama, 2005 [1], Fig.1) based on in depth destructive etching of the CR-39 detectors, allowing us to obtain track diameter evolution vs. removed depth, to the Pd electrodeposition experiment.
- To apply the CR-39 technique to in-situ neutron detection near an electrolytic cell. To compare the results with that obtained in Blank (H₂O electrolysis) and Background (no cell) experiments as well as with a BF₃ proportional detector count rate.

A series of experiments have been performed where Pd was electrodeposited onto Ag-wire cathodes with CR-39 plastic track detectors separated from the electrolyte and electrodes, with the cell placed in an external magnetic field [3]. The Blank (H₂O electrolysis) and Background (CR-39 2 m from the cell) experiments were performed using same series Landauer CR-39 sheet as used in the original D₂O experiment. Contrary to earlier studies, the CR-39 detectors in this study were not in contact with the cathode or electrolyte, protecting the CR-39 surface from mechanical stress and electrostatic (discharge) damage during electrolysis. In addition to the CR-39 detector, a low self-efficiency proportional BF₃ spherical neutron dosimeter was employed in each experiment.

2. Experimental

The same lot of CR-39 chips (2cm x 1cm, Landauer Inc.) were used in all experiments and calibrations. After exposure the chips were immediately exposed to 6N NaOH at 70°C for 7 hours yielding an etch rate of 1.3 μ m/hr. Pd was electrodeposited onto Ag-wire cathodes with CR-39 plastic track detectors separated from the electrolyte and electrodes, with the cell placed in an external magnetic field [3]. The detectors from the #7 and #5 experiments were separated from the cathode and electrolyte by sheets of 6 μ m Mylar® and 60 μ m polyethylene, respectively. The blanks were performed using the same electrochemical parameters, salts, and CR-39 placement as in the #7 and #5 experiments substituting H₂O for D₂O. The background CR-39 detectors were held 2m from the operating cell. A Ludlum proportional BF3 spherical neutron dosimeter with self-efficiency of 2.5x10⁻³ (with respect to Cf-252 fast neutrons) was employed in each experiment.

Calibration chips were exposed to proton beams of 1.0 - 2.5 MeV from a Van DeGraaf accelerator—and etched at 1.3 μ m/hr. Fig. 1 shows the raw data and the calibration curve obtained from proton bombardment on CR-39 chips identical to those used in the electrolysis experiments. During analysis the CR-39 detectors were etched three more times, at a bulk etch of rate 1.3 μ m/hr. Track detection was performed manually using the “PAVICOM” track processing facility in Lebedev Physics Institute, Russian Academy of Sciences, Moscow.. Proton recoil track distributions from a weak Cf-252 neutron source (120 n/s) are presented in Fig.2.

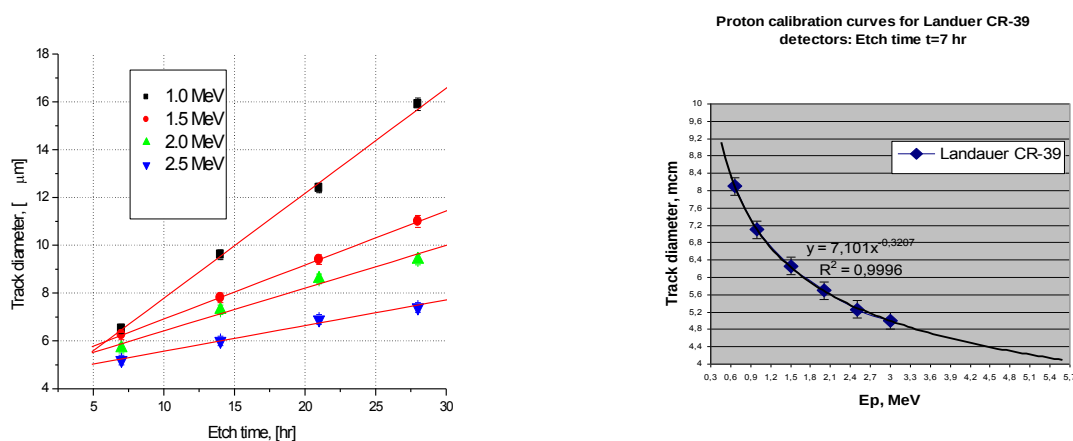


Fig.1 - Track diameter vs. etching time for four different proton energies (left). Proton calibration curve (right).

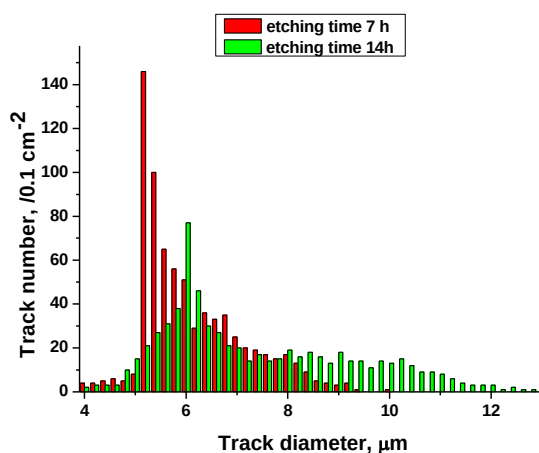


Fig.2 - Proton recoil track distributions (track number vs. track diameter) obtained with Cf-252 neutron source.

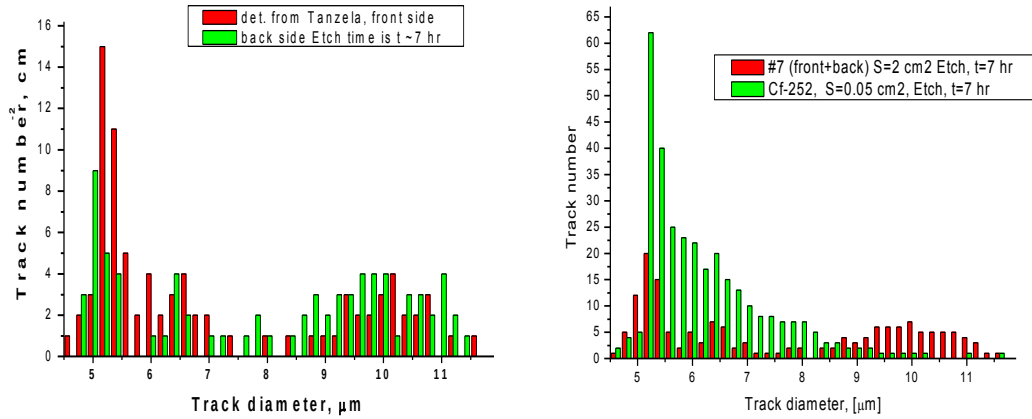


Fig.3 - Tracks from #7 detector, after 1st etch (left picture); Comparison to neutron calibration (right picture).

3. Results

After the 7-hr etch the proton recoil spectrum from experiment #7 is located between 4.5 and 9.0 μm track diameter with a maximum near 5.2 μm . This maximum is consistent with the mean recoil proton energy in the range of 2.2-2.5 MeV. The broader recoil spectrum after the 14-hr etch is between the 5.0 and 12.0 μm proton recoil track diameters with the maximum near 6.0 μm . This shift in maximum track diameter from 5.2 to 6.0 μm is consistent with 2.2-2.5 MeV protons. The neutron detection self-efficiency of CR-39 after the second etch (1.2×10^{-4}) is about factor of 1.3 higher than that after the first etch (0.9×10^{-4}) due to the increase in proton recoil critical angles at the greater depth. Fig. 3 shows the track diameter results measured from both sides of the #7 detector after the first etch compared to that for Cf-252 recoil. For the front side: the total number of circular and elliptic tracks (normal and oblique incidence) is $N=77 \text{ cm}^{-2}$, with about 30 % of all tracks having elliptical shape. For the backside: $N=40 \text{ cm}^{-2}$. In the range of 4.5-8.0 μm the track diameter plot for #7 looks similar to that for Cf-252.

Fig. 4 shows a comparison of #7 data with that from the H_2O experiment and the Background after the 1st etch. The Blank and the Background data show no sign of proton recoil from fast neutrons proving that there was no accidental neutron irradiation of CR-39 sheet during transit.

Fig.5 compares all above background tracks from the #7 (D_2O) track detector after the 2nd etch with that from the Cf-252 calibration. The above background track distribution in the range of 4.5-11.0 μm is nearly identical to that from the Cf-252 recoil measurements. The D_2O detector showed 101 tracks/ cm^2 . Fig.6 compares all above background tracks from the #7 (D_2O) track detector after the 2nd etch with that from the H_2O experiment and the background detector. Fig.7 shows a rough reconstruction of the protons recoil spectra for CR-39 detectors obtained during the D_2O electrolysis run #7 and during exposure to a Cf-252 neutron source after the 2nd etch. The reconstruction was

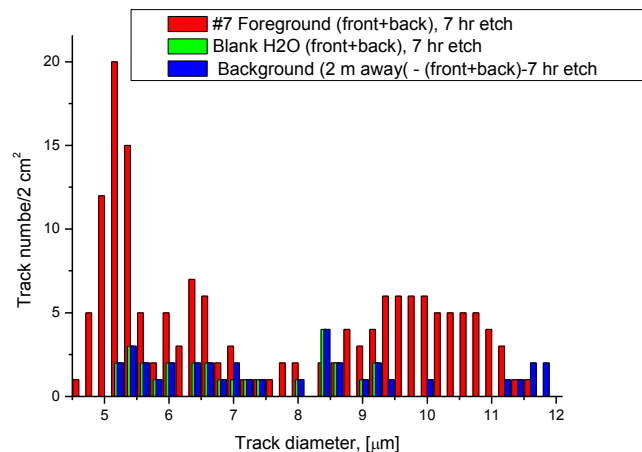


Fig.4 - Comparison of #7 data after 1st etch with that from Blank experiment and Background.

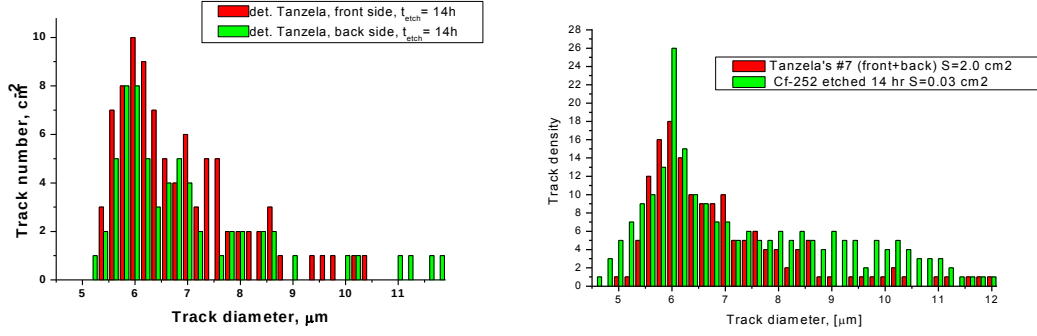


Fig.5 - Comparison of the #7 track detector distribution after the 2nd etch with that of the Cf-252 recoil .

deduced from the track density vs. track diameter histograms, taking into account the track diameter vs. proton energies after the 2nd etch and the critical incidence angle θ_c vs. proton energy.

We also noted that statistically significant counts were recorded by the BF₃ dosimeter during the D₂O runs #5 and #7.

3. Discussion

After the 1st etch the average track density on both sides of the detector $\langle N(\text{fg}) \rangle$ is 58.5 tracks/cm². The total background track density on both sides of blank detector $\langle N(\text{bg}) \rangle$ is 6.0 tracks/cm². After subtraction $\langle \Delta N \rangle$ is 52.5 ± 8.0 track/cm². Assuming a “neutron source” was a cathode wire in a 2π -geometry with respect to the CR-39 surface, the neutron count rate/intensity (I_n) would be $2\langle \Delta N \rangle / (t \times \epsilon_s)$, where the CR-39 self-efficiency after the 1st etch (ϵ_s) is 9.2×10^{-5} and t is the electrolysis time. Assuming that the neutrons were emitted when the current was greater than 0.5 mA ($t = 15$ days), $I_n = 0.90 \pm 0.14$ n/s. If we assume that the neutron emission was observed only when neutron dosimeter read above its background ($t = 4$ days), $I_n = 3.38 \pm 0.53$ n/s. So, the neutron emission rate in the D₂O run #7 is in the range of 1.0-3.0 n/s. After the 2nd etch, $\langle N(\text{fg}) \rangle = 88$ cm⁻², while $\langle N(\text{bg}) \rangle = 26$ cm⁻², and $\epsilon_s = 1.17 \times 10^{-4}$. I_n is again in the range of 1.0-3.0 n/s as shown after the 1st etch.

The #5 CR-39 detector used in SRI BE010-5 PdD_x deposition electrolysis experiment had a 60 µm polyethylene film adhered to both faces while immersed in the electrolyte and in contact with the cathode. Although the front face was found to be covered with high density pits (defects) making it almost impossible to distinguish real nuclear tracks from defects, the rear face of #5 detector shows proton recoil tracks similar to those found on both faces of the # 7 CR-39 (with a track density 50 -70% of that of #7). These pit densities are shown in Fig. 8 and actual pits are shown in Fig. 9.

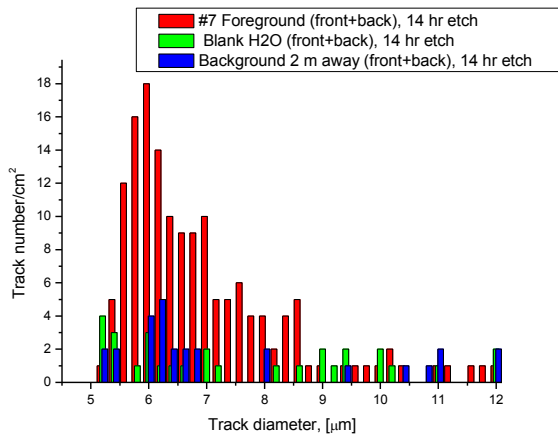


Fig.6 - Comparison of Foreground #7 data (taken from both sides) with that from Blank experiment (H₂O electrolysis) and the Background (detector is placed 2m away of the electrolytic cell) - 14 hr etch

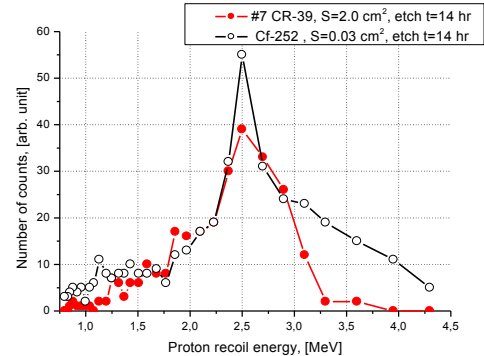


Fig.7 - Rough reconstruction of the protons recoil spectra from both the D₂O run and the Cf-252 exposure.

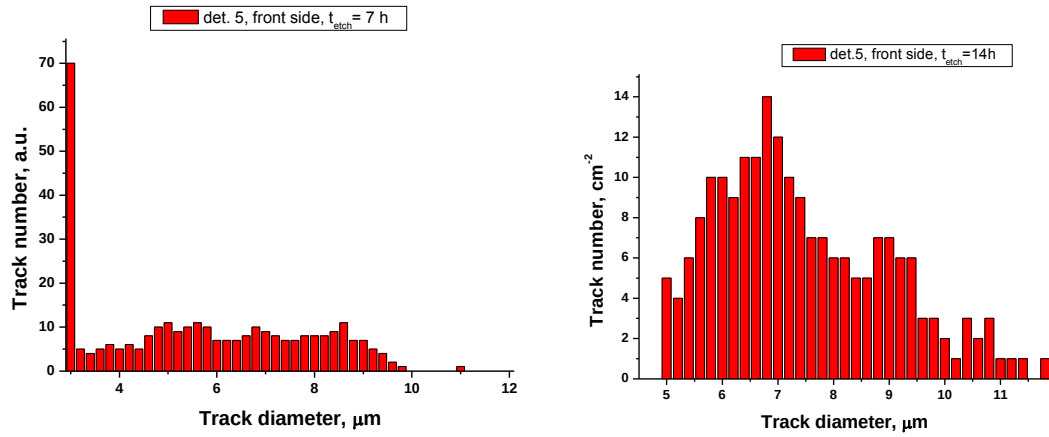


Fig.8 - Individual pit density at the front side of #5 detector: 7 hr (left) and 14 hr (right) etch

The analysis of the back side of detector #5 after the 1st etch showed $N(\text{Fg}) = (30.0 \pm 5.5)$ recoil protons/cm², $N(\text{Bg}) = 6 \pm 4$ cm⁻², $\Delta N = 24.0 \pm 6.8$ p/cm², and $\langle \text{In} \rangle = 2\langle \Delta N \rangle / (t\epsilon_s) = 0.30 \pm 0.08$ n/s. After the 2nd etch (back side only): $N(\text{Fg}) = 45$ cm⁻², front $N(\text{Fg}) = 63$ cm⁻², $\langle N(\text{fg}) \rangle = 54.0 \pm 7.3$ cm⁻². Background $\langle N(\text{bg}) \rangle = 26 \pm 5$ cm⁻², $\Delta N = 28 \pm 9$ cm⁻², and $\langle \text{In} \rangle = 2\langle \Delta N \rangle / (t\epsilon_s) = 0.29 \pm 0.09$ n/s in 2π solid angle. If $t = 1$ day $\text{In} = 6.0 \pm 1.6$ n/s in 2π solid angle. These results are shown in Fig. 10.

At a self-efficiency to fast neutrons $\epsilon_s = 7.6 \times 10^{-3}$ ($R \sim 0$ cm) and detector-source distance of 10 cm, the total efficiency of BF₃ sphere for fast neutrons (ϵ_t) would be 7.6×10^{-5} . The sensitivity of the detector to fast neutrons (minimal detectable emission rate) can be expressed as: $S = 3[\langle N_b \rangle / (\epsilon_t 2\tau)]^{1/2}$, where $\langle N_b \rangle$ is the averaged background count rate, and τ is the duration of neutron detection. For detector #7: $\langle N_b \rangle \approx 6.0$ cps, $\tau = 15$ days, resulting in $S \approx 150$ n/s, (300 n/s, when $t=4$ days). This results is 100 times higher than that measured by the CR-39 detector in that experiment. This is also true for the results measured in experiment #5.

4. Conclusions

- Entire results of two CR-39 detectors analysis show that a weak, but statistically significant emission of fast neutrons has been observed in the SRI's #7 and #5 runs replicating SPAWAR Pd-deposition experiment (in the presence of an external electromagnetic field).

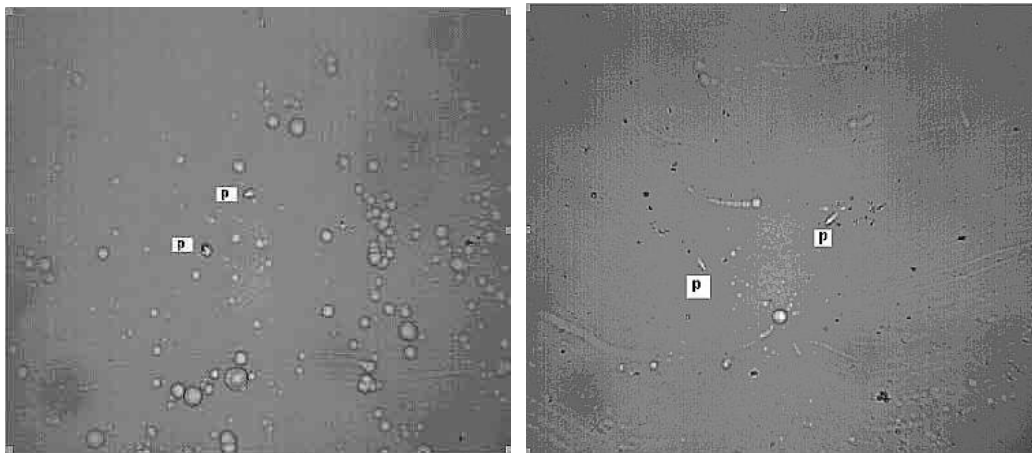


Fig.9 - Proton recoil tracks at the front side of #5 detector and the defects ("ground beef") after 2nd etch.

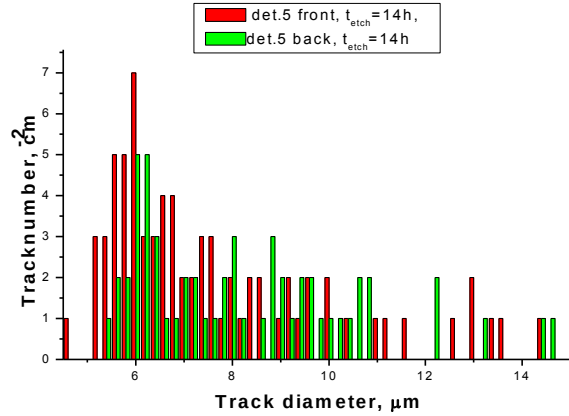


Fig.10 - Comparison of the back and the front side proton recoil spectra at t = 14 hr etch

- The #7 detector separated from the electrolyte by a 6 μm Mylar® film shows “clean” front and back faces, containing only nuclear tracks (proton recoil). While the #5 detector, submerged in the electrolyte but covered with a 60 μm PE film, had vast areas covered by defects (“ground beef”) on the front face lower (than #7) proton recoil density at the back side
- The small diameter defect pits were eliminated by in-depth etching (>18 μm) allowing us to distinguish real proton recoil tracks caused by neutrons as well as by energetic charged particles (protons and alphas) emitted from the PdD_x powder being deposited on top of the detector during electrolysis.
- Comparison of proton recoil spectra (track number vs. their diameter) of the analyzed detectors with that of their respective Blank and Background runs and with the tracks from Cf-252 source gives solid evidence for a fast neutron emission taking place during the runs #7 and #5.
- Comparison of the neutron emission rates obtained from CR-39 analysis with that deduced from SRI (proportional BF₃ detector) measurements shows a of the results, suggesting orders of magnitude higher neutron emission recorded by SRI detector than that calculated from the noiseless CR-39 measurement data .
- Because of the huge discrepancy between the CR-39 and BF₃ dosimeter results and since the dosimeter has very low neutron sensitivity we assume that the excess dosimeter counts contain significant electromagnetic noise, induced by the electrolysis power supply.
- In order to provide additional confirmation for our CR-39 results on neutron emission in SRI experiments, a high-efficiency neutron spectrometer would be desirable.

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On the products of nucleus reactions formed during deuterium diffusion through palladium membrane

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Abstract. We report on the results of experimental observation of interaction of deuterons in a palladium membrane in deuterium gas under the pressure of $P=0,07$ Mpa. The temperature fluctuation with an amplitude of $\Delta T=4\div 5^{\circ}\text{C}$ was observed. After a 42 hour experiment, a significant increase in the number of tritium (^3T) atoms, $N>10^9$, has been revealed, while no traces of ^4He have been found.

Introduction. The results of the investigation of cold nuclear fusion by M. Fleischmann and S. Pons published in 1989 [1] are not accepted by scientific community until now because of rather small amount of products of nucleus reactions and difficulties with reproduction of their experimental results in other laboratories. The aim of our work is to develop experimental equipment capable of synthesizing essential amount of such products. Our idea is based on the assumption that the composition and the structure of the material saturated by deuterium may have an essential influence on the processes occurring in the solid body at low energy reactions. On our opinion, the intrinsic properties of the metallic matrix determine not only the ability of the material to accumulate deuterium but also the possibility for deuterium nucleus to move and interact.

In our work [2] we have reported on the results of deformation of titanium saturated with deuterium and on the process of saturation. It was concluded that the results depend on the initial structure of the sample. On the basis of the analysis of our results and the results available in the literature, we have proposed a mechanism of nuclear fusion via tritium channel [3].

To confirm the proposed mechanism one should carry out an experiment on generation of a large number of products of low energy reactions. Our experimental setup is based on the following prerequisites:

1. the synthesis of cold fusion products should be continuous,
2. the experiments should be performed at high temperature in order to increase the rate of deuterium diffusion,
3. it is necessary to provide a directed motion of deuterium through metal.

The simplest possibility to satisfy all three conditions is to conduct the experiment in the gaseous atmosphere of deuterium. Since the process takes place at the metal surface [4], the reaction should be facilitated during deuterium diffusion through a membrane. The directed motion can be achieved by a glow discharge at one side of the membrane.

Experimental procedure. In Fig. 1, the experimental equipment is schematically shown.

Fig. 1. Schematic of the experimental equipment: 1 reaction chamber, 2 ceramic tube, 3 nichrome curl of the furnace, 4 stainless steel cylinder, 5 Pd membrane, 6 high voltage vacuum feedthrough, 7 anode, 8 low voltage vacuum feedthrough, 9 control thermocouple, 10 measuring thermocouple, 11 adjustable power supply of the furnace, 12 adapter, 13 computer.

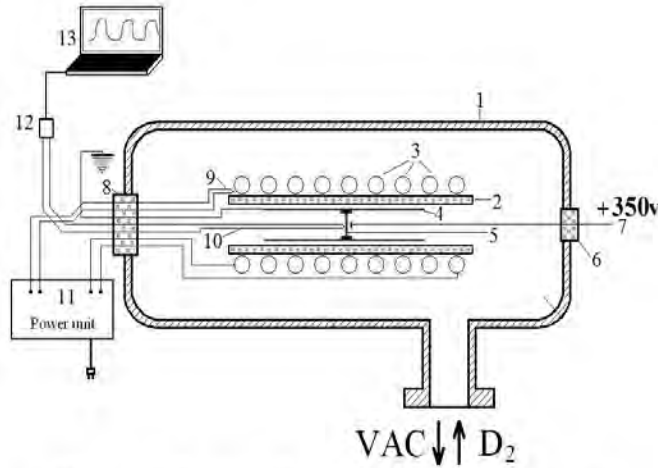


Fig. 1 Schema of experimental chamber

The structure of a palladium foil (Pd -99,8) having thickness of $s = 0.1$ mm was processed in accordance with the principles developed in [2]. The disk type membrane was sealed in the tube made of stainless steel. The induction furnace provides heating of the tube up to $T=700^{\circ}\text{C}$. After vacuumization of the reactionary volume, it was filled with deuterium under $P<0,07$ MPa. Glowing discharge was applied (DC), ($I=40$ ma, $U=350$ v).

Mass-spectrometric analysis of gas content before and after the process was made on the mass-spectrometer "Thermo Finnigan MAT 95 XP" (the resolution $R=10000$, the scanning range of mass numbers 1 – 18, the ionization energy 70 eV).

The concentration of tritium was measured by a scintillation method according to the procedure described earlier [2].

For the level of neutrons and gamma-quanta measurement a spectroscopic radiometer SRPS-2 was used. The threshold level of neutrons $N_{\text{ПН}} = 30 \pm 2$ 1/50 sec and gamma-quanta $N_{\text{ПГ}} = 700 \pm 15$ 1/5 sec was not exceeded during the experiment.

Experimental results. Temperature in the vicinity of the membrane was recorded constantly and it is shown in Fig. 2. It can be seen that after two hours the temperature starts to fluctuate, while the discharge current remains constant.

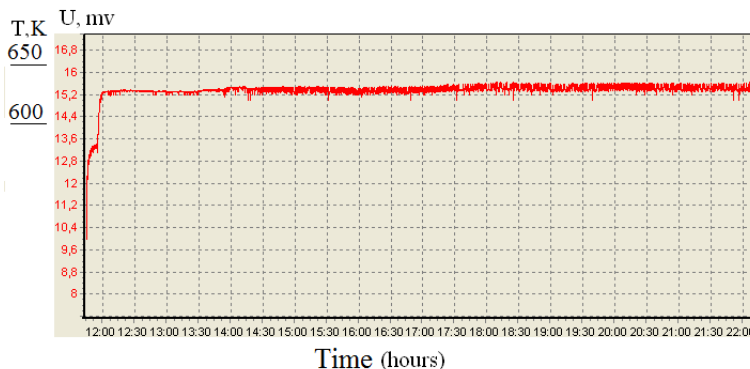


Fig.2 Change in temperature near the membrane

Fig. 3 shows temperature fluctuations in an increased scale. The fluctuations are not stable since the duration of intervals with relatively small and relatively large temperature change. The presence of temperature fluctuations can be explained in terms of the model of low temperature fusion due to resonant transfer of neutron from

deuteron proposed in [3]. Deuterons are accumulated in the vicinity of the membrane surface. Afterwards they move to the structure defects and form pairs of quasi-ions D_2^+ . During this process the internal stresses grow in the membrane. When these stresses attain certain value, the

quasi-ions leave the metal interior and move in the field of a crystal lattice. There occurs a resonant transfer of neutron from one deuteron to another, resulting in formation of proton and triton nuclei accompanied by heat emission. Since a large number of deuteron pairs participate in this reaction, the temperature fluctuations can be detected even by a thermocouple. When internal stresses are decreased the motion of deuterium pairs ceases, high thermal conductivity of hydrogen isotope gas results in sharp cooling and the temperature of the membrane decreases. Then the process repeats.

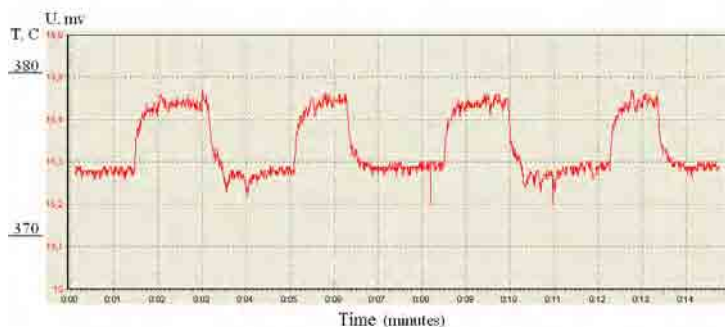


Fig. 3 Fluctuation of temperature after $t=36$ hours of discharge applied

level.

During the experiment, the neutron and gamma quanta did not exceeding the background level. Tritium was measured by scintillation method, and the total amount was $N>10^9$ atoms.

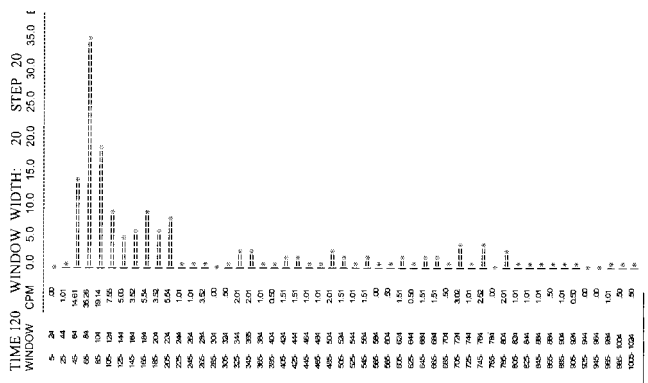


Fig.4 Energy spectrum of tritium solution

Conclusions. A device producing heat and tritium was proposed.

Temperature fluctuations with the amplitude of $\Delta T=4-5^{\circ}\text{C}$ were recorded.

The essential increase in the amount of tritium, $N>10^9$ atoms, was registered.

It was shown that the low temperature reaction in deuterium medium occurs via the tritium channel.

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Hot Spots, Chain Events and Micro-nuclear Explosions

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Abstract. In 1990 the BARC group presented results at several fora, based on our neutron multiplicity studies as well as tritium measurements, that suggested micro-nuclear explosions seem to occur at localized hot spots in which both Tritium and neutrons are generated, subject to the n/T branching ratio anomaly. It was estimated that about 10^8 to 10^{10} tritium generating lenr reactions take place in these hot spots accompanied by a very small fraction of neutrons. During the last few years several researchers have reported detecting a variety of transmutation reaction products in localized sites, often associated with some type of crater formation. Other experimenters have reported online detection of flashes of “thermal hot spots” in their cathodes. It is therefore tempting to speculate that perhaps the concept of micro-nuclear explosions can be extended to heat generating helium producing reactions too, as well as nuclear reactions responsible for transmutation products. Many theoretical models such as those that depend on the catalyzing role of some exotic intermediate agent (such as Bose-Einstein condensates, deuteron clusters, Erzsions, poly neutrons, trapped neutrons etc) seem to point to the possibility of occurrence of chain events. Two decades into the CMNS era, it is therefore worthwhile re-examining the merits of the micro-nuclear explosion hypothesis and seek independent experimental evidence to either corroborate or refute such a hypothesis.

1. Summary of the early BARC findings

Two decades of wide ranging research has shown that low energy nuclear reactions take place primarily on the surface rather than in the bulk metal, the growing preference for thin films, small diameter wires and nano powders being an indication of this. Further there is convergence of perception that even on the surface, these reactions occur only at certain special locations referred to as “Nuclear Active Environment” (NAE) [1] which are thought to be created during the dynamic transport of deuterons (or protons) in and out of the metal, often initiated by some type of triggering mechanism. However the exact nature of the NAE continues to be elusive.

In the present paper we wish to bring into the conversation the aspect of “localised time” in addition to localised space, governing the occurrence of these reactions. In other words we raise questions regarding the temporal characteristics of the NAE. It is reasonable to expect that NAEs will not all be created simultaneously and uniformly over the entire host metal surface and also, once created, would not be able to continue catalyzing nuclear reactions for “ever”. Thus it may be postulated that NAEs are continuously generated and destroyed and during their “lifetime” they trigger a certain number of nuclear reactions. A pertinent question that then arises is : what could be the duration of the lifetime of the NAEs ? Could it be possible that their lifetimes is as small as nanoseconds or microseconds?

This line of thinking leads us to postulate that the lenr phenomenon could comprise of a series of “bursts” of nuclear reactions, each burst composed of “x” numbers of nuclear reactions generated by an NAE site during its lifetime. What could be the temporal characteristics of the reactions within a single nuclear “burst”? Could these individual reactions be “chain correlated”, with each new reaction being triggered by the previous or an “exotic” agent or particle responsible for catalyzing these reactions? Alternately the entire “x” numbers of reactions could all take place simultaneously in a coherent fashion, in a “flash”; In either case we are presented with a micro-nuclear explosion!

These speculative considerations are not entirely imaginative but arise out of the multiplicity distribution of neutron counts measurements that our group had carried out during the first few years following the Fleischmann-Pons announcement, with both electrolytically loaded Pd cathodes as well as gas loaded Ti targets. These early measurements led us to conclude, even as far back as 1989 [2], that micro-nuclear explosions are possibly responsible for the generation of tritium in highly localised hot spots. In this paper we first review the sequence of experimental findings that led us to such a conclusion and then go on to examine whether there is any case for extending the concept of micro-nuclear explosions to other nuclear reactions that have been observed in the lenr field.

2. Summary of the early BARC findings

Within days of the Fleischman-Pons announcement in march 1989 a dozen independent groups from various divisions of BARC set up electrolytic cells using whatever materials were readily available. Clear evidence was obtained for the production of neutrons and tritium, signatures of the occurrence fusion reactions, but with the difference that tritium production was higher by several orders of magnitude as compared to neutrons. A comprehensive review of these early BARC results in which over 50 researchers were involved [3] has just been re-published [4]. The main findings are summarised below :

2.1 BARC finding # 1 - Neutron to tritium branching ratio: Majority of the BARC cells produced both neutrons and tritium [5] with the neutron to tritium yield ratio being in the range of $\sim 10^{-7}$ rather than the expected value of unity. BARC groups were among the first to publish [2] this unexpected feature of neutron and tritium production in electrolytic cells. This so called “branching ratio anomaly” has since been observed by several other groups also, inclusive of with devices where in the deuterium loading into titanium samples was effected by gas loading methods. The branching ratio anomaly essentially signifies that on an average one neutron is generated for every 10 million tritons. Surprisingly neutron and tritium production was also noticed in a couple of instances even after the cell current had been switched off in the case of electrolytic cells or with unperturbed TiD_2 targets just sitting on the table, a behaviour which has since come to be alluded as “life after death” in CMNS literature.

2.2 BARC finding # 2 - Simultaneity of production of neutrons and tritium: In electrolysis experiments neutron yield is measured online using standard neutron pulse detector set ups (BF_3 counters, proton recoil type scintillators etc), while tritium production is measured off line employing liquid scintillation techniques, with the electrolyte being sampled typically once or twice a day or at times once in a few days. In the BARC experiments it was noted that invariably the tritium levels indicated a jump only after one or more neutron emission “spikes” had been detected. Figs 1 & 2 reproduced from Reference [5] bring out this behavior.

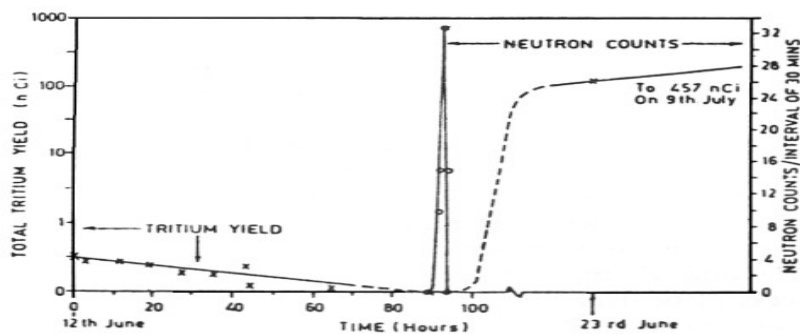


Fig. 1 - Concomitant generation of neutrons and tritium during run 2 of the first Milton Roy cell.

It was inferred from these that neutrons and tritium are probably produced simultaneously. Simultaneity in time would also imply co-generation at the same spatial location as a product of the same event, since it is difficult to conceive of a mechanism responsible for concomitant generation from spatially separated sites since otherwise we are faced with an action-at-a-distance problem.

2.3 BARC finding # 3 - Multiplicity distribution of neutron emission: BARC groups were the first [2,6] and perhaps the only group so far, to have carried out a detailed experimental analysis of the

statistical characteristics of the neutrons emitted by lenr devices. The question we asked ourselves was : Are the neutrons put out by these devices being emitted one at a time following Poisson statistics or are they emitted in bunches of 2, 10 or 100s ? We were inspired to ask such a question primarily because one of us had, decades earlier, carried out a Masters thesis study on the neutron density (or flux) fluctuations in a zero energy experimental fission reactor using the so called Feynmann alpha method [7]. He had the experimental background and familiarity with the statistical analysis methodology readily available to quickly set up the hardware to measure the multiplicity distribution of neutron emission. The details of this are elaborated on further in Section 3 below in view of its central importance to the main theme of the present paper.

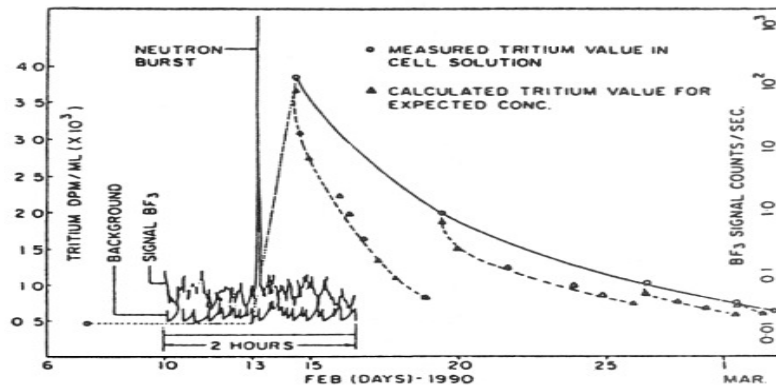


Fig. 2 - Increase of tritium concentration in electrolyte following neutron burst in ROMG cell.

The results of neutron multiplicity studies, repeated on many different lenr devices, clearly indicated that a non negligible fraction (6 to 15%) of the neutrons produced were in bunches of 20 to 400, the exact fraction and magnitude of the bunches being dependent on the efficiency of the neutron detection set up, the characteristics of the lenr device and the type of the deuterium loaded target metal. The intriguing question raised by this finding which has puzzled this author for the last two decades is : what could be the mechanism by which such bunched neutron generation takes place?

2.4 Implication of BARC findings 1, 2 and 3 taken together: If for every neutron produced 10 million tritons are generated “simultaneously” and if say a 100 neutrons are emitted in a bunch then it could be surmised that 10^9 tritons are produced in the form of a micro-nuclear explosion. In this context we have already considered arguments which suggest that all this must be taking place at a highly localized site, because otherwise we would be obliged to invoke an appropriate action-at-a-distance mechanism. In the following it is shown that this is precisely what the autoradiographic images seem to indicate.

2.5 BARC finding # 4 – Tritium found mainly in hot spots in gas loaded Ti targets: BARC groups deployed autoradiography as a very powerful tool to identify the location of tritium embedded in deuterated titanium targets [8]. The samples were placed close to but not touching medical x-ray films giving exposure times in the region of 20 to 60 hours. Both deuterium and hydrogen loaded palladium and titanium samples were investigated. We also carried out a number of basic studies to understand the mechanism of production of images in photographic films deploying various thin absorbers between the target and the photographic film. Such experiments clearly ruled out the possibility that these images could be artifacts caused by chemical reaction of the metallic sample being in direct contact with the emulsion of the photographic film. Besides, in the case of titanium targets, the presence of tritium in the surface layers of the target could be cross checked by measuring the 4.5 kev Ti K- α x-ray, as well as the direct measurement of the 18 Kev tritium β s [9]. In the case of Pd samples however the threshold for production of Pd K- α x-ray is too high for the 18 Kev tritium β s and only direct counting of the tritium β particles needs to be adopted.

It was conclusively established in a variety of gas/plasma loaded titanium target experiments that in the case of machined (cold worked) samples, the tritium generated by low energy nuclear reaction processes is invariably lodged in lattice defect spots and crevices where the metal was subject to severe cold working (edges for example) [10]. For example the plasma focus anodes which were subject to several

charge discharge shots in particular gave spectacular images of the top surface [11]. The auto-radiographic images of rod TA 1, repeatedly measured again and again over a period of five years were remarkably reproducible showing that tritium remains entrenched for years in the same spot in titanium. This observation is indicative of the fact that the tritium must have been produced at these spots and could not have migrated and accumulated there after being generated elsewhere.

Thus as concluded in sec 2.4 the first three BARC findings alone are adequate to support the micro-nuclear explosion hypothesis. But the spotty autoradiographs in titanium further strengthens this speculative hypothesis.

3. Brief review of the neutron multiplicity measurements

3.1 Basis of time resolved detection of individual neutrons of a simultaneously emitted bunch:

When a bunch of simultaneously produced fast neutrons impinges on a large hydrogenous moderator assembly in which one or more thermal neutron detectors such as BF_3 or He^3 gas proportional counters are embedded, because of the statistical time spread (typically about 25 μs) that occurs during the neutron slowing down process, a certain fraction of the total number of neutrons emitted would get separately and individually detected in a time resolved manner, the exact fraction depending on the geometrical efficiency and other factors. The resultant time series of electronic pulses issuing from the neutron detector set up can then be analysed for its statistical properties, especially the degree of departure from Poissonian nature, in order to yield information on the neutron multiplicity spectrum.

3.2 Experimental techniques for statistical analysis:

Two different techniques were used to determine the statistical characteristics of the pulse train issuing from the BF_3 or He^3 neutron counter banks. In the first method the frequency distribution of counts in 20 ms time bins was recorded [6]. In each sweep of the pulse train there were 1000 such bins, with a 280 ms separation between the 20 ms bins (as required by the data acquisition system), consuming in all a real time duration of 5 minutes per 1000 bin sweep. (The duration of the counting interval selected, namely ~20 ms, was a compromise between the total volume of data required to be stored and the resolution time of the study.)

The second approach to measuring the statistical characteristics of the pulse train was an adaptation of the “artificial dead time” method [6,12] developed originally for investigating neutron density fluctuations in experimental fission reactors [7,13] as well as for the passive neutron assay of plutonium in the safeguards field [14,15]. When more than one neutron from a neutron burst is registered by the BF_3 or He^3 detectors, the corresponding electronic pulses will all be time correlated and closely spaced within about 100 μs of each other. In such events the second, third and subsequent pulses of the “family of pulses” are diverted by a 100 μs wide “artificial dead time gate” into a separate “burst counts analyzer”, while the leading pulses are totalized separately. The computerized burst counts analyzer then carries out a frequency of counts analysis to give the multiplicity spectrum of the neutron counts.

3.3 Theoretical considerations[16] :

For a purely random (Poisson) pulse series wherein N_0 is the average count rate and τ is the counting bin time interval (in this case 20 ms) and for the case when $N_0\tau$ is $\ll 1$, the probability of registering one count in a single 20 ms interval is $N_0\tau$, while $[(N_0\tau)^2]/2!$ gives the probability of getting doubles, $[(N_0\tau)^3]/3!$ that of getting a multiplicity of three counts and so on. Note that the probability of getting higher order multiplicity counts decreases steadily, since $N_0\tau$ is much less than unity.

If now there are ζ burst events per second generating ν neutrons per burst, superimposed on the random background and the neutron detection efficiency is ϵ , then the contribution of the burst events to the overall count rate would be $\zeta\nu\epsilon$. The probability of getting r counts in time τ from burst events is governed by a binomial distribution. Table I of ref. [16] summarizes the expressions for the contribution to the various orders of multiplicity counts from random and burst events. Table II of the same paper gives numerical examples with typical parameters for the expected frequency distribution of counts for random and bunched neutronic events. The main point brought out is that whereas for random events and low count rates, the probability of getting doubles, triples etc. is extremely small, in the case of burst

events these probabilities are non-negligible. It is noteworthy that for burst events the peak of the multiplicity distribution actually shifts to higher multiplicity values as the product $v\varepsilon$ increases. Thus when the product $v\varepsilon$ exceeds unity (as for example when a bunch of 100 neutrons are emitted in a single event and detection efficiency ε is 10% in which case the magnitude of $v\varepsilon$ is 10) the probability of registering three or four counts per interval could be even higher than that of singles or doubles counts!

4. Summary of neutron multiplicity measurement results

Neutron Multiplicity measurements were carried out both with a large cathode area Milton Roy type Pd-D₂O electrolytic cell [3,5] as well as some gas/plasma loaded TiD₂ targets. In these “first attempt” experiments conducted in 1989 only the frequency spectrum type analysis was performed. Unfortunately the overall neutron detection efficiency was only around 1 to 1.5%, primarily due to the poor geometrical arrangement of the detector assembly with respect to the source of neutrons. In general we were happy to note that the equipment functioned very satisfactorily, with the no source background counts both of the foreground detector as well as the background detector strictly obeying Poisson statistics. Never were multiplicities beyond doubles ever recorded in background runs. One of the unexpected surprises, as already commented upon, was that both a shut off but previously operated electrolytic cell, as well as stand alone TiD₂ targets, produced neutrons even in an unperturbed state. In all these runs the neutron yield was in the form of distinct spikes superimposed on a steady background.

The 1994 campaign was conducted with a newly procured Milton Roy cell. This time the electrolyte used was LiOD instead of NaOD which was used in the 1989 runs. (The manufacturer recommended only NaOD. This is being emphasized since use of LiOD could have had a bearing on the neutron production characteristics of the new Milton Roy cell.) We used a large annular neutron detector set up inside the central location of which the electrolytic cell was mounted giving a neutron detector efficiency as high as ~ 10%. For statistical analysis of the pulse train the improved artificial dead time technique discussed earlier was employed. The experiment was conducted over a two month period: The first 15 days were used to collect background data. The second one month was with the fully operating Milton Roy cell in place; For the last 15 day run LiOD electrolyte was replaced by LiOH. We thought we were doing a control run; but it turned out that the Pd cathodes probably still had deuterium loaded from the previous one month run. It was evident from the neutron counts data that the deuterium was slowly getting replaced with hydrogen over the 15 day period.

Detailed descriptions of all these measurements and results are available in refs. [2 to 6, 12,16]. In all the runs the foreground counter gave clear evidence of several higher order neutron multiplicity events. In some cases in the 1989 campaign the peak of the multiplicity spectrum was in the 4 or 5 neutron pulses region. Since the overall neutron detection efficiency in those runs was only ~ 1 % this would imply that in these runs approximately 400 to 500 neutrons were produced in each of the “explosive bursts”. In the 16th June 1989 run with the first Milton Roy cell for example wherein a two hour long neutron spike episode occurred multiplicities as high as 15 were recorded during the last 5 minute interval, implying that a burst of 1500 neutrons was produced in a flash incident.

In the 1994 campaign during the D₂O run with the new Milton Roy cell in spite of the higher neutron detection efficiency, the maximum multiplicity recorded was only around 8 counts, pointing to a burst strength of not more than 80 neutrons. It must however be noted that in this experiment the average magnitude of the neutron output was only ~ 10 % above the background values and there were no clearly distinguishable spikes superimposed on the background values. In response to a possible criticism that a mere 10 % above background levels could be “suspect”, it may be pointed out that when the LiOD was replaced with LiOH the neutron count rate steadily decreased to background values over a 15 day period confirming that the neutrons are indeed produced by lenr processes [12].

5. Discussion and Conclusions

On the whole there is unmistakable evidence that whenever lenr sources produce neutrons, a significant fraction (6.5% to 25%) [6,12] of these are emitted in the form of bunches of magnitude varying from 20 to several hundreds, the exact magnitude depending on the type of lenr source. In this context it is however worth emphasizing that, for example, if the neutron detection efficiency ε is say 1 % and one neutron count is registered it could still have resulted from a single burst of 100 neutrons on account of

the 1% detection efficiency! Thus the balance 75% to 93.5 % which although detected as singles counts could still have resulted from bunched neutron emission. The key to successful observation of neutron multiplicity is high neutron detection efficiency and perhaps use of the dead time method.

We are suggesting that each of the hot spots where tritium was found to be concentrated in our measurements could perhaps be associated with an NAE site discussed in lenr literature [1]. Based on the BARC findings we therefore postulate that once an NAE is formed a rapid cascade of 10^8 to 10^{10} tritium producing nuclear reactions takes place in rapid succession in this local site, in a sort of chain or cascade event, during which process on an average for every ten million tritium nuclei generated one neutron is also emitted as a very low probability offshoot side reaction event!

We then go on to further speculate that if neutrons and tritium could be produced in micro-nuclear explosions then possibly other nuclear reactions such as those responsible for heat and helium as well as transmutation products could also possibly take place in similar micro-nuclear explosions. As noted earlier the observed craters in post run cathodes could be an indication of such events.

However we emphasize that the main experimentall measured parameter fuelling all these speculations is neutron multiplicity and hence statistical analysis experiments of the type described in this paper warrant attempts at replication.

Acknowledgements

The author wishes to place on record the significant contributions of his former colleagues and co-authors of many of the referenced papers in the conduct of the experiments reviewed here, notably P.K.Iyengar, S.B.Degwekar, A.Shyam, T.C.Kaushik, R.K.Rout and L.V.Kulkarni.

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Comparison Between Piezonuclear Reactions and CMNS Phenomenology

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Abstract. The purpose of this paper is to place side by side the experimental results of Piezonuclear reactions, which have been recently unveiled, and those collected during the last twenty years of experiments on low energy nuclear reactions (LENR). We will briefly report the results of our campaign of experiments on piezonuclear reactions where ultrasounds and cavitation were applied to solutions of stable elements. These outcomes will be shown to be compatible with the results and evidences obtained from low energy nuclear reaction experiments. Some theoretical concepts and ideas, on which our experiments are grounded, will be sketched and it will be shown that, in order to trigger our measured effects, it exists an energy threshold, that has to be overcome, and a maximum interval of time for this energy to be released to the nuclear system. Eventually, a research hypothesis will be put forward about the chance to raise the level of analogy from the mere comparison of results up to the phenomenological level. Here, among the various evidences collected in LENR experiments, we will search for hints about the overcome of the energy threshold and about the mechanism that releases the loaded energy in a suitable interval of time.

First of all we would like to warn the reader that due to the limited length allowed for the manuscript we will only mention the results and the main experimental features both for piezonuclear reactions and CMNS experiments and leave the comprehensive descriptions to the references. The subject will be dealt with on a qualitative level since the goal of this paper is only to show a new possible perspective and promote discussion on it.

1. Evidences of Piezonuclear reactions

All of the experiments that we have carried out, involved the application of ultrasounds with a frequency of 20 kHz and suitable power (between 100 and 130 Watts) to liquids either bidistilled deionised water [1, 2, 3] or solutions of bidistilled-deionised water and some standard stable chemical elements [4, 5]. In [1, 2] we report two evidences: an increase of the proportion of a few high mass number stable isotopes (including uranium) and an increase of the proportion of a few nuclear species within the particular atomic mass range $238 < M < 264$ (including transuranic elements). In the third experiment [3], aimed at detecting elements in the so called rare-earth mass range, ICP mass gave evidence of a significant peak corresponding to a nuclide with atomic mass (137.93 ± 0.01) amu and half-life 12 ± 1 sec, identified as Eu_{63}^{138} . The candidate identified, Eu_{63}^{138} , does not exist in nature; it is an artificial (discovered in 1995-97 [6]) that can be produced at the present time in nuclear reactors and by synchrotrons. The ionising radiation measurements, by LR115 detectors, that were carried out during the application of ultrasounds in all of these experiments, did not provide any evidence of ionising radiation above the background level. Further experiments were designed in order to try and detect possible neutron emission [4,5]. We subjected to cavitation, bidistilled deionised water, solutions of Lithium, Aluminium, and Iron. Being equal all the experimental conditions, but the element, we obtained reproducible evidences of neutrons bursts only with Iron. A further unusual circumstance was the lack of any gamma radiation (above the background level) that usually comes along with the emission of neutrons. Neutrons were measured by

three techniques: bubble detectors, Boron screened CR39 and Boron Trifluoride. A further experiment was performed in order to verify the effects of these new mechanisms induced by ultrasounds and cavitation on radioactive nuclei [7,23,24]. The evidences indicated that the initial quantity of Thorium became half in a interval of time 10000 times faster than Thorium half life. However it turned out that this process was not a mere acceleration of the usual Thorium decay by emission of alpha particles, since the number of tracks on the CR39 detectors that monitored the radioactive process was not compatible with this possibility [23,24].

2. Evidences of Low Energy Nuclear reactions

We will try and group the apparently anomalous results obtained by different teams and techniques in LENR in order to point out the possible analogies among these outcomes and those collected in the experiments of piezonuclear reactions. We will summarise the results by referring to the book "The Science of Low Energy Nuclear Reactions" by Edmund Storms [8]. Independently from the method used to induce LENR there were clear signs of transmutations and most of the times the resulting products were Fe, Zr, Cu, Ni, Cr and other nuclides with comparable mass and binding energy per nucleon. Besides, the nuclides belonging to the substrates, used in all of the experiments, had considerable atomic mass ranging from 48 up to 197 amu (Ti, Ni, Pd, W, Au). The environment, in which the substrate was immersed, contained different substances and chemical compounds which contained much lighter nuclides like H, D, Li, Na, K, C, N, O, Cl, and sometimes other heavier ones compatible with the atomic mass of the nuclides of the substrate. Both in piezonuclear reactions experiments and in LENR experiments there are transmutations that involve medium weight or heavy mass number nuclides and produce other intermediate and heavy mass number nuclei¹ (neither fusion nor fission can be invoked [8]). In LENR neutron emission was very low and infrequent while in piezonuclear reactions it was not infrequent but nevertheless it was low and apparently not compatible with known nuclear reactions because of the lack of gamma rays (above the background level). Gamma rays are expected either to follow emissions of neutrons or, at least, to come from the interaction of neutrons and matter (mostly Hydrogen in this case). However, further and more discriminating measurements will certainly be necessary. As to other kinds of radiation emitted during LENR, many different types were detected, which, however have not helped in identifying clear common features among the different experiments and techniques. Among all of them it is worth noting that some teams detected a strange radiation showing unknown features and behaviour [8, 9] which, from our point of view, could be put beside the strange lack of gamma rays which, at least from hydrogen neutron capture, should be emitted. As it will become clear from the next section, it was not our goal to perform extra power or heat measurements during piezonuclear reaction experiments, and hence no comparison can be made on this ground.

3. Local Lorentz Invariance Breakdown

The theoretical background, on which our experiments have been designed and carried out, is based on the concept of breakdown of Local Lorentz Invariance (LLI) [10, 11, 12]. Our phenomenological theory concentrates on the structure of local (microscopical) space-time (flat and rigid according to LLI) when LLI is broken. The coefficients of the local Minkowski metric tensor are hypothesised to be function of the energy of the process. This means that space-time is locally deformed and plays an active part in the dynamics of the physical process whose features and flow deeply depart from their usual appearance. The theory predicts that the space-time of strong interactions begins to be deformed when the energy of the process overcomes a threshold equal to 367.5 GeV [10, 11]. Besides it clearly states that there is no isochrony between the time of the experimenter and that of the hadronic process. To put it in a more practical way, this means that in order to deform space-time around a nucleus (or nuclei) and hence trigger "anomalous" processes, in the fashion of those presented above from piezonuclear reactions, one has to use a microscopical mechanism that loads an amount of energy higher than the energy threshold and then it is capable to release it in a suitable interval of time or in other words it is capable of a

¹ In piezonuclear reactions the heavy nuclides which can be placed side by side to the LENR substrate are those contained in the alloy of the sonotrode.

suitable power (energy divided by time). This theoretical background shows that our experiments were not in wake of the LENR ones, but their target was to obtain some evidences that would corroborate the two predictions mentioned above about the threshold energy and the release mechanism².

4. LLI and anomalous nuclear processes

It has been shown that the results of LENR experiments and those of piezonuclear reactions are compatible. Thus, despite the apparent diversity of the experimental set-ups and conditions, it is possible to hypothesise that similar outcomes are brought about by similar microscopical mechanisms that trigger alike anomalous nuclear processes. Now, let us evidence the phenomenological aspects that, within piezonuclear experimental set-ups, fulfil the two conditions mentioned above. Once that these aspects are clear we will try and analyse some LENR set-ups and evidences in order to make out similar features. The collapse of a generic bubble under the huge pressure of ultrasounds, that induces shock-waves on its surface, is regarded as the microscopical mechanism to fulfil the two requirements. As mentioned before, we obtained neutrons only with the solutions of Iron and their emission took place after 40 – 50 minutes the ultrasounds had been turned on, which can be interpreted as the time to reach and overcome the energy threshold. However, the overcoming the energy threshold needs to be referred to the context and the environment where the process takes place and in particular to the types of nuclides involved. The collapse of the bubble concentrates energy in a smaller and smaller region of space (which is actually space-time whose volume is still an open question of the theory), making the energy density higher and higher. In this region of space-time nuclear species are forced. The overcoming of the threshold is achieved by the complementary contributions of the external energy (ultrasounds) and internal energy, i.e. that of the nuclides taking part in the collapse. In this sense, the first preliminary clue is that the higher the atomic mass the less external energy and the shorter time interval it takes to deform locally the space-time. Thus, a first preliminary phenomenological sketch of piezonuclear reactions can be depicted as follows: pressure combined with a mechanism that allows an abrupt release of energy within a suitable interval of time bring about piezonuclear effects. The pressure is produced by ultrasounds, the mechanism is the collapse of the bubble³. Their synergy along with nuclides with high atomic mass form the Nuclear Active Environment (NAE) in our experiments. Now let us try and see if it is possible to spot within LENR experimental set-ups, where ultrasounds are not used, the counterparts of pressure and bubble collapse. Due to the preliminary character of these ideas we will focus our attention on one of the many different techniques and in particular on the evidences collected by an electrochemical cell with Pd/D co-deposition which, first of all, is the LENR technique more similar to that used by Fleischmann and Pons and more over it seems the farthest from the piezonuclear reactions set-up. In particular, we refer to the experimental set-up and procedure used by Mosier-Boss et al. which is described in [15]. In their experiments the metals used for the cathode were Ni, Ag, Pt, Au and the solution contained $PdCl_2$ and $LiCl$ or KCl in heavy water. In control experiments $PdCl_2$ was substituted for $CuCl_2$. We will not go through the description of the experimental process, but we will only say that the procedure comprises different phases when the Pd/D co-deposition is formed and when current is periodically increased and an intense electric or magnetic fields is applied. All the details can be found in [15, 16, 17, 18] and the references cited in them. Our target is to look through these details and make out those features that may fulfil the two requirements mentioned above: energy threshold (pressure or energy density) and releasing time (releasing mechanism). Bubble collapse is a far from equilibrium process where energy is locally concentrated around the surface of the bubble and suddenly released with great intensity. Thus, we will have to search in the electrolytic technique for leads pointing toward these three characteristics (far from equilibrium, local loaded energy, local abrupt release of it). From the description in [16] the researchers state that “the experimental protocol covers three time periods” and that the third period of time is used “to put the system in a far from equilibrium condition” which is obtained by applying an intense static electric or magnetic field and by letting the electrolysis proceed by keeping increasing the current from time to time. It is fairly reasonable to consider that a co-deposition of Pd/D is in itself an unstable structure in which atomic bonding between Palladium atoms are deformed, stretched, and weakened by

² This explains why we have never used deuterated substance, never look for Helium or Tritium and never attempted to measure the presence of extra heat.

³ Critical parameters are the dimension of the bubble and the number of ions of the specific nuclide present on the its surface.

the presence of Deuterium. To confirm this, one can put forward the fact that LENR experiments have begun to be carried out in the last few years not by loading Deuterium in bulky Palladium, but rather by co-depositions Pd/D or by nanostructured Pd. These methods produce greater quantities of anomalous evidences than those with solid Pd [8, 15, 19]. That the loading of mechanical energy in Pd is brought about by Deuterium, is confirmed by experiments in which the solution contained CuCl_2 instead PdCl_2 . Copper does not absorb Deuterium, no lattice deformation is brought about, no mechanical energy gets loaded and hence no reactions take place [15]. The statements by Storms [8] in his book seem to move in the same direction. He reports that "...the basic material used as cathode is not active initially even when it is made of Palladium - activation is required. Nevertheless, the base material does affect the morphology and subsequent activity of the deposited layer...". All of these conjectures can be considered a sound and promising lead⁴ from the experimental conditions about the possible fulfilment of the first requirement of LLI breakdown hypothesis: existence of an energy threshold. We concentrate now on the second requirement: the mechanism to release this loaded energy. In the experimental accounts [16, 20] the researchers mention a shape change in some areas of the cathode at the end of the electrolysis. Indeed, the structure at the cathode is a complicated and microscopically feeble equilibrium of three layers: the substrate (Ni, Ag, Pt, Au), the co-deposition Pd/D and the solution. We reckon that the application of an electric or magnetic field and the increasing current during electrolysis may generate microscopical conditions compatible with those found in piezonuclear reaction experiments where cavitation took place. As a bubble is a local frail inhomogeneity within a liquid which can be squeezed and deflated⁵ by squeezing it using ultrasounds, the locally frail structure of Pd/D co-deposition presents local inhomogeneities or hollows (e.g. gradients of the density of Pd and/or D atoms) whose sudden and violent collapse can be induced by bringing the systems to a far from equilibrium condition (electric or magnetic field, periodical increase of current, continuous flow of Deuterium through the co-deposited layer). As Iron atoms (not light elements) are entrapped in the interface gas/liquid of bubbles and are launched against each other during the collapse and forced in a smaller and smaller volume of space-time until the energy threshold is reached and overcome in a precise interval of time, Palladium atoms might endure similar processes as hollows in Pd/D co-deposition are made collapse. In [8] cracks are indicated as "...the only environments obviously common to all successful experiments...". Always in [8] it is said that Palladium expands as it is loaded with Deuterium and cracks of different dimensions form during this process. Besides cracks are said to be present in Pd/D co-depositions or Palladium black. Some questions are raised as to how cracks are involved in the cold fusion process, or as to how cracks operate to allow Coulomb barrier penetration, or as to how dimensions of cracks influences the formation of a NAE. Eventually, cracks are said to be good candidates to be a NAE. From our point of view and from these statements, cracks can be considered in this experimental system the counterparts of bubbles in cavitation [21,22]. However we reckon that it is not correct look at the NAEs that form in our experiments and in all of the LENR/CMNS experiments from the point of view of the well known nuclear processes and all the concepts involved in them like Coulomb barrier and other quantum mechanical concepts. We believe that this statement is more than corroborated by loads of compatible anomalous evidences collected in these 20 years by different institutions and researchers, different techniques spread all over the world. Before concluding, we would like to point out one more thing. We said that, high atomic mass nuclides contribute to facilitate the overcoming of the energy threshold when they are forced in a smaller and smaller region of space-time. This qualitative picture may induce to think that starting from Palladium, one should obtain heavier nuclei like in a sort of new type nuclear fusion. However in [16] it is reported of transmutations whose products were Aluminium, Magnesium, Chlorine, Silicon which are all lighter nuclides than Palladium. Since these transmutations are thought to be brought about by space-time deformation, it is possible that a heavy nuclide be ripped apart into lighter nuclides by tidal forces i.e., in more picturesque way, as an astronaut would be as he were falling into a black-hole.

⁴ A lead in the sense that deeper investigation, experimental, theoretical and phenomenological will have to be carried on from this point.

⁵ We remind that in our phenomenological model the generic bubble deflates while being squeezed by a shock-wave. In other words it is not treated as mean to compress the gas contained in it in order to reach hot fusion conditions.

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Piezonuclear reactions in inert solids revealed by neutron emissions from brittle fracture

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Abstract. Neutron emission measurements by means of ³He neutron detectors were performed on solid test specimens during crushing failure. The tests were carried out at the Laboratory of Fracture Mechanics of the Politecnico di Torino. The materials used were marble and granite, selected in that they present a different behaviour in compression failure (i.e., a different brittleness index) and a different iron content. All the test specimens were of the same size and shape. Neutron emissions from the granite test specimens were found to be of about one order of magnitude higher than the natural background level at the time of failure. These neutron emissions should be caused by nucleolysis or piezonuclear “fissions” that occurred in the granite, but did not occur in the marble: $\text{Fe}_{26}^{30} \rightarrow 2\text{Al}_{13}^{14} + 2 \text{ neutrons}$. The present natural abundance of aluminum (7-8% in the Earth crust), which is less favoured than iron from a nuclear point of view, is possibly due to the above piezonuclear fission reaction.

1. Introduction

We consider samples of marble and granite rocks, containing different amounts of iron, loaded in compression until failure [1,2]. As ultrasounds induce cavitation in the liquids and then bubble implosion accompanied by the formation of a high-density fluid or plasma [3], so shock waves due to compression rupture induce a particularly sharp strain localization in the solids and then material interpenetration accompanied by an analogous formation of a high-density fluid or plasma [2]. Our experiment follows a different path with respect to those of other research teams, where only fissionable or light elements (deuterium) were used, in pressurized gaseous media [4,5], in liquids with ultrasounds and cavitation [6], as well as in solids with shock waves and fracture [7-12]. We are treating with inert, stable and non-radioactive elements at the beginning of the experiments (iron) [1,2,13], as well as after the experiments (aluminum). During the experiments neutron emissions in thermal and fast energy range were detected.

The materials selected for the compression tests –performed at the Laboratory of Fracture Mechanics of the Politecnico di Torino (Director Prof. Alberto Carpinteri)– were Carrara marble (calcite) and green Luserna granite (gneiss). This choice was prompted by the consideration that, test specimen dimensions being the same, different brittleness numbers [14] would cause catastrophic failure in granite, not in marble. The test specimens were subjected to uniaxial compression to assess scale effects on brittleness [15]. Four test specimens were used, two made of Carrara marble, consisting mostly of calcite, and two made of Luserna granite, all of them measuring 6x6x10 cm³. The same testing machine was used on all the test specimens: a standard servo-hydraulic press with a maximum capacity of 500 kN, equipped with control electronics. This machine makes it possible to carry out tests in either load control or displacement control. The tests were performed in piston travel displacement control by setting, for all the test specimens, a velocity of 10⁻⁶ m/s during compression.

Neutron emission measurements were made by means of a ³He detector placed at a distance of 10 cm from the test specimen and enclosed in a polystyrene case so as to prevent the results from being altered by acoustical-mechanical stresses. During the preliminary tests, thermodynamic neutron detectors of the bubble type BD (bubble detector/dosimeter) manufactured by Bubble Technology Industries (BTI) were used, and the indications obtained persuaded us to carry on the tests with ³He detectors [2].

2. Testing and neutron measurements

The neutron detector used in the tests is a ^3He type with electronic of preamplification, amplification and discrimination directly connected to the detector tube, which is of the type referred to as “long counter”. This detector was calibrated for the measurement of thermal neutrons; its sensitivity is 65 cps/ n_{thermal} ($\pm 10\%$ declared by the factory) i.e., the flux of thermal neutrons was 1 thermal neutron/s cm^2 , corresponding to a count rate of 65 cps. The laboratory neutron background was measured at 600 s time intervals to obtain sufficient statistical data. Before starting the tests the average background count rate was:

$$3.8 \times 10^{-2} \pm 0.6 \times 10^{-2} \text{ cps}$$

corresponding to an equivalent flux of thermal neutrons of

$$5.8 \times 10^{-4} \pm 0.9 \times 10^{-4} n_{\text{thermal}}/\text{s cm}^2.$$

During the compression tests neutron emissions were measured on four specimens, two made of marble, denoted with P1, P2, and two of granite, denoted with P3, P4. The test specimens were arranged with the two smaller surfaces in contact with the press platens, with no coupling materials in-between, according to the testing modalities known as “test by means of rigid platens with friction”.

The electronics of the ^3He detector was powered at least one hour before the background estimation, in order to avoid intrinsic thermal effects. The neutron background was measured during 600 s time intervals repeatedly, so to obtain sufficient statistical data for a preliminary period of more than three hours. Then the background measures were performed fixing at 60 s the acquisition time to make sure there were no variations. The acquisition time was fixed at 60 s and the results of count rate measurements are given in Fig. 1a and b together with the diagrams of the force applied to the test specimens as a function of the time elapsed since the beginning of its application. The measurements of neutron emissions obtained on the marble test specimens yielded values comparable with the background, even at the time of test specimen failure. The neutron measurements obtained on the two granite test specimens, instead, exceeded the background value by about one order of magnitude at the test specimen failure.

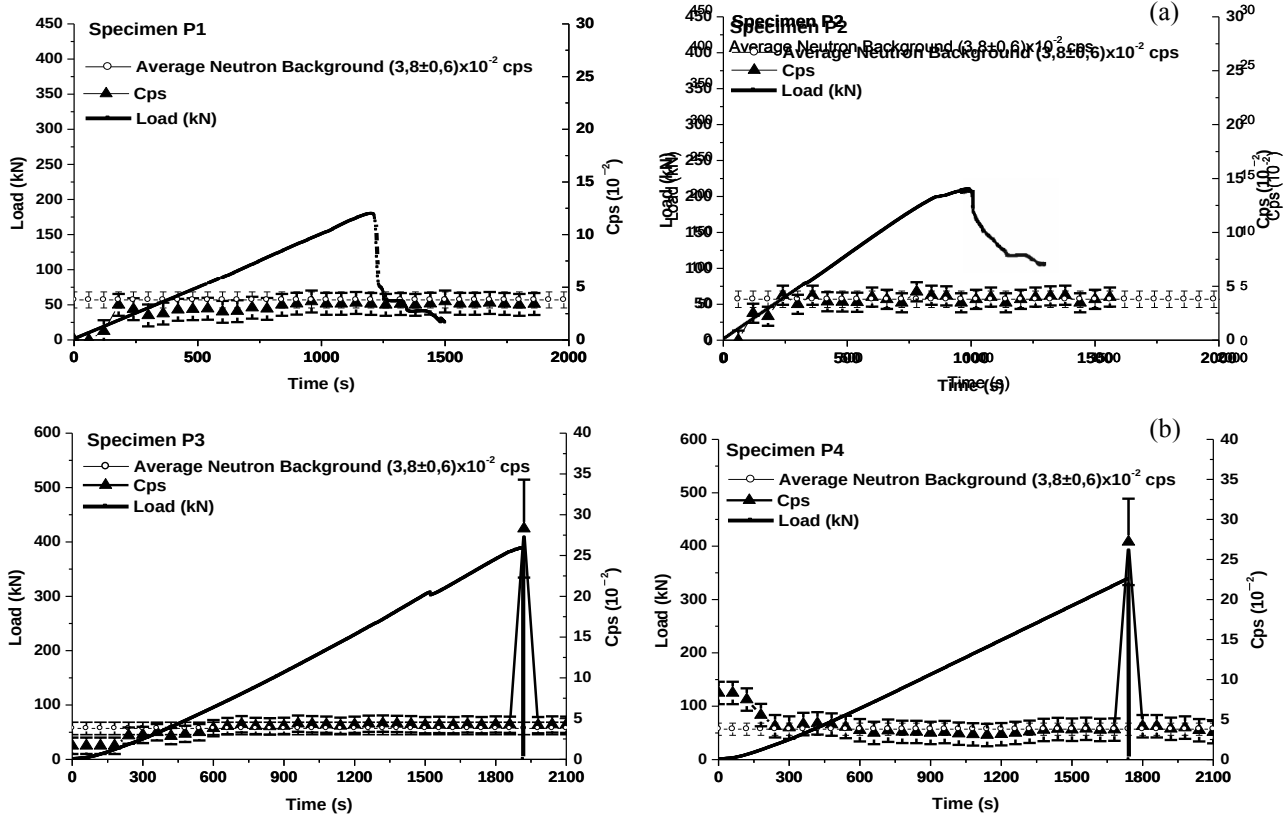


Fig. 1 – (a) Load vs. time and cps curves for test specimens P1 and P2 in Carrara marble, and (b) for test specimens P3 and P4 in Luserna granite.

After 20 min, test specimen P1 reached a peak load of ca 180 kN, corresponding to an average pressure on the bases of 50 MPa; after 15 min, test specimen P2 reached a peak load of ca 200 kN, corresponding to an average pressure on the bases of 55.6 MPa.

Test specimen P3 reached at time $T(P3) = 32$ min a peak load of ca 400 kN, corresponding to an average pressure on the bases of 111.1 MPa. When failure occurred, the count rate was found to be

$$28.3 \times 10^{-2} \pm 5.7 \times 10^{-2} \text{ cps}$$

corresponding to an equivalent flux of thermal neutrons of

$$43.6 \times 10^{-4} \pm 8.8 \times 10^{-4} n_{\text{thermal}}/\text{s cm}^2.$$

Test specimen P4 reached at time $T(P4) = 29$ min a peak load of ca 340 kN, corresponding to an average pressure on the bases of 94.4 MPa. When failure occurred, the count rate was found to be

$$27.2 \times 10^{-2} \pm 5.5 \times 10^{-2} \text{ cps}$$

corresponding to an equivalent flux of thermal neutrons of

$$41.9 \times 10^{-4} \pm 8.5 \times 10^{-4} n_{\text{thermal}}/\text{s cm}^2.$$

Notice how the above neutron measurements occurring in P3 and in P4 at failure are well beyond the background interval and how the value obtained on P3 is greater than the value measured on P4. We believe that this result, albeit with the due caution, may be ascribed to the unstable failure of these test specimens and the greater quantity of energy released by P3 compared to P4 at the time of failure. Figure 1a and b summarise the evolution of the neutron count rates together with the load vs. time curves for the four test specimens.

3. Discussion and remarks

Experimental data from rocks tested in compression generally indicate that this is a brittle material, since it exhibits a rapid decrease in load carrying capacity when deformed beyond a peak load. When the softening diagram is very steep, or even shows simultaneously decreasing strain and stress values, the material is said to present a snap-back or catastrophic behaviour. This is in contrast with ductile materials which retain considerable strength beyond the peak as shown in Fig. 2 [14-19].

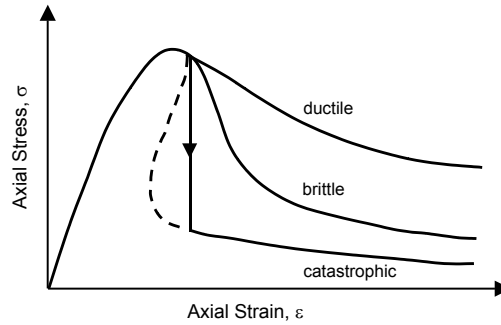


Fig. 2 – Ductile, brittle, and catastrophic behaviour.

In this study, all compression tests were conducted through feedback control of the axial displacement of piston travel on test specimens having the same dimensions. The complete failure process was observed only for P1 and P2 marble specimens, whose behaviour was seen to be ductile compared to the brittle catastrophic failure behaviour displayed by granite specimens P3 and P4. For the latter two, in fact, failure occurred instantaneously, without showing the descending branch of the load-time curve (Fig. 1a and b).

The elastic strain energy accumulated in the test specimens up to failure, ΔE , is given in Table 1. Moreover, for each test specimen, it is possible to draw some conclusions on the release rate of the elastic energy accumulated.

Table 1. Elastic strain energy at the peak load, ΔE .

Test specimen	Material	ΔE [J]	ΔE [eV $\times 10^{20}$]
P1	Carrara marble	124	7.75
P2	Carrara marble	128	8.00
P3	Luserna granite	384	24.00
P4	Luserna granite	296	18.50

One of the conditions to be met for piezonuclear reactions to take place is that the ratio, r , between the power of released energy, $W = \Delta E / \Delta t$, and the power threshold [13,21]:

$$W_{\text{strong}} = 7.69 \times 10^{11} \text{ W} = 4.8 \times 10^{30} \text{ eV/s} \quad (1)$$

be greater than or equal to 1 [13,20]:

$$r = W / W_{\text{strong}} \geq 1. \quad (2)$$

Accordingly, based on the data obtained from the tests, the time interval of released energy, Δt , in granite test specimens in which piezonuclear reactions have occurred, should satisfy the following relationship:

$$\Delta E / \Delta t \geq W_{\text{strong}}, \quad (3)$$

and hence:

$$\Delta t \leq \frac{\Delta E}{W_{\text{strong}}} = \frac{384}{7.69 \times 10^{11}} = \frac{24 \times 10^{20}}{4.8 \times 10^{30}} = 0.5 \times 10^{-9} \text{ s} = 0.5 \text{ ns} \quad (4)$$

Equation (4) was written by considering the energy accumulated in P3 which was greater than the energy accumulated in P4. For the marble test specimens, in which peak load is clearly followed by a softening branch, energy release surely occurred over a period of time too long to permit the production of piezonuclear reactions.

Considering that the elastic strain energy accumulated in specimen P3 is released at the pressure wave velocity v (for granite $v \sim 4000$ m/s), the extension of the energy release zone results to be equal to:

$$\Delta x = v \Delta t \sim 4000 \text{ m/s} \times 0.5 \text{ ns} \sim 2 \mu\text{m}.$$

Such energy release band width Δx could correspond to the critical value of the interpenetration length w_{cr}^c assumed by Carpinteri and Corrado [19] to explain the critical conditions for the catastrophic behaviour of solids in compression (Fig. 3). Accordingly, neutron emissions in granite may be accounted for by the fact that the power threshold for piezonuclear reactions is exceeded, as well as by the type of catastrophic failure that occurs, which entails a very fast energy release, over a time period of the order of a nanosecond.

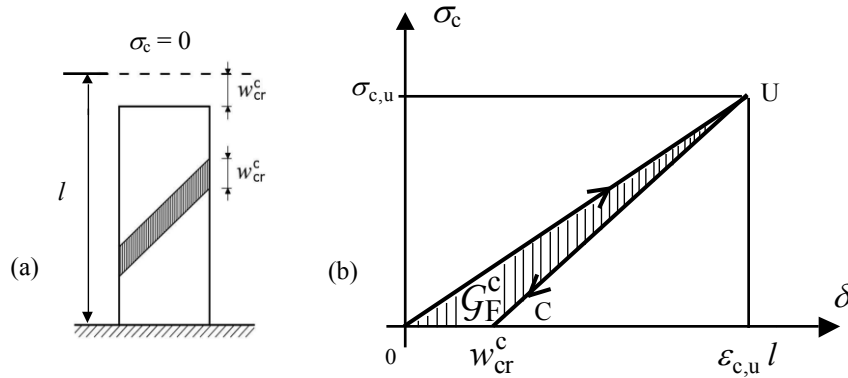


Fig. 3 – Catastrophic behaviour in a solid specimen during compression. (a) Conditions of complete interpenetration and critical value of the interpenetration length w_{cr}^c . (b) Stress vs. displacement response; $\sigma_{c,u}$ = ultimate compression strength; $\epsilon_{c,u}$ = ultimate compression strain; $\delta = \epsilon_{c,u} l$ = ultimate displacement, G_F^c = crushing energy.

If we consider the elastic energy stored in the sample and the temperature equivalent to this energy together with the final pressure before fracture, the material of the sample is in a region of the phase-space corresponding to a transition from solid to liquid phase. Our conjecture is that in the interpenetration layer of thickness w_{cr}^c the conditions are realized for a high density fluid, over-saturated but in metastable conditions. On the other hand, these locally extreme conditions could catalyse in the interpenetration band the formation of a plasma from the gases which are present in the solid materials (even at room conditions).

From this experiment it can be clearly seen that piezonuclear reactions giving rise to neutron emissions are possible in inert non-radioactive solids, in addition to liquids [1-3,13]. Anyhow, it is also evident that the availability of an amount of stored energy for the reactions exceeding the microscopic nuclear deformed space-time threshold

$$E_{0, strong} = 5.888 \times 10^{-8} \text{ J} = 3.675 \times 10^{11} \text{ eV}$$

is not sufficient *per se* [21]. The energy must be contained in a space-time (and energy) hypervolume such that $r \geq 1$, i.e., such that the phenomenon will actually develop in deformed space-time conditions [13,20]. From Table 1, in fact, it can be seen that it was $\Delta E > E_{0, strong}$ in all the test specimens loaded in compression, but r was greater than 1 only in granite test specimens. Hence, even for piezonuclear reactions in solids, the notion of stored energy must be combined with the notion of speed of energy release as is the case for liquids [1-3].

Another factor to be taken into account is the composition of the materials in which piezonuclear reactions may be produced. As we have already specified in the Introduction [1,2], the fact that the marble used in the tests contains only iron impurities (not more than 0.07% of Fe_2O_3), and granite instead contains a considerable amount of iron (around 3% of Fe_2O_3), could be another factor contributing to the phenomenon in question, by analogy with the case of piezonuclear reactions in liquids. In fact, piezonuclear reactions with neutron emissions were obtained in liquids containing iron chloride or iron nitrate subjected to ultrasounds and cavitation [3,13]. In the experiments on liquid solutions [3,13], aluminum atoms appeared at the end in a final quantity as large as about seven times the small initial quantity [22]. More precisely, they increased from 3.99 ppb to 27.70 ppb, without evident reasons, if we exclude possible transmutations.

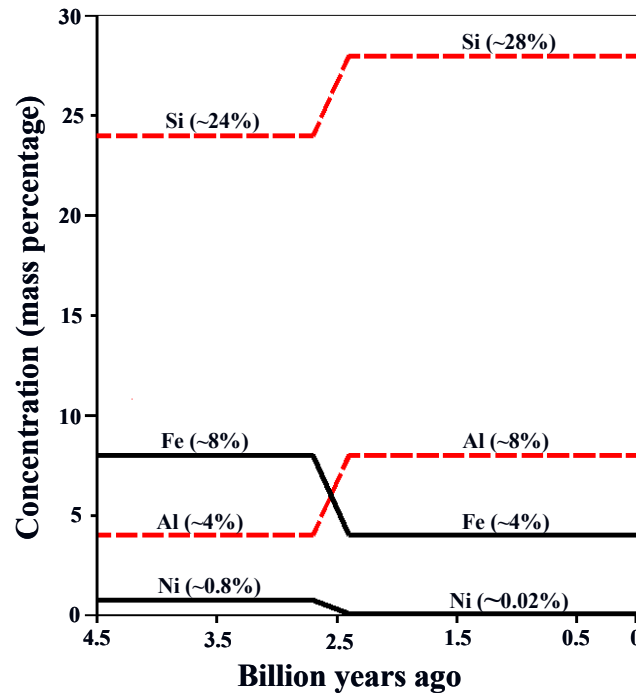
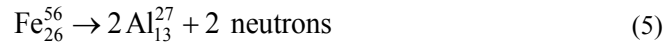


Fig. 4 – Evolution in mass percentage concentration of Si, Al, Fe and Ni in the Earth crust during the last 4.5 billion of years (age of the planet Earth).

Therefore, our conjecture is that the following piezonuclear fission reaction should have occurred also in the compression tests on granite specimens [1,2]:



In addition to the previously reported and still unpublished observations in liquid experiments, other strong reasons of a very general nature push us to emphasize this type of explanation.

The present natural abundance of aluminum (7-8% in the Earth crust), which is less favoured than iron from a nuclear point of view (it has a lower bond energy per nucleon), is possibly due to the above piezonuclear fission reaction. This reaction –less infrequent than we could think– would be activated where the environment conditions (pressure and temperature) are particularly severe, and mechanical phenomena of fracture, crushing, fragmentation, comminution, erosion, friction, etc., may occur. If we consider the evolution of the percentages of the most abundant elements in the Earth crust during the last 3 billion years (Fig. 4), we realize that iron and nickel have drastically diminished, whereas aluminum, silicon and magnesium have as much increased [23-25]. It is also interesting to realize that such increases have developed mainly in the tectonic regions, where frictional phenomena between the continental plates occurred.

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Li+D and D+D Fusion Assisted with Acoustic Cavitation

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Abstract. We have studied the Li+D and D+D fusion reactions in liquid Li by bombarding deuteron beams with energies below 70 keV. In the present work, an ultra sonic target system was developed to form acoustic cavitation bubbles in the liquid Li, in order to investigate the effect of the enhanced dynamic motion of the target. It was found that the ultra sonic effect strongly depends on a target condition and the D+D reaction could be enhanced very much due to the liquid Li cavitation. In addition, the D+D reaction rate is not constant but time dependent. Preliminary analyses indicate that decrease of the Coulomb energy barrier is about 2000 eV for a relatively stable condition. On the contrary, the Li+D reaction shows no meaningful effect for incident energies down to 30 keV. The present results indicate that not only density increase but also another mechanism enhancing reaction rates should be exist in liquid Li acoustic cavitation process.

1. Introduction

It has been shown that the nuclear reaction could be strongly affected by target condition and environment, and has been suggested that a dynamic mobility of deuteron in condensed matter is an essential factor to enhance the D+D reaction rate as well as a high deuterium density. In this paper, we try to establish unusual target conditions and to show enhanced nuclear reactions in such conditions. We employed a liquid metal (Li) as a host material where the D+D and Li+D reactions occur; the advantage of the liquid metal to the solid is possible existence of a screening effect of positive charges due to freely moving ions in addition to that of negative charges. Furthermore, the acoustic cavitation is applied to enhance the effects due to a dynamic motion of the target. In order to achieve these conditions, we developed an ultra sonic target system incorporated into a vacuum chamber to form Li cavitation bubbles in the target.

The reaction rates of the Li+D and D+D reactions in the Li cavitation bubbles were measured for the deuteron beam bombardment with energies below 70 keV; the density and kinematical effects were investigated. We also tried to detect bubble fusion under such a dynamic condition.[1-3]

2. Experiment

2.1 Ultrasonic System and Li Cavitation

Figure 1 (left) shows a schematic view of the ultra sonic system with the situation of vibration amplitudes depending on the position. It should be noted that the sonic wave is not transverse but longitudinal wave to form alternate dense and sparse conditions. A bolt-clamped Langevin-type transducer (BLT) generates a high amplitude sonic wave. A piezoelectric element is lead zirconate titanate (PZT). When the BLT is driven with an appropriate frequency, it outputs a high amplitude wave because of vibration resonance with four piezoelectric elements. Since the resonance condition is determined by the wavelength of the sonic wave, the total length of the system is an important factor. We designed the total length in such a way that the Li target is placed at an anti-node and that the resonance frequency is near 19 kHz. An aluminum horn connected to the BLT amplifies the vibration amplitude; the maximum amplitude is 10 μm . The horn has a flange at the node position of the sonic wave and is fixed with the vacuum chamber.

A situation of bubble growth and collapse through ultra sonic cycles is shown in Fig. 1 (right). At the sparse timing, a nucleus is born, the bubble shrinks and expands through a several cycles and it finally

collapses at the dense timing. Thus, it is considered that the state with high pressure, density and temperature can be achieved and light emission, so called sonoluminescence, occurs.

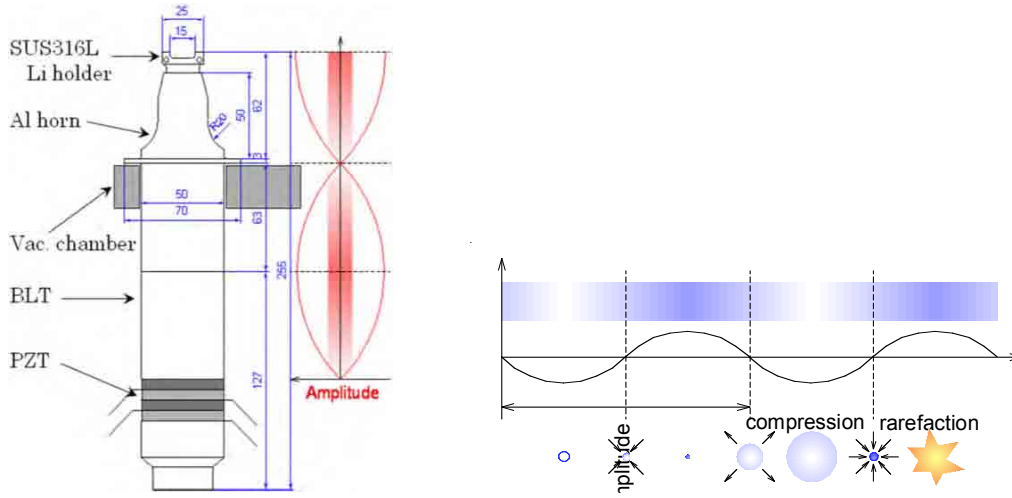


Fig. 1 – (left) A schematic view of an ultra sonic system. (right) Bubble growth and collapse through ultra sonic cycles.

However, the acoustic cavitation is a very complex process and there is no general theory to explain the mechanism and characteristic. Furthermore, almost no reports are found on the cavitation of the liquid metal. In a simple model, the threshold pressure for cavitation formation is mainly determined by surface tension of the liquid $\sigma(T)$ and expressed as

$$P_{th} \sim P_0 - P_s + \sqrt{\frac{16\pi(\sigma(T))^3}{3kT \cdot const.}}, \quad (1)$$

$$P_{th}(Li) \sim 10 \times P_{th}(H_2O) \sim 1.6[GPa]. \quad (2)$$

From the empirical eq. (1), we need ten times higher pressure than water to produce cavitation bubbles.

Figure 2(a) shows a surface of clear liquid Li in the vacuum chamber; we see a distinct reflection of the light from outside of the chamber. When we apply the ultra sonic wave, the cavitation occurs and bubbles reflect the light diffusely; we see countless white dots as shown in Fig. 2(b). We note that these white dots are not sonoluminescence but diffused light reflection since they appear just as a reflection of the light. The cavitation bubbles cover all Li surface as shown in Fig. 2(c).

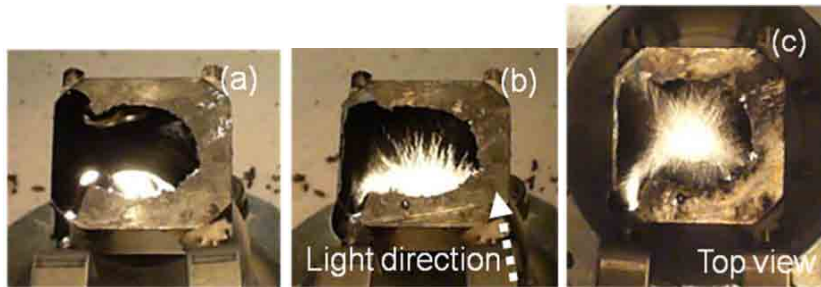


Fig. 2 – Liquid Li cavitations. (a) Clear liquid Li surface without ultra sonic wave. (b, c) Li cavitation bubbles. White dots are bubbles reflecting the light.

2.2 Li+D and D+D Measurement

We used enriched ${}^6\text{Li}$ metal, consisting of 95% ${}^6\text{Li}$ and 5% ${}^7\text{Li}$. The Li metal is very active material, and the surface is easily oxidized and/or contaminated. Therefore we designed and constructed a new vacuum chamber which has a glove box. In order to keep the surface clean, we handled the Li metal in Ar atmosphere in the glove box. The contamination, however, cannot be avoidable because of the residual gas when the chamber is evacuated. Thus, we removed the contamination every 1 or 2 hours by using a scraper attached to the chamber. We kept the Li temperature considerably higher than the melting point (180 °C). Below 300 °C, the vapor pressure of Li (10^{-6} Pa) is much lower than the vacuum of the chamber (typically 5×10^{-5} Pa). Thus Li evaporation can be avoided even in the cavitation condition.

The liquid Li was irradiated by deuteron beams with energy ranging from 30 to 70 keV. We kept the input power constant to be about 500 mW, in order to stabilize the ultra sonic effect. The beam was injected to the chamber at an angle of 60° with respect to the vertical direction. A Si detector placed at 125° was used to detect charged particles emitted in the nuclear reactions.

In order to elucidate the ultra sonic effect, we compared the yields of the Li+D and D+D reactions for the ultra sonic ON and OFF measurement. However, it was found that the target condition was very sensitive and was easily changed within a several minutes due to high activity of Li. Therefore a data acquisition system, in which the measurements with and without the ultra sonic were performed alternatively, was developed to reduce systematic errors. As is shown in Fig. 3, the beam was turned OFF and ON every 3 or 10 seconds while the ultra sonic wave was turned OFF and ON every 13 seconds so as to accumulate the 4 data sets in one cycle.

In Fig. 3, the reading of the infrared thermometer, which is considered to show the temperature of the Li surface, is also shown. It periodically increases and decreases synchronized with the ultra sonic ON/OFF cycle. It is not plausible that the change of the reading corresponds to real change of the temperature because of its instant response. At present, we conjecture that near-infrared lights are emitted in the Li cavitation as the sonoluminescence.

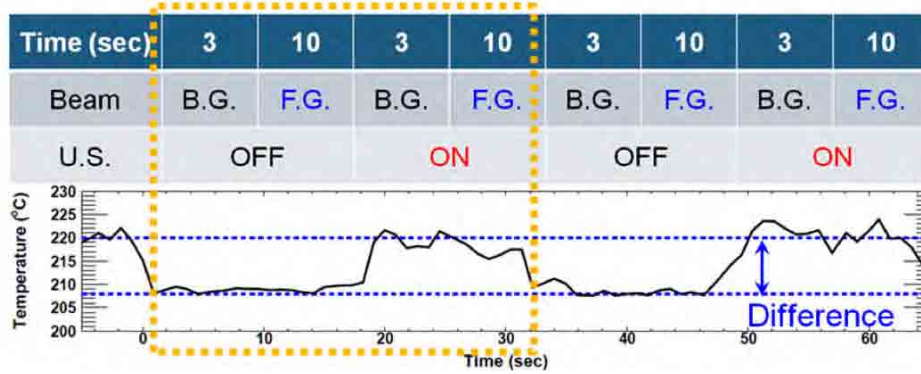


Fig. 3 – An alternate data acquisition cycle and infrared thermometer output.

3. Result

A typical energy spectrum is shown in Fig. 4. The blue peak is the 11.2-MeV α particle from the ${}^6\text{Li}+\text{D}$ reaction. During the deuteron bombardment, deuterons are being accumulated in the Li target and an incident deuteron collides with them to make the D+D reaction. The red peak is 3-MeV proton from the D+D reaction. We can estimate the deuteron density in the Li liquid by counting α and proton counts as

$$\frac{Y_p}{\frac{1}{2}Y_\alpha} = \frac{\int N_D(x) \cdot \sigma_{D+D}(x) \cdot dx}{N_{Li} \cdot \int \sigma_{Li+D}(x) \cdot dx} \Leftrightarrow \frac{N_D}{N_{Li}} \sim \frac{2 \int \sigma_{Li+D}(E)(x) \cdot \frac{1}{dE/dx} \cdot dE}{\int \sigma_{D+D}(E) \cdot \frac{1}{dE/dx} \cdot dE} \cdot \frac{Y_p}{Y_\alpha} \quad (3)$$

The maximum deuteron density deduced in the present measurements is 0.1% of the Li.

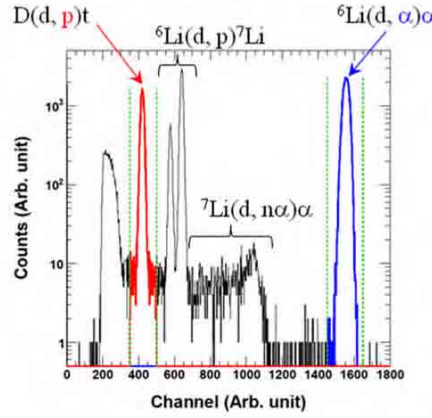


Fig. 4 – Energy spectrum.

We show an example of measurements in Fig. 5. We plot the yield of the Li+D and D+D reactions as a function of elapsed time with black marks for ultra sonic OFF and blue marks for ON. In the case of the Li+D reaction shown in Fig. 5(a), the yield is constant and the difference between the ultra sonic ON and OFF is within the error. On the other hand, the yield of the D+D reaction increases gradually probably due to increase of deuteron density in the liquid Li. Of particular significant, however, is the fact that the D+D reaction is enhanced by the ultra sonic wave. In Fig. 5(c) one already sees large difference between ON and OFF. Figure 5(b) shows the ratio of the yield for the ultra sonic ON to that for OFF. One can see that the D+D reaction with the ultra sonic is really enhanced several times, while no enhancement is observed for the Li+D reaction. In this run, we obtained the averaged ON/OFF ratio to be 3.5 for the D+D reaction. After 2 hours, the ultra sonic effect was lost and the ratio became back to unity.

Fig. 5(d) shows time spectra of events; the abscissa is the correlated time with the ultra sonic. The BLT is driven with the resonance frequency of 18.85 kHz, corresponding to a 53- μ s cycle. We measured the time difference between the standard signal and the event signal. In the case of the ultra sonic OFF, the reaction occurs randomly and the time spectrum is flat as is shown with a black line. However, we cannot find clear time correlation with the ultra sonic, either, as shown with a blue line up to now.

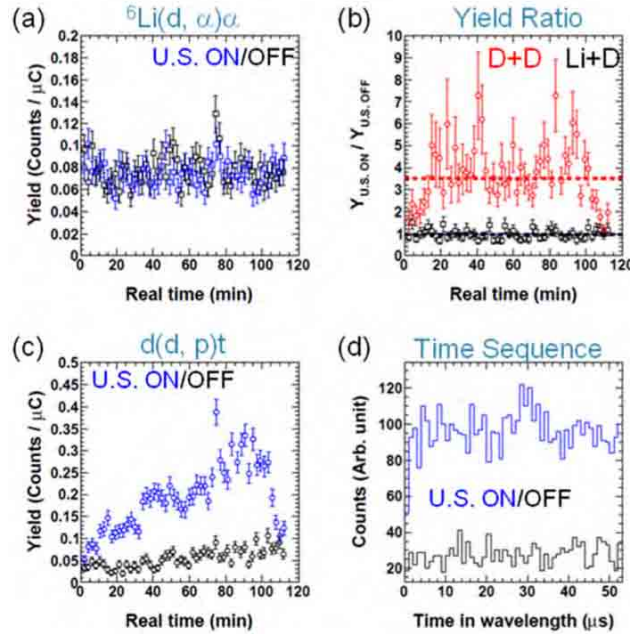


Fig. 5 – Time behaviors of Li+D and D+D reaction yields. (a) Li+D reaction yield, (b) yield ratio: ultra sonic ON/OFF, (c) D+D reaction yield, (d) micro time sequence of D+D reaction.

Fig. 6 (left) shows a histogram on the time correlation between two successive events; the abscissa corresponds to the time interval of the two successive events. It is known that reactions occur randomly and constantly, i.e., for Poisson distribution, the expected spectrum shows an exponentially decreasing function. For the generalized Poisson process in which the reaction rate is not constant but varies as time, the probability expressed

$$P = \frac{(\lambda(t))^k}{k!} e^{-\lambda(t)}, \quad (4)$$

$$f(t) \sim e^{-\lambda(t)}, (\lambda(t) = \int_0^t r(x) dx)$$

where $f(t)$ and $r(t)$ are reaction interval and reaction rate, respectively.

In Fig. 6 (left), a histogram for the measurement without the ultra sonic (the black line) shows an exponential curve as expected. On the contrary, the blue line for the ultra sonic ON has three components; (1) homogeneous Poisson process (high reaction rate), (2) homogeneous Poisson process (low reaction rate) and (3) non- homogeneous Poisson process. The reaction rate $r(t)$ for each process is estimated as shown in Fig. 6 (right). First, there is a high density phase (1) that is 13 times larger than the normal phase (2). Furthermore, we found the shoulder, not exponential component, in the time interval spectrum as shown in red curve (3). That means the reaction rate is not constant λ_0 but has time dependence $\lambda(t)$.

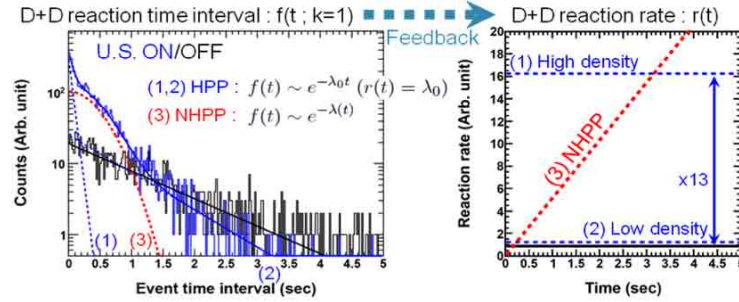


Fig. 6 – D+D reaction time interval (left) and reaction rate (right).

Vibration amplitude dependences and incident energy dependences of the Li+D and D+D reactions are shown in Fig. 7. In the figure, Y axis corresponds to the ultra sonic ON/OFF ratio. The intensity of cavitation is obviously increased with increase of the vibration amplitude. However, the yield ratio decreases for the D+D reaction because the intense cavitation stirs the liquid Li and absorbed deuterons diffuse out immediately from the spot where part of the beam is being accumulated. We carried out many measurements and found that the cavitation effect strongly depends on the target condition. Up to now, we have not found the way to keep the good condition for a long period.

We selected the data measured under a relatively stable condition and show the energy dependence of the yield ratio in Fig. 7 (right); i.e., the data under the condition of vibration amplitude of 1.9 μm , surface temperature of 220 $^{\circ}\text{C}$, and beam input of 500 mW. The D+D reaction yield ratio has obvious energy dependence. As the incident energy becomes lower, the yield ratio increases. If the reaction is enhanced by the change of the deuteron density only, the energy dependence cannot be observed. Thus, the observed dependence on the incident energy clearly indicates that not only density effect but another mechanism to enhance the reaction should be effective in the liquid Li cavitation process. We fitted the experimental ratios to the calculations with the following equation

$$\frac{\sigma_{U.S.ON}(E)}{\sigma_{U.S.OFF}(E)} \sim \frac{\sigma(E+U)}{\sigma(E)} \sim \exp(15.64z_1z_2\sqrt{\mu}\frac{U}{E^{3/2}}), \quad (5)$$

and obtained an effective energy difference U . If we assume that the enhancement is caused by Gamow factor only, the effective energy difference is $U = 1980$ eV for D+D fusion in center of mass system as shown in solid lines in Fig. 7.

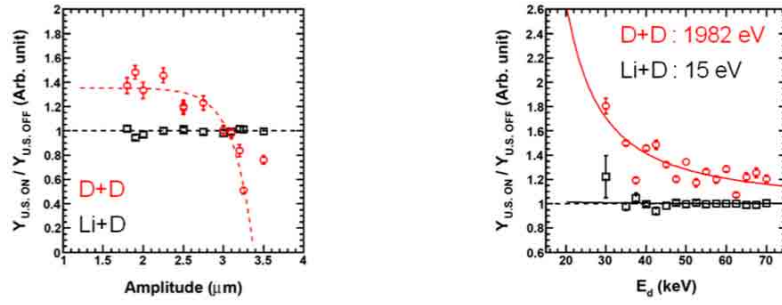


Fig. 7 – Vibration amplitude dependence and incident energy dependence of Li+D and D+D reactions.

4. Conclusion

We have developed an ultra sonic target system to form the Li acoustic cavitation bubbles in the vacuum chamber. The Li+D and D+D fusion reactions were measured during the low energy deuteron bombardment to the Li target. In this paper, we show the first experimental result with acoustic cavitation. It is found that the ultra sonic effect strongly depends on the target condition, the D+D reaction could be quite enhanced under the cavitation, and the reaction rate is not constant but time dependent. The decrease of the Coulomb energy barrier is about 2000 eV for the relatively stable condition. On the contrary, the Li+D reaction shows no meaningful effect. The present results indicate that not only density effect but also another mechanism to enhance the reaction rate should exist in liquid Li acoustic cavitation.

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The effects of nuclear reactions in solids on the phonon dispersion relation

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Abstract. In this study, theoretical predictions about the effects of nuclear reactions in solids on the phonon dispersion relations are shown. As an initial model, we have tried to treat one dimensional palladium deuteride and have obtained possible changes of phonon dispersion relations due to DD reactions. This method will be applied to the detection of nuclear reactions in solid by using nuclear scattering or Raman spectroscopy.

1. Introduction

In solid state physics, phonon dispersion relation is one of the most important information, because it includes not only the geometric and the electronic structures of the crystals but also the interaction between ions or electrons. For example, a lattice with only one atom in a primitive cell only has acoustic lattice vibration. However, a lattice with more than one atom in a primitive cell has acoustic and optical modes of vibration. Furthermore, interactions between impurity ions are also effective on the features of phonons. If nuclear reactions occur in solids, they will change the lattice and electronic structures and interactions between impurity ions and so on. Therefore, the changes of phonon dispersion relations will give us the evidences of nuclear reactions in solids. In this study, the possible changes of the phonon dispersion relation due to the nuclear reaction in solid were discussed. In this section, the theories of phonon dispersion relation of solids [1,2] are introduced briefly. Firstly, we define the equilibrium positions of ions in crystalline solids as $\mathbf{R}_{nm} = \mathbf{r}_n + \mathbf{k}_m$, where $\mathbf{r}_n$ and $\mathbf{k}_m$ mean position of the n-th primitive cell and position of the k-th ion in the cell, respectively. Then the total kinetic energy is defined using displacement vector $\mathbf{u}_{nm}$ from $\mathbf{R}_{nm}$ as

$$K = \frac{1}{2} \sum_{nmj} M_m (\dot{u}_{nm}^j)^2, \quad (1)$$

where M_m is the mass of the m-th ion in the primitive cell and the summation for j is done over Cartesian components. And the total potential energy is written in the 2nd order approximation as

$$V = V_0 + \frac{1}{2} \sum_{nmj} \sum_{n'm'j'} C_{nmn'm'}^{jj'} u_{nm}^j u_{n'm'}^{j'}, \quad (2)$$

where C is the second order partial derivative of V with respect to the displacement. They give the equation of motion for each ions which is written as

$$M_m \ddot{u}_{nm}^j = - \sum_{n'm'j'} C_{nmn'm'}^{jj'} u_{n'm'}^{j'}. \quad (3)$$

In this equation, every components of the displacement satisfy Bloch theorem

$$u_{nm}^j = e^{i\mathbf{q} \cdot \mathbf{r}_n} u_{0m}^j \quad (4)$$

and coefficient C has a symmetry

$$C_{nmn'm'}^{jj'} \rightarrow C_{mm'n'}^{jj'}(\mathbf{h}) \quad (\mathbf{h} = \mathbf{r}_{n'} - \mathbf{r}_n). \quad (5)$$

Defining the Fourier transformed formula as

$$\sum_{\mathbf{h}} C_{mm'}^{jj'}(\mathbf{h}) e^{i\mathbf{q}\cdot\mathbf{h}} \equiv G_{mm'}^{jj'}(\mathbf{q}) \quad (6)$$

and assuming the oscillatory solution as

$$u_{nm}^j(t) = e^{-i\omega t} u_{nm}^j(0), \quad (7)$$

we obtain phonon dispersion relation as

$$\sum_{m'=1}^M \sum_{j'=1}^3 G_{mm'}^{jj'}(\mathbf{q}) u_{0m}^{j'}(0) = M_m \omega^2 u_{0m}^j(0) \quad (8)$$

where M is the number of ions including in a primitive cell. For the case of a monatomic lattice which has only one ion in a primitive cell, eq.(8) is rewritten as

$$\begin{pmatrix} G^{11} & G^{12} & G^{13} \\ G^{21} & G^{22} & G^{23} \\ G^{31} & G^{32} & G^{33} \end{pmatrix} \begin{pmatrix} u^1 \\ u^2 \\ u^3 \end{pmatrix} = M\omega^2 \begin{pmatrix} u^1 \\ u^2 \\ u^3 \end{pmatrix}. \quad (9)$$

This equation has three solutions. One corresponds to the longitudinal mode, and the other two corresponds to the doubly-degenerated transverse mode. The typical solutions are sketched in Fig.1. For the case of a diatomic lattice with a heavy and a light ion in a primitive cell, eq.(8) is rewritten as

$$\begin{pmatrix} G_{11}^{11} & G_{11}^{12} & G_{11}^{13} & G_{12}^{11} & G_{12}^{12} & G_{12}^{13} \\ G_{11}^{21} & G_{11}^{22} & G_{11}^{23} & G_{12}^{21} & G_{12}^{22} & G_{12}^{23} \\ G_{11}^{31} & G_{11}^{32} & G_{11}^{33} & G_{12}^{31} & G_{12}^{32} & G_{12}^{33} \\ G_{21}^{11} & G_{21}^{12} & G_{21}^{13} & G_{22}^{11} & G_{22}^{12} & G_{22}^{13} \\ G_{21}^{21} & G_{21}^{22} & G_{21}^{23} & G_{22}^{21} & G_{22}^{22} & G_{22}^{23} \\ G_{21}^{31} & G_{21}^{32} & G_{21}^{33} & G_{22}^{31} & G_{22}^{32} & G_{22}^{33} \end{pmatrix} \begin{pmatrix} u_1^1 \\ u_1^2 \\ u_1^3 \\ u_2^1 \\ u_2^2 \\ u_2^3 \end{pmatrix} = \omega^2 \begin{pmatrix} M_1 u_1^1 \\ M_1 u_1^2 \\ M_1 u_1^3 \\ M_2 u_2^1 \\ M_2 u_2^2 \\ M_2 u_2^3 \end{pmatrix}. \quad (10)$$

The typical solutions are sketched in Fig.2. In real case, these relations should be calculated for each directions of wave propagation.

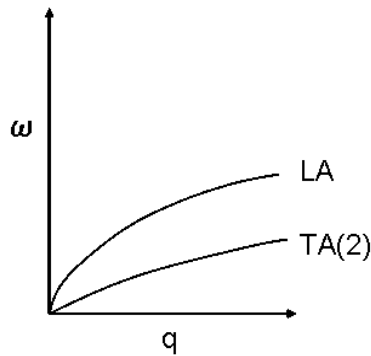


Fig. 1 - Phonon dispersion relation of monatomic lattice. Characters LA and TA(2) mean longitudinal acoustic and doubly-degenerate transverse acoustic modes, respectively.

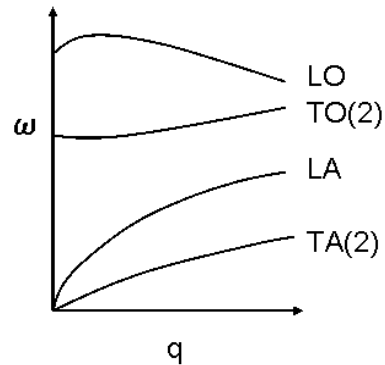


Fig. 2 - Phonon dispersion relation of diatomic lattice. Characters LA and TA(2) mean longitudinal acoustic and doubly-degenerate transverse acoustic modes, respectively. Characters LO and TO(2) mean longitudinal

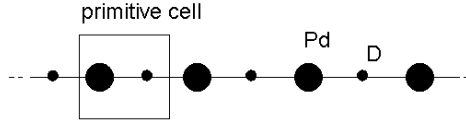


Fig. 3 - One-dimensional PdD lattice

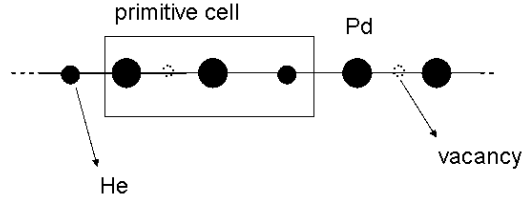


Fig. 4 - A model of structure changed one dimensional PdD lattice due to nuclear reaction

2. Change of the phonon dispersion relation due to the nuclear reaction

We discuss the phonon dispersion relation of palladium deuteride using the one dimensional PdD lattice. It is a very simple model which is illustrated in Fig.3. In this case, the dimension of the dynamical matrix is 2×2 with 2 solutions. The solutions are easily obtained by using the method described in section 1. And the typical dispersion curves are similar to Fig.2. If we consider some nuclear reactions and they change the structure of the lattice in Fig.3, they will also change phonon dispersion relation. For example as illustrated in Fig.4, if deuterons are disappeared and He's are produced, a primitive cell contains two palladiums, one He and one vacancy. This lattice roughly corresponds to the He concentration of 10^{22} atom/cm³ in the three-dimensional lattice. It is unrealistic situation. However, our model gives possible changes of phonon dispersion relation by assuming the lowest dimensional lattice and the highest deuteron concentration. For example, the occurrence of the nuclear reactions at a definite small domain with high deuteron concentration in the palladium deuteride may influence the phonon states of the whole lattice. At the moment, phonon dispersion relation will be changed under the influence from the domain. It will be detected by using neutron scattering or Raman spectroscopy. Of course it suggests the DD reaction. At this time, the dimension of the dynamical matrix is changed into 3×3 with 3 solutions. This means that some unknown phonon dispersion branches are created at the reaction. Therefore, if we measure the phonon dispersion relation of palladium deuteride and find unknown extra dispersion branches, they may be evidences of nuclear reactions. It is a model with oversimplification. In real case, more complicated and local reactions should be considered. For example, multi-body fusion or more complicated reaction [3] should be considered. However, the structure changes due to the nuclear reaction always tend to increase dispersion branches

Here, we would like to show the examples by doing one dimensional calculation of longitudinal mode for the lattices illustrated in Figs.3 and 4. Firstly, calculation for PdD lattice illustrated in Fig.3 has done. It is a simplified one dimensional lattice with alternate arrangement of Pd and D atoms. If we only consider the vibrations along the line, it means longitudinal mode. In this case, the total kinetic energy is written as

$$K = \frac{1}{2} M \sum_n \dot{u}_{2n}^2 + \frac{1}{2} m \sum_n \dot{u}_{2n+1}^2, \quad (11)$$

where M and m mean mass of Pd and mass of D, respectively. And the total potential energy in harmonic approximation with neighboring interaction is written as

$$V = \frac{1}{2} k \sum_n (u_n - u_{n+1})^2, \quad (12)$$

where k means elastic constant. Using them, the equations of motion are derived as

$$\begin{aligned} M \ddot{u}_{2n} &= -k(2u_{2n} - u_{2n+1} - u_{2n-1}) \\ m \ddot{u}_{2n+1} &= -k(2u_{2n+1} - u_{2n+2} - u_{2n}), \end{aligned} \quad (13)$$

where displacement u_n for the n -th atom is a function of time. Using a similar procedure with the general case in section 1, we obtain secular equation

$$\begin{vmatrix} 2k - M\omega^2 & -2k \cos(qa) \\ -2k \cos(qa) & 2k - m\omega^2 \end{vmatrix} = 0. \quad (14)$$

The well known solutions of eq.(14) are

$$\omega_{\pm}^2 = k \left(\frac{1}{m} + \frac{1}{M} \right) \pm k \sqrt{\left(\frac{1}{m} + \frac{1}{M} \right)^2 - \frac{4 \sin^2(qa)}{mM}}. \quad (15)$$

They give phonon dispersion relation which has one acoustic mode and one optical mode. Secondly, we consider one dimensional lattice illustrated in Fig.4. In this case the total kinetic energy is written as

$$K = \frac{1}{2} M \sum_n \dot{u}_{3n}^2 + \frac{1}{2} (2m) \sum_n \dot{u}_{3n+1}^2 + \frac{1}{2} M \sum_n \dot{u}_{3n+2}^2, \quad (16)$$

where the 1st, the 2nd and the 3rd terms mean total kinetic energy of Pd sitting on the left side of He, of He and of Pd sitting on the right side of He, respectively. The total potential energy is written as

$$V = \frac{1}{2} \alpha \sum_n (u_{3n+2} - u_{3n+1})^2 + \frac{1}{2} \alpha \sum_n (u_{3n+1} - u_{3n})^2 + \frac{1}{2} \beta \sum_n (u_{3n} - u_{3n-1})^2. \quad (17)$$

In this equation, the 1st and the 2nd terms mean interactions between neighboring Pd and He with elastic constant α . The 3rd term means interaction between neighboring Pd's with elastic constant β . Equations of motion for each atom are written as

$$\begin{aligned} M \ddot{u}_{3n} &= -(\alpha + \beta) u_{3n} + \alpha u_{3n+1} + \beta u_{3n-1} \\ 2m \ddot{u}_{3n+1} &= -\alpha (2u_{3n+1} - u_{3n+2} - u_{3n}) \\ M \ddot{u}_{3n+2} &= -(\alpha + \beta) u_{3n+2} + \beta u_{3n+3} + \alpha u_{3n+1}. \end{aligned} \quad (18)$$

And the secular equation is obtained as

$$\begin{vmatrix} \alpha + \beta - M\omega^2 & -\alpha e^{iql} & -\beta e^{-iql} \\ -\alpha e^{-iql} & 2\alpha - 2m\omega^2 & -\alpha e^{iql} \\ -\beta e^{iql} & -\alpha e^{-iql} & \alpha + \beta - M\omega^2 \end{vmatrix} = 0. \quad (19)$$

Expanding the secular equation, we obtain a cubic equation for ω^2 as

$$mM^2 \omega^6 - \{\alpha M + 2(\alpha + \beta)m\} M \omega^4 + \alpha(\alpha + 2\beta)(m + M) \omega^2 - \alpha^2 \beta \{1 - \cos(3ql)\} = 0, \quad (20)$$

which has three positive real solutions. They correspond to one acoustic mode and two optical modes. For the case of $q=0$, this equation reduces to

$$\omega_0^2 [mM^2 \omega_0^4 - \{\alpha M + 2(\alpha + \beta)m\} M \omega_0^2 + \alpha(\alpha + 2\beta)(m + M)] = 0. \quad (21)$$

The solution for acoustic mode is $\omega_0=0$ and the solutions for the optical mode are

$$\omega_{0\pm}^2 = \frac{\alpha M + 2(\alpha + \beta) \pm |\alpha M - 2\beta m|}{2mM}. \quad (22)$$

For the case of $\alpha M > 2\beta m$, we obtain

$$\omega_{0+}^2 = \alpha \left(\frac{1}{m} + \frac{1}{M} \right) \quad \text{and} \quad \omega_{0-}^2 = (\alpha + 2\beta) \frac{1}{M}. \quad (23)$$

For the case of $\alpha M < 2\beta m$, we obtain

$$\omega_{0+}^2 = (\alpha + 2\beta) \frac{1}{M} \quad \text{and} \quad \omega_{0-}^2 = \alpha \left(\frac{1}{m} + \frac{1}{M} \right). \quad (24)$$

They give the difference of two optical mode at $q=0$. If we find these changes of dispersion relation, we can know the change of the structure from the lattice in Fig.3 to the lattice in Fig.4. This corresponds to the detection of some nuclear reactions in solids.

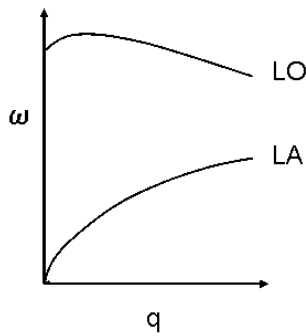


Fig. 5 - Phonon dispersion relation of the longitudinal vibration of the one dimensional lattice illustrated in Fig.3.

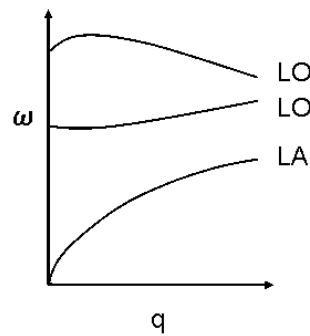


Fig. 6 - Phonon dispersion relation of the longitudinal vibration of the one dimensional lattice illustrated in Fig.4.

3. Conclusions

If some nuclear reactions have happened in solids, the lattice structure is changed and the number of the ions in a primitive cell is increased. Even if these changes are spatially inhomogeneous, this tendency is unaltered. In this case, the dimension of the dynamical matrix becomes larger and this causes an increase of dispersion branches. Therefore, if we measure the phonon dispersion relation of palladium deuteride and find unknown extra dispersion branches, they may be evidences of nuclear reactions. These discussions can be applied to the analysis of Raman observation of the palladium deuterides [4,5] .

Acknowledgments

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Nuclear Transmutation in Non- equilibrium Systems by Ultra-closed Range Casimir Effect

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Abstract. Quantum physics predicts the existence of an underlying sea of zero-point energy at every point in the universe. The breakthrough of seeing, understanding and devising a converter of the energy available in quantum oscillation might be the opening point of an energy filled 21st century for humanity.

It is well known that phenomena of electrical discharge always bring on transient energy concentration temporally and spatially. Highly localized nuclear activation in electrochemical systems and other electrical discharge processes had been observed at many laboratories in the world. Based on the theory of vortex dynamics, the strange phenomena of “cold fusion”, such as the excess heat, anomalous nuclear transmutation and so forth, are considered to be interpretable by torsion coherence with the zero-point energy induced by localized intense field emission of micro-protrusion of the cathode, and the dynamic Casimir effect of transient evolution of triple region of gas, liquid solution, and electrode protrusion. In fact this process induces a variety of high energy, deterministic nuclear fusion reactions between relatively large nuclei, “triggered” by low input energies, generally not considered possible in the conventional physics frame. A logical extrapolation of this discovery is that the strong force of the nucleus is in fact an ultra-close range Casimir effect. Fusing ions capturing electron to convert excess protons to neutrons is a common occurrence and a key to the production of stable isotopes without neutrons or radiation.

A system as an anomalous transmutation reaction discovered by Yuguang Zhang is described in this paper. A micro-emission exhaust gas handling device(publication number of patent: WO 2008 083530) due to nuclear transmutation by vortex dynamics, is provided, which is a container only having inlets. A model of sonic black hole with the acoustic version of Hawking radiation by using de Laval nozzle is supposed to explain the behaviors of micro-emission exhaust for the system.

1. Introduction

“No problem can be solved from the same level of consciousness that created it “—Albert Einstein.

Researchers fail to explain the phenomena related to so called “Cold Fusion” within the framework of main stream physics. The theories of tapping the zero point energy, dynamic Casimir effect and the torsion field including the spin and rotation movement, are suggested to be used for describing the phenomena of “cold fusion”[1,2].

Many scientists have long been aware that our earth is immersed in an extremely dense sea of energy, which permeates every nook and cranny of the universe[3]. Recently it was realized that this huge reservoir could be an available source of usable energy. Science employs a variety of names to describe

this new field: space energy, vacuum energy, dark energy, the quantum vacuum, and Zero Point Energy (ZPE). Until about twenty years ago, scientists did not consider it possible to tap it for practical use. Nikola Tesla, the genius who gave birth to alternating current, said in a talk to electrical engineers in 1891: "Ere many generations pass, our machinery will be driven by a power obtainable at any point in the universe. ...Throughout space there is energy." Trying to unravel this mystery has taken many paths, Cold Fusion, bubble fusion, LENR, cavitation and Casimir cavities to name a few.

For Bohm, "an invisible, intrinsic connectedness uniting everything in the universe was merely perceived, but fundamentally real." In his words: " Ultimately, the entire universe (with all its 'particles,' including those constituting human beings, their laboratories, observing instruments, etc.) has to be understood as a single undivided whole, in which analysis in separately and independently existent parts has no fundamental status."

Kovac explains the cold fusion and transmutation processes in term of Gauss' pseudosphere-catenoid geometry determining the bending of space to form the toroid knots[4]. The tightly wound toroid (centripetally bound and compressed) mass can then either unwind back through its axis(as it turns inside-out) as energy production (heat, electricity, and light), or it can unwind equatorially as a catenoid spiral in secondary mass formation to form various elements.. Thus mass-energy transmutations occurring as in Russell' descriptions of motion to and from wave field cube well boundaries to and from mass spherical center boundary. The creation of mass 5 element is offered as support for the notion that cold fusion, ultra subatomic particles, electricity, and magnetism are each a consequence of special interrelated geometric formation moving in microscopic space

2. Nuclear transmutation in non-equilibrium system

For discuss of nuclear transmutation, the issues of low-energy nuclear synthesis and transmutation of stable and radioactive isotopes in non-equilibrium systems listed as following: such as (1)diffusion processes of hydrogen and deuterium gases in a new type "Solid Fusion Reactor" of two types of nanomaterial (ZrO₂_Pd₃₅ and ZrO₂_Ni₃₀Pd₅) by Arata and Y.C. Zhang; (2) piezonuclear reactions occurring in stable iron nuclides contained in aqueous solutions of iron chloride or nitrate by A. Carpinteri, F. Cardone, G. Lacidogna; and (3)the anomalous characteristics of nuclear transmutation by V. Vysotskii and A. Kornilova observed in biological cells (including numerous Kervran's experiments evidencing the nuclear transmutation of chemical elements in animals and plants) should be mentioned.

Sonoluminescence can be explained in terms of quantum radiation by moving interfaces between media of different polarizability. The long distance quantum radiative phenomenon associated not with atoms but with fast moving surfaces in the collapsing bubble following the dynamical Casimir effect..

3. Vortex dynamics and torsion field

During the period of March to May, 1989, Xingliu Jiang detected nuclear tracks with solid detector of CR-39 by on site of the tip of cathode electrode in a electrolyte cell. A manuscript, "Micropinch in cold nuclear fusion" about the experimental results by Xingliu Jiang, Ning Xu and Lijun Han was sent to Editor of Nature magazine at September 1989, Dr. Philip Ball, Assistant Editor wrote on this manuscript (Registration no: J10535 PB/HH):" The referee finds your results interesting", "The referee clearly feels that your experiments represent an interesting approach to studies of cold fusion". For the referee, he wrote: "I found manuscript J10535 quite interesting and recommend that you publish it ".The tracks of



Fig. 1 - Tracks of nuclear reaction products on the CR-39 detector under the torsion field effect.

highly directional particles (Fig. 1) might be products of nuclear reactions in the electrolyte cell, such as protons and alpha particles including clusters of high density charge of electrons with different size according the experimental results by Shoulders. Such pattern of tracks offers the evident factors for channeling effect of crystalline metal electrodes and particle acceleration by torsion field.

The experimental results of anomalous nuclear reaction reported by Jiang, Borkris, Miley and Patterson plus similar results reported by Mizuno, et al challenge the current atomic model[5,6,7].. The phenomenon seems highly reproducible. It appears that there are situations in which nuclei split open at the stimulus only chemical energies. Ronald J. Kovac reported [3]that elemental transmutation appears to have occurred when a vacuum tube containing only nitrogen(^{14}N) was exposed to an electromagnetic force field. Gas spectrometer analysis revealed that the contents in the tube after electromagnetic shaping included substantial amounts of helium ^4He and lithium ^5Li .

Recently, Ron Kovac and Toby Grotz of Colorado, repeated Russell's 1927 work, which was verified at the time by Westinghouse Laboratories. Russell found a novel way to change the ratio of hydrogen to oxygen in water vapor inside a sealed quartz tube, or to change the vapor to completely different elements. Their conclusion agrees with Russell: the geometry of motion in space is important in atomic transmutation. Kovac short hands that idea to geometry of space-bending. It is well known “matter” is a wave form energy-pattern in the medium. Quanta turned out to be more like waves than like corpuscles. According to Russell’s description of the Wave of Creation: The wave is described as causing “the integration of matter at poles and disintegration at equators. Matter integrates by the contraction of one pair of spirals around the shafts which wind it into spheres by the way of its poles, and disintegrates it by the expansion of the other pair which unwinds it by the way of equators”.

A system as an anomalous transmutation reaction discovered by Yuguang Zhang is described in this paper. An micro-emission exhaust gas handling device (publication number of patent: WO 2008 083530) is provided, which is a container only having inlets. At least two stages of exchangers (2) are provided in series in the container from an exhaust gas inlet (1) and a mixing gas chamber (3) is arranged at the communicating location between two stages of exchangers. An exchanging gas chamber (23) in the first stage of the exchanger (2) is provided with an orifice (4) communicating with air and each of the mixing gas chambers (3) from the second to the last stage of exchangers is disposed with a return pipe (4) communicating with the inlet of the first stage of the exchanger.

For the gas handling device, the straight pipes or cylinder channels with the geometry similar to the de Laval nozzle will generate supersonic gas flow with vortexes in the form of turbulence in order to brake the flow of straight line, laminar motion [8]. A model of the sonic black hole with Hawking radiation

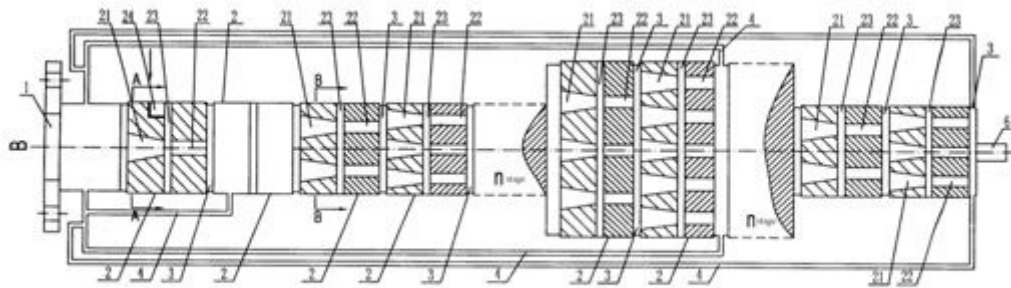


Fig. .2 - A micro-emission exhaust gas handling device

could be used to describe the annihilation of exhaust gas [9,10]. Thus the vortex body and the mass of the medium is affected toward the dissipation and breaking apart. Such dissipation, expansion and slow explosion of many natural elements could be observed in the micro-emission exhaust gas handling device due to dynamic Casimir effect and torsion coherence with zero point energy [1]. The polarization of particle spin and angular moment generate the torsion field. The filamentation of turbulence flow shows the effect of dynamic Casimir force with the zero point electromagnetic fluctuation. The axial acceleration and memorial effect (heat after death) of character for torsion field have been observed in many laboratories.

4. Conclusion

The vacuum is the matrix that contains all matter and all energy. Our current understanding of science is like a puzzle with a large missing piece-quantum vacuum zero point energy. Various scientists have been discovering anomalies of phenomena attributed to the conversion of the zero point energy.. The combination of ion vortex or vortex rings with abruptly pulsed bucking electromagnetic field or turbulence fluid could result in the direct manifestation of energy and matter transformation. Based on the theories of quantum vacuum zero point energy, torsion field, further study of sonic black hole should be carried out for explanation of anomalies [10].

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A Practical Way to Generate Protons (Deuterons) of Energy Between 500 and 1000 eV.

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Abstract. *Research tools used in the field of d/d fusion are protons (deuterons) accelerators producing ion beams of energies between 10 keV up to several MeV. Another source of protons (deuterons) are low pressure electrical discharge, yielding ions of energies between 1 to some tens of eV. Based on this second source, a way to generate protons (deuterons) in the range 500 to 1000 eV is described.*

1. Introduction

It was recently proposed [1] to study d/d fusion reactions initiated by bombarding targets loaded with deuterium, with deuterons of energies between 500 and 1000 eV. These levels of energy can easily be achieved by using ion generators of several kW power, that are now available on the market (surface treatment, electronic industry). They can produce ion (proton, deuteron) beams of high intensity (several A) with ion energies in the range 100 to 4000 eV and are thus able to work in the 500 to 1000 eV energy window. Due to budget limitations, such an equipment cannot be envisaged for the time being. The existing laboratory accelerators are limited on the low energy side to some 5 to 10 keV. A device was thus developed, based on the acceleration of ions generated in a low pressure (50 Pa) glow discharge. Ionic current up to 30 μ A, with ion energies of some 850 eV are expected.

2. Principle of the device

Glow discharges in hydrogen isotopes at pressures between 10 to 50 Pa, mainly yield H^+ (D^+) ions and atomic hydrogen (deuterium). The principle of the device is described in Fig 1. Technical features to control operating conditions (pressures cascades for instance) are given in Fig 2.

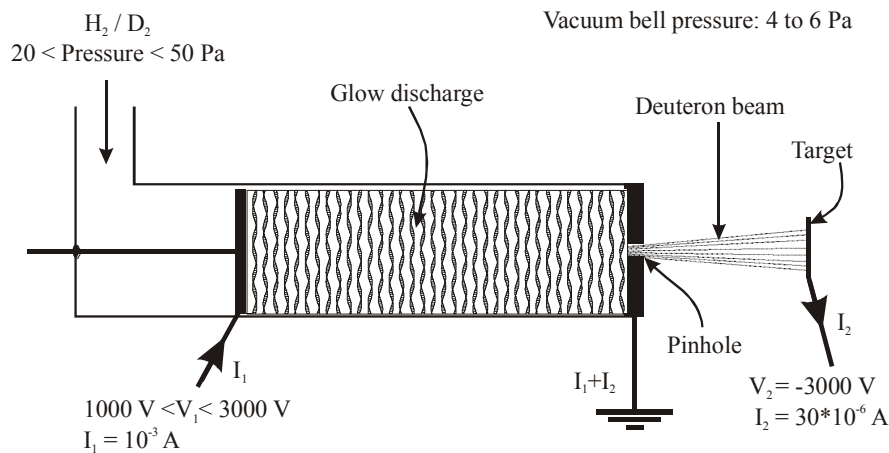


Fig. 1 – Principle of the device of glow discharge

The concentration of molecular deuterium entering the system is some $8 \cdot 10^{21} \text{ m}^{-3}$ (at a representative pressure of 30 Pa) and the current I_1 of the main glow discharge is measured to be 10^{-3} A for a voltage $V_1 = +2000 \text{ V}$. Part of the deuterons, generated in the glow discharge, go through a pinhole (0.5 mm diameter) in the earthed electrode and are collected on the target. At low voltage of the target, the current I_2 is some $5 \cdot 10^{-6} \text{ A}$, increasing from 30 to $40 \cdot 10^{-6} \text{ A}$ when V_2 reaches 3000 V. At a pressure of 5 Pa, the mean free path of hydrogen (deuterium) is round 2 mm. For $V_2 = 3000 \text{ V}$ and a distance between the grounded electrode and the target of 5 mm, the mean energy of the D^+ ions impinging the target can be estimated to be some 850 eV (See below more details on the modeling of the discharge)

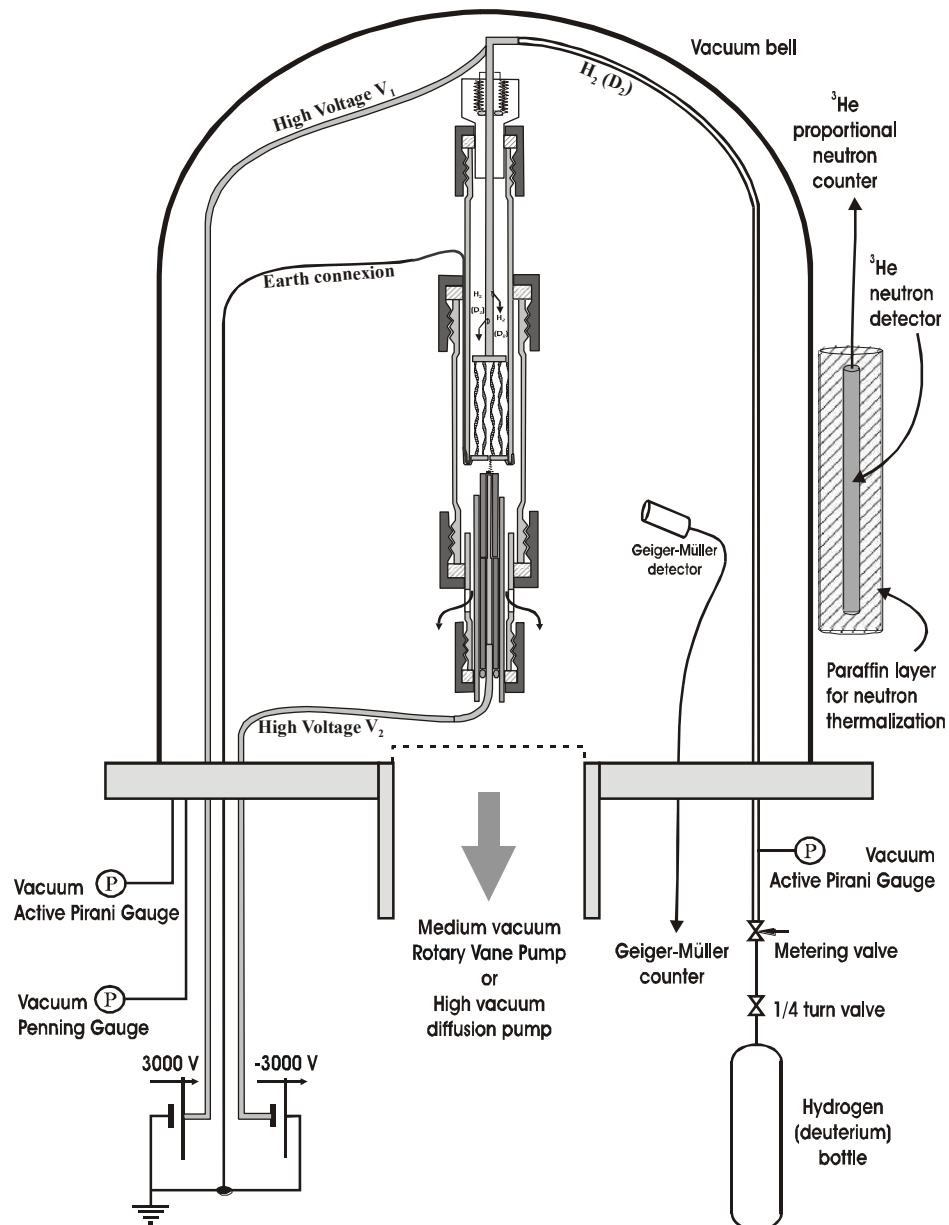


Fig. 2 – Overall experimental set-up

3. Detailed description of the device

3.1 Over all experimental set-up:

The overall experimental set-up is given *Fig 2*.

The reactor is placed in a vacuum bell. Pressures down to 1 Pa can be reached when using the medium rotary pump and down to 10^{-2} Pa when using the combination rotary/diffusion pumps. The pressures before and after the reactor are measured by 2 Pirani gauges, when the rotary pump only is used (1 Pirani before and 1 Penning gauge after the reactor when the combination rotary/diffusion pumps is used). Hydrogen (deuterium) gas is fed into the reactor through a metering valve. The pressure drop through the pinhole of the glow discharge cathode is measured by the pressure gauges. The glow discharge cathode (tantalum) is connected to earth. The glow discharge anode (stainless steel) is connected to a positive high voltage generator (GAMMA High Voltage Research) delivering a regulated current up to 3 mA under a regulated voltage up to 20 kV. The target is connected to a negative high voltage generator (HP 6110 A) delivering a regulated current up to 6 mA under a regulated voltage up to 3 kV. Pressures, currents and voltages are monitored, using an AOIP LS20 monitoring device.

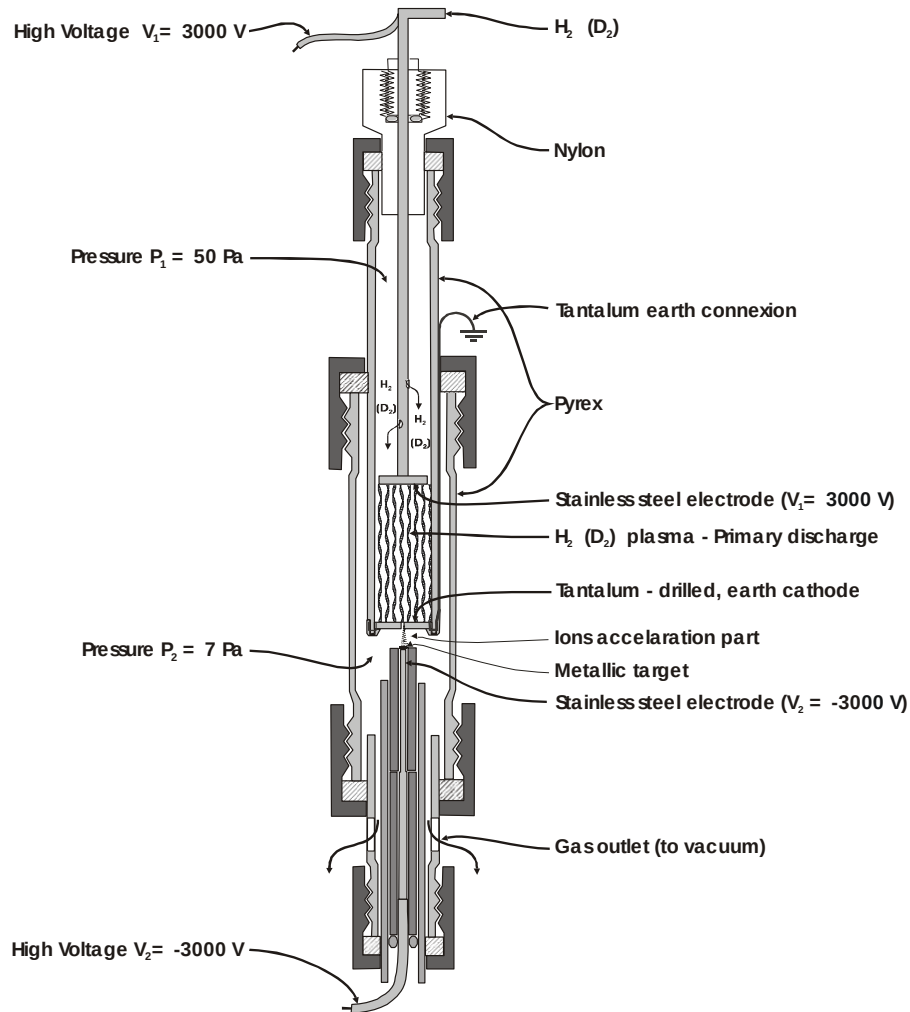


Fig. 3 – Reactor design

3.2 Reactor design

The reactor is shown on Fig 3.

The glow discharge is struck between the stainless steel anode and the tantalum cathode. A pinhole (surface $S_{Pin\ Hole}$) in the cathode (surface $S_{Cathode}$) allows the hydrogen (deuterium) flowing through the glow discharge at a pressure P_1 of a few tens of Pa, to expand down to a pressure P_2 of a few Pa. A current of protons (deuterons) also flows with the expanded hydrogen (deuterium), through the pinhole and is accelerated, under vacuum, by the high negative voltage of the target. Energies of the ions up to some 850 eV are expected (see below modeling of the discharge).

An helium 3 neutron detector with 2 cm paraffin thermalization covering is placed outside the vacuum bell (see above)

4. Modeling of the process

4.1 The glow discharge

The principles for a global model of a glow discharge can be found in [2]. The particles balance yields the temperature of the electrons T_e and the power balance yields the ions (and electrons) concentrations $n_0 = n_i = n_e$. If l is the length, R the radius of the plasma of the cylindrical discharge (Fig 4) and n_g the neutral gas concentration, the particles balance expresses that the charged particles production through ionization (coefficient K_{IZ} $m^3 s^{-1}$) is equal to the charged particles lost by recombination in the gas (axial losses, dimensionless fraction h_l) and on the surface of the reactor (surface losses, dimensionless fraction

$$K_{IZ} n_g n_0 \pi R^2 l = (2\pi R^2 h_l n_0 + 2\pi R l h_R n_0) u_B, \text{ with } u_B = \sqrt{\frac{kT_e}{m_i}} \text{ (Bohm velocity of the ions, mass } m_i)$$

From this balance, the following relation is obtained:

$$\frac{K_{IZ}(T_e)}{u_B(T_e)} = \frac{1}{n_g d_{eff}} \quad (1)$$

with $d_{eff} = \frac{1}{2} \frac{Rl}{Rh_l + lh_R}$, (m) linear dimension describing the geometry of the plasma.

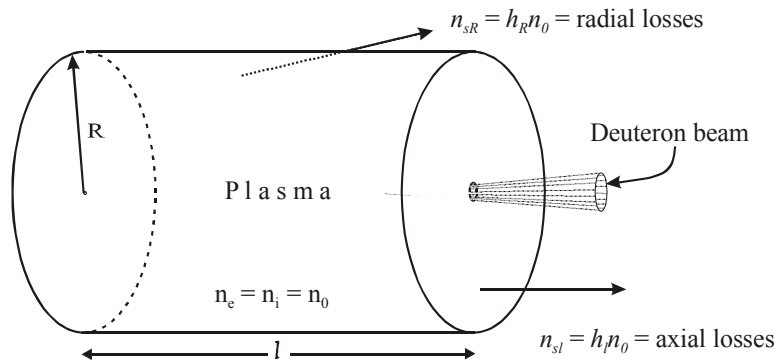


Fig. 4 – The glow discharge

The energy balance can be written $P_{abs} = (h_i n_0 2\pi R^2 + h_R n_0 2\pi R l) u_B E_T$ expressing that the total power absorbed P_{abs} is used for electron-ion pair production, E_T being the total energy required per pair (ionization, excitation, ion acceleration...)

From this balance, the following relation is obtained:

$$n_0 = \frac{P_{abs}}{A_{eff} u_B E_T} \quad (2)$$

with $A_{eff} = 2\pi R(Rh_i + lh_R)$, (m^2) surface dimension describing the geometry of the plasma.

Relations (1) and (2) combined with the relation:

$$A_{eff} d_{eff} = \pi R^2 l, \quad (m^3) \text{ (plasma volume)} \quad (3)$$

allow the calculation of the parameters of the discharge (n_0 and T_e), using the experimental relation between T_e and $n_g d_{eff}$ given by Fig 5 which is valid for any discharge. T_e is used as the fitting parameter.

Typical values for the conditions used ($P_1 = 50$ Pa, $V_1 = 3000$ V, $I_1 = 3$ mA) are $n_0 = 2 \cdot 10^{16} \text{ m}^{-3}$, temperature of the electrons $T_e = 4,2$ eV and energy of the ions leaving the cathode 2 eV.

4.2 The positive ions acceleration zone

A fraction of the positive ions (protons, deuterons) generated in the discharge (in the ratio $S_{Pin\ Hole} / S_{Cathode}$) are expanded, with the neutral atoms, from P_1 to P_2 , through the pinhole of the cathode, which they leave with an energy of a few eV (see above). They are accelerated by the target negative voltage. Their mean free path λ is assumed to be the same as atomic hydrogen,

$\lambda_H (mm) = \frac{100}{P_2 (Pa)} 10^{-1}$. For a distance cathode-target of 5 mm and a target voltage of -3000 V, the

energy of the protons (deuterons) impinging on the target will be some 850 eV for $P_2 = 7$ Pa, assuming that the expansion is complete at a few (2 to 3) mm from the cathode.

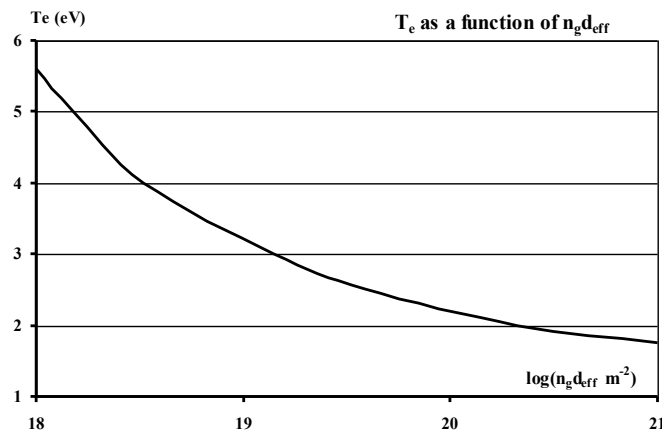


Fig. 5 – T_e as a function of $n_g d_{eff}$

5. Monitoring the fusion reaction

To monitor the fusion reaction, the production of neutrons will be measured, using a ^3He detector (active detection surface $S = 100 \text{ cm}^2$). The active part of the detector is surrounded by a cylindrical layer of paraffin, resulting in a paraffin thickness of 2 cm. The spectra are recorded using a CANBERRA 2006 pre-amplifier, an ORTEC 570 amplifier and a CANBERRA AccuSpec NaI multi-channel analyser. The back ground of the laboratory has been measured and found to be equal to $1.5 \pm 0.2 \cdot 10^{-2}$ cps, corresponding to a background neutron flux $\Phi_{N-back.}$ of some $1.5 \cdot 10^{-4}$ cps/cm².

Assuming an efficiency of 100% of the detection chain, the neutron activity $A_{N-meas.}$ of the target, will be evaluated from the measured neutron flux $\Phi_{N-meas.}$ by $A_{N-meas.} = 4\pi R^2 (\Phi_{N-meas.} - \Phi_{N-back.})$, (Bq), with R being the distance target/detector (taken as 25 cm which is the minimum distance between the cylindrical detector and the target). Thus calculated, $\Phi_{N-meas.}$ gives a low side value of the neutron activity of the target, that will then be compared to the value $A_{N-mod.}$, computed from the model described in [1].

In order to detect possible γ emission from the target, a Geiger counter has been placed inside the vacuum bell.

6. Conclusion

The proposed device will be used to test various targets (diameter 2 to 4 mm). The choice of these targets (nature of the metal and its physical and chemical characteristics) will be guided by the results already obtained in the field. In a first step, the objective will be to verify the validity of phenomenological model. In a second step, the possibility of gaining a better knowledge of the mechanisms involved could result in a further improvement of the targets.

Finally, in case of success, ion generators, with kW power level and energies of the ions in the range 200 to 4000 eV, that are now available on the market (surface treatment and electronic industries) could be used for an industrial up-scaling.

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Lithium Fluoride X-ray Imaging Film Detectors for Condensed Matter Nuclear Measurements

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Abstract. A novel thin-film imaging detector for X-rays, based on photoluminescence from aggregate color centers in lithium fluoride, has been proposed and tested. The detector consists in a radiation-sensitive thin film of lithium fluoride thermally evaporated on a glass substrate. The morphological properties of the lithium fluoride thin films, which influence the detector performances, have been investigated.

1. Introduction

Among alkali halides, lithium fluoride (LiF) is particularly interesting because it is practically not hygroscopic, it possesses good physical and optical properties and it can host laser active electronic defects stable at room temperature (RT). Various kinds of radiation can generate stable primary and aggregate defects, known as color centers (CC) [1] in LiF crystals and thin films. Some of these CC are optically active and emit photoluminescence efficiently in the visible spectral range at RT, under optical pumping. The primary CC is the F one, which consists of an anionic vacancy occupied by an electron. Its absorption band is located at around 248 nm and up to now the photoluminescence originating from the F defect in LiF has not been detected unambiguously. The aggregate centers F_2 and F_3^+ (two electrons bound to two and three anion vacancies, respectively) possess almost overlapping absorption bands, around 450 nm, generally called M band [2]; under optical pumping in this spectral region, at RT they emit broad photoluminescence bands peaked at 678 nm and 541 nm for F_2 and F_3^+ CC, respectively. Due to these properties, LiF is a radiation-sensitive dielectric material well-known in dosimetry [3] and utilized in optoelectronic devices [4-7].

2. Novel lithium fluoride imaging film detectors

In recent years the area of growth, characterization and coloration of LiF thin films has seen a considerable expansion [8]. Polycrystalline LiF films grown by thermal evaporation were proposed for gamma dosimetry [9], as nuclear sensors for neutrons [10,11] and as novel soft X-ray imaging detectors [12] based on F_2 and F_3^+ photoluminescence.

Recently the use of LiF thin films as innovative X-ray imaging detectors based on photoluminescence from optically active CC in LiF thin films [13] has been successfully extended to higher energies, up to 10 keV [14]. Their main peculiarities [12,14], which are intrinsic high spatial resolution on a large field of view, wide dynamic range, easiness of handling and versatility make a very powerful tool to reveal X radiation eventually emitted during low energy nuclear reactions (LENR) experiments.

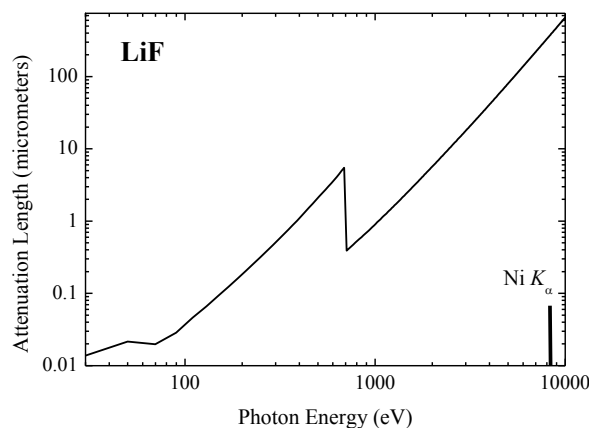


Fig. 1 – Attenuation length of X-rays in lithium fluoride as a function of their energy.

3. Experimental results and discussion

The electro-magnetic radiation interacts with the matter by three processes: photoelectric effect, Compton effect and electron-positron pair creation. Depending on X-rays energy, their penetration in LiF ranges from few tens of nanometers to several hundreds of micrometers; the deposited energy per unit length is constant in a certain material and the radiation intensity along the depth decreases as an exponential function, approximately. Figure 1 shows the attenuation length of X-rays in LiF as a function of their energy, below the Ni K_{α} edge (8.333 keV). The exposure to X-rays produces the stable formation of CC in LiF in layers of thickness comparable with their attenuation length.

Uniform thickness, good optical quality, polycrystalline LiF films of different thicknesses, from 0.1 to 4 μm , have been grown by thermal evaporation [8] on heated amorphous and crystalline substrates. The substrates were clamped to a rotating plate, controlled at fixed temperatures up to 350 $^{\circ}\text{C}$ during the deposition process. The starting material consists of LiF microcrystalline powder (Merck Suprapur, 99.99% pure), heated at about 800 $^{\circ}\text{C}$ in a tantalum crucible, placed below the substrate at a distance of 22 cm, under a typical vacuum pressure below $5 \cdot 10^{-6}$ mbar. The evaporation rate, monitored in situ by an INFICON quartz oscillator, was controlled at a fixed value of 1 nm/s during the growth. The total thickness of the deposited films was also directly measured by using a Tencor Alpha-Step 200 profilometer. The morphological analysis was performed by an Assing Perception Device Atomic Force Microscope (AFM) equipped with a Veeco MLCT-AUNM-10 tip operating in contact mode, maximum scan area of $(25 \times 25) \mu\text{m}^2$ and a z-axis range of 5 μm . The estimated relative error for x, y and z axis is $\sim 3\%$. Measurements are performed with a resolution of 257×257 points on xy plane (sample plane).

The structural, morphological and optical properties of the films grown on optically transparent amorphous substrates, like glass and silica, are dependent on the deposition parameters, in particular the substrate temperature, which influences the features of films of different thickness and the stable formation of primary and aggregate color centers [15].

Figure 2 shows the two-dimensional (2D) AFM image $(5 \times 5) \mu\text{m}^2$ of the surface of a LiF thin film deposited by thermal evaporation on a glass substrate kept at 28 $^{\circ}\text{C}$ and of total thickness = 1.9 μm .

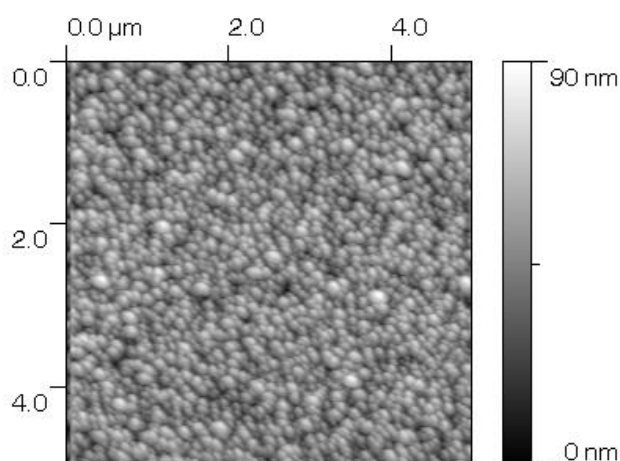


Fig. 2 – 2D AFM image of a LiF film, of thickness 1.9 μm , thermally evaporated on a glass substrate kept at 28 $^{\circ}\text{C}$.

The images show a quite compact grain structure with regular and uniform grain size distribution; average grain size is about 10 nm and the Root Mean Square (RMS) roughness value compute from the image is 11 nm on the $5 \times 5 \mu\text{m}^2$ mapped area, which is comparable with the typical roughness of a thicker LiF film grown on glass microscope slides.

X-rays of energy higher than 2 eV are entirely absorbed by this film, as it can be deduced by the curve of Fig. 1, making it coloured along its full thickness. The CC produced in the LiF film by the X-rays exposition can be made visible by blue light excitation of the photoluminescence of the F_2 and F_3^+ defects, which emit in the red and green spectral regions, respectively.

The exposed LiF film is analyzed by using a Confocal Laser Scanning Microscope (CLSM) Nikon Eclipse C1-80i equipped with a coherent CW Argon laser operating at 458 nm. It allows to integrate, acquire and store the signature of the emitted radiation in a fluorescence image reaching a spatial resolution below 300 nm at the used wavelength. The same optical microscope was used in different optical operation modes, with white and blue light lamp illumination, in order to exclude and/or distinguish artifacts in the registered fluorescence image. The presented morphological investigation confirm the good surface quality of the LiF-film based detector.

3. Conclusions

Novel LiF-film based X-ray detectors were proposed, realized and characterized. These two-dimensional imaging detectors found application in photonics, biology, material science, device investigation and in the characterization of intense X-ray sources, including very short duration ones [16]. They allow great versatility, as they can grown in the form of thin films by well-assessed physical deposition techniques. The stored fluorescence images, based on the stable formation of aggregate electronic defects in the exposed areas, can be directly read without the need of any development procedure, which could introduce some artifacts. A good optical quality and a uniform surface of the deposited LiF film, which is the radiation-sensitive element in the X-ray detector, improve the quality of the images and reduces reading artifacts. Further studies are in progress on the LiF films growth on several substrates and their characterization in order to improve the optical quality and adhesion properties, as well as progress are under way in the full spectral analysis of the stored fluorescence images.

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Arguments for dideuterium near monovacancies in PdD

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Abstract. Molecular D₂ does not form in bulk PdD because the electron density sufficiently high so that antibonding orbitals are occupied. The electron density can be lower in the vicinity of a vacancy. We examine the possibility that sigma-bonded dideuterium can occur at the lowered electron density near a monovacancy in PdD.

1. Introduction

Excess heat has been observed in many Fleischmann-Pons experiments over the years, generally supporting the claims made by Fleischmann and Pons in 1989 [1,2]. The many negative results found in the early experiments of 1989 can be attributed in part to a lack of understanding of basic requirements that were clarified later on [3-5]. A remarkable feature of the effect is that a prodigious amount of energy is produced; much greater than can be attributed to chemical reactions (for which physical evidence is absent). The conjecture that the energy is due to a new nuclear process has historically been met with much skepticism, due to the absence of commensurate energetic particles which would be expected if nuclear reactions were responsible [6]. In a nuclear reaction, the energy produced is expressed as energetic particles as a consequence of local energy and momentum conservation. Excess energy produced in the Fleischmann-Pons experiment without commensurate energetic particles challenges long established ideas about how nuclei react, suggesting that there is a new kind of physical process in which nuclei interact in some new way in which the energy is expressed through other degrees of freedom.

We have described in earlier publications a new mechanism which is capable of coherent energy exchange between two-level systems and an oscillator under conditions where the transition energy of the two-level system is a great many times the characteristic energy of the oscillator [7,8]. This mechanism seems to be capable of converting an MeV-level nuclear energy quantum into a very large number of meV-level phonons under conditions relevant to the Fleischmann-Pons experiment. We have proposed a two-step reaction mechanism that involves first the transfer of excitation from the hindered D₂/He system to unhindered two-level systems which then convert the nuclear energy quantum to phonons using this new energy conversion mechanism. Under conditions where the excitation transfer step is the "bottleneck" which determines the overall rate for the two-step reaction, the reaction rate can be estimated from the associated excitation transfer matrix element. We have recently computed the nuclear part of this matrix element using a brute force numerical calculation, and we find that it is sufficiently large to account for the rate of excess heat production if the screening energy [9] is about 150 eV.

For the process consistent with our model to occur, molecular D₂ must be present in the lattice. In this respect, our model differs from other models which are currently more popular [10,11]. In our view, many practical aspects of the Fleischmann-Pons experiment and related experiments can be understood in terms of maximizing molecular D₂ inside the lattice. In this proceedings paper, we will focus on the issue of D₂ in PdD, which will focus our attention on issues related to the local electron density and vacancies.

2. Preferred electron density

Our arguments in this paper are based on the notion (from embedded atom theory [12-14]) that there exists a preferred electron density that deuterium or dideuterium wants to see, that is similar in molecular or solid state environments. If so, then we might use PdH as a reference for deuterium in Pd, and PdH₂ as

a reference for dideuterium in Pd.

In the case of PdH, we make use of the results of Balasubramanian et al [15] who give an atomic separation of 1.53 Angstroms. For PdH₂, we use the results of Balasubramanian et al [16], who give an a separation between the Pd atom and the center of the H₂ molecule to be 1.67 Angstroms. In this case, the two hydrogen atoms bond as a molecule with a separation of 0.81 Angstroms. To estimate the Pd electron density at 1.67 Angstroms for PdH₂, we performed a Dirac-Fock calculation for atomic Pd in the ground state (4d)¹⁰ configuration (which was found by Balasubramanian et al to be the dominant Pd configuration), and found the Pd electron density to be 0.0332 electrons/Angstrom³ (see Figure 1). A similar computation for the Pd (4d)^{9.35}(5s)^{0.65} configuration leads to an electron density at 1.53 Angstroms of 0.0686 electrons/Angstrom³.

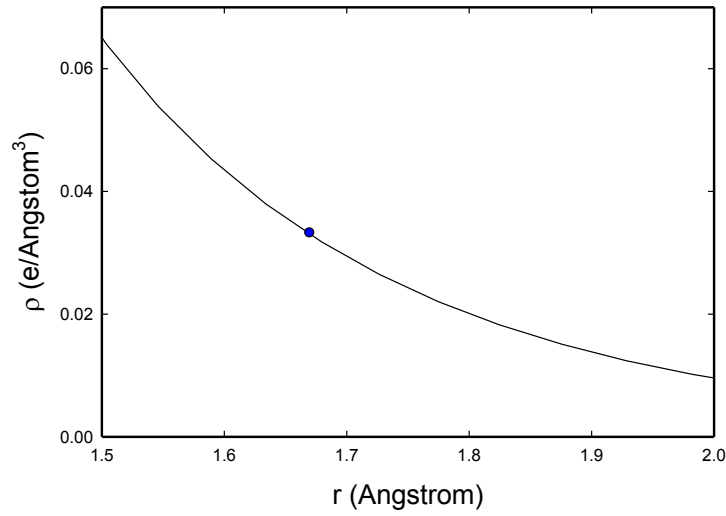


Fig. 1. – Electron density from a Dirac-Fock calculation of Pd (4d)¹⁰ configuration in the vicinity of 1.67 Angstroms relevant to the PdH₂ molecule.

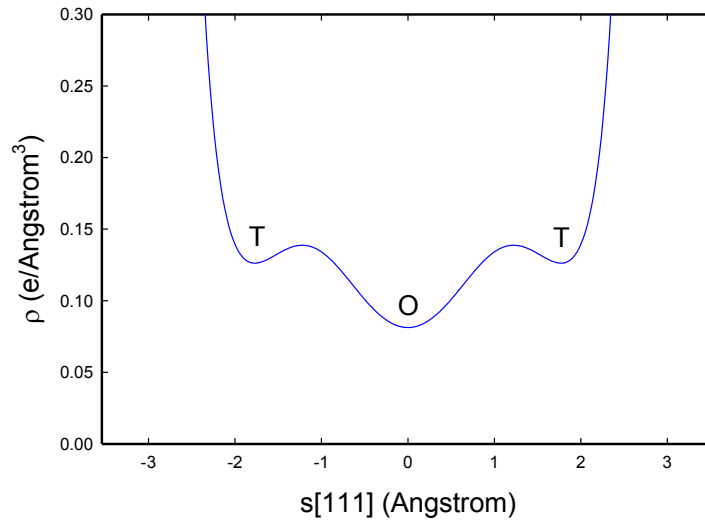


Fig. 2. – Model electron density due to Pd in the vicinity of an octahedral site in PdH.

3. Pd electron density in PdH

If we consider the electron density due to only the Pd atoms in PdH from a simple superposition of the atomic orbitals, we obtain the result for a scan centered at an octahedral site along the [111] direction shown in Figure 2. We see that the electron density is lowest at the octahedral site in this model, with a density of 0.081 electrons/Angstrom³. The electron density in this model is significantly higher at the tetrahedral sites, indicating that one would expect hydrogen in PdH to occupy the octahedral sites since the Pd electron density at these sites is closer to the Pd electron density in molecular PdH.

A computation of H₂ in electron gas at an electron density of 9.3×10^{-3} electrons/a₀³ was published by Christensen et al [17]. This electron density corresponds to 0.0628 electrons/Angstrom³, and is reasonably close to the octahedral site electron density in PdH from above (0.081 electrons/Angstrom³). The equilibrium distance between the two hydrogen atoms in this case is about 1.9 a₀, which is 1.005 Angstroms. This perhaps provides the closest connection to the discussion above. The electron density once again is higher than in the case of σ -bonded PdH₂, and the H₂ molecule responds by increasing its separation because of the occupation of antibonding states.

4. Electron density near a monovacancy in PdH

We next consider the electron density due Pd atoms near a monovacancy in PdH. In Figure 3 we show the Pd electron density from a simple superposition of Pd atomic orbitals, where the vacancy is indicated at -3.54 Angstroms, and where the along the [111] direction the electron density is equal to the preferred electron density of molecular H₂.

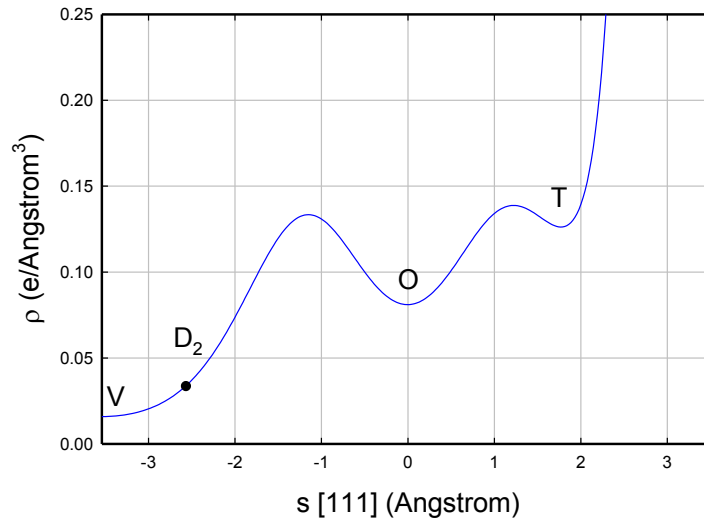


Fig. 3. – Model electron density due to Pd near a monovacancy in PdH.

We note that this model gives an electron density at the octahedral site location near the vacancy to be very close to the optimum for single H as judged by the PdH molecule. The calculation of Velikova et al [18] is consistent with a displacement of 0.26 Angstroms for single H occupation from the octahedral site location.

5. Statistical mechanics

To estimate the probability that a D_2 molecule is present in a monovacancy, we require a statistical model. Binding energies for single hydrogen atoms in octahedral sites have been estimated by several authors, including Nordlander et al [14] and Velikova et al [18]. The binding energies of Velikova et al are relative to hydrogen in solution at low concentration, which suggests that we need consistent models for deuterium in the bulk and trapped in vacancies. We begin with the bulk model, where the chemical potential can be related to the loading above the beta phase boundary through

$$\mu(x) - E_D(0) = k_B T \ln \frac{x}{1-x} + \Delta E + (x - 0.60) \frac{d\mu}{dx} \quad (1)$$

Here $E_D(0)$ is the deuterium binding energy in dilute PdD_x ; the variable x is the D/Pd ratio; and ΔE is the binding energy at D/Pd = 0.60 minus the binding energy at D/Pd=0. We have used $\Delta E = -135$ meV [19], and

$$\frac{d\mu}{dx} = 514 \frac{\text{meV}}{D} \quad (2)$$

This is consistent with the measurements of Chun and Ra [20].

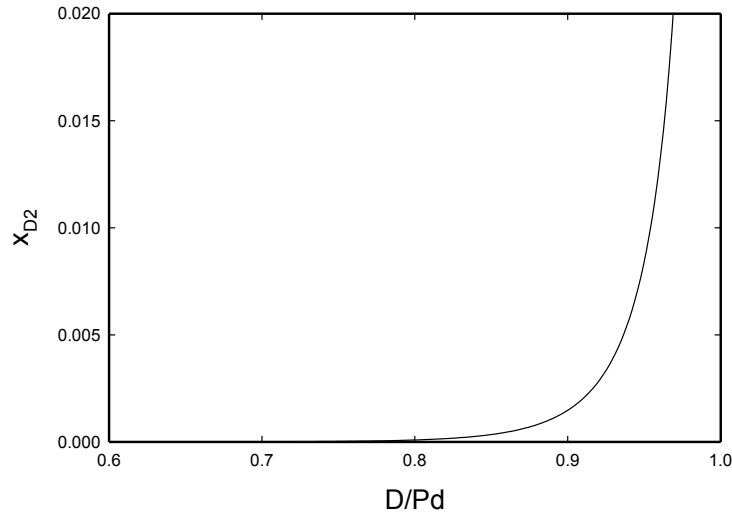


Fig. 4. – Model calculation of occupation of D_2 near monovacancies.

For the occupation of the octahedral sites in the vicinity of a vacancy, we can use a model based on

$$p_m = \frac{g_m e^{-(E_m - \mu_m)/k_B T}}{\sum_n g_n e^{-(E_n - \mu_n)/k_B T}} \quad (3)$$

For the degeneracy g_m , we have included the spin and statistical factors; for the energies E_m , we have used the results of Velikova et al [18]. From the computations in [18], we know that a dideuterium molecule is unstable in the presence of unoccupied octahedral sites in the vicinity of a monovacancy. So we have added the possibility of D_2 occupation only when there are 7 deuterons in the vicinity of the monovacancy. This is consistent with the computations of Liu et al for hydrogen in W [21]. In the

calculation of Velikova et al, the energy of the D_2 molecule is about 1 eV above deuterium atom occupation of the octahedral sites. Unfortunately, we do not as yet have a good number for the D_2 energy relative to bulk deuterium for $5D+D_2$ occupation around a monovacancy. In the computation shown in Figure 4, we have assumed that the additional D has to go up by 200 meV from $E_D(0)$ to make a D_2 molecule.

The amount of D_2 in this model increases with loading above a threshold near 0.85. We recall that the excess heat increases with loading above a threshold in much the same way. This is consistent with models that we have put forth which start with D_2 in the lattice as a prerequisite for the reactions which result in excess power and 4He .

6. Conclusions

Excess heat in the Fleischmann-Pons experiment has been seen in a large number of experiments. At present there is no consensus among those in the field as to what physical mechanism is responsible. Our attention over the past decade has been focused on new reaction mechanisms which are driven by D_2 to 4He transitions, with the energy converted into phonon excitation. For this reaction mechanism to work, we require D_2 to be present in the lattice, which is not an easy thing to happen if the lattice is PdD. Molecular D_2 cannot form in bulk PdD because the electron density is too high. According to the arguments here, D_2 can form near vacancies, and we have focused on the occurrence of D_2 near a monovacancy. Since the electron density due to Pd is reduced near the site of a missing Pd atom, the electron density in our simple models drops to levels at which D_2 normally binds to Pd.

We have been of the opinion for many years now that important aspects of the Fleischmann-Pons experiment can be understood simply if we are trying to maximize D_2 occupation. Since D_2 doesn't form in bulk PdD, and since there are very few vacancies initially in Pd, the cathodes start out with essentially no ability to host molecular D_2 . So, according to the discussion above, we need to create vacancies. Vacancies are stabilized when Pd is highly loaded with deuterium [22-23]. Previously we estimated that a D/Pd loading of about 0.95 was required in order for the vacancies to become favored thermodynamically. However, since the diffusion coefficient for vacancies is so small near room temperature, vacancies have great difficulty diffusing in from nearby surfaces. Instead, it seems more probable that inadvertent codeposition of Pd on highly loaded Pd is responsible. This is consistent with observations of impurities below the outer surface of cathodes, and it is consistent with the very long time that cathodes need to remain loaded prior to observations of excess power. Codeposition has been verified as being able to produce superabundant vacancies [24]. The short onset time of excess power in the Szpak experiment is consistent with this point of view. Vacancies in this scenario would be created near the outer surface, so that only the near-surface region would be active. This is consistent with the observation of produce 4He in the gas phase, which could not diffuse if created in the interior.

Once vacancies have been produced, then they need to be filled with molecular D_2 . According to the model described above, this requires high loading above D/Pd of about 0.85. The correlation between loading and excess power has been observed in experiments [3], and the results are consistent if one assumes that the level of excess power production is correlated with D_2 occupancy. It remains to compute the D_2 binding energy in a monovacancy with 7 deuterium atoms present.

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Bose-Einstein Condensation Nuclear Fusion: Theoretical Predictions and Experimental Tests

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Abstract. It is shown that theory of Bose-Einstein condensation nuclear fusion (BECNF) [1] is capable of explaining many diverse experimental results of deuteron induced nuclear reactions in metals, observed in electrolysis and gas loading experiments. The theory is based on a single conventional physical concept of Bose-Einstein condensation of deuterons in metal and provides a consistent theoretical description of the experimental results. The theory also has predictive powers as expected for a quantitatively predictive physical theory. It is shown that the fusion energy transfer can be accomplished by the stopping power of metal without invoking hypothesis of fusion energy transfer to metal lattice vibrations. It is also shown that observed anomalous tritium production can be explained by incorporating a sub-threshold resonance reaction mechanism into the BECNF theory. The basic concept and important features of the BECNF theory is presented, and theoretical explanations of the experimental observations are described. Key experimental tests of theoretical predictions are proposed and discussed.

1. Introduction

Recently, it has been shown that the BECNF theory [1] can provide a consistent conventional theoretical explanation for anomalous results of deuteron induced nuclear reactions in metal at ultra low-energies [2-5]. Two decades ago, Fleischmann and Pons reported excess heat generation in electrolysis experiment using the negatively polarized Pd/D – D₂O system [2]. Since then, many others have reported experimental observations of excess heat generation and anomalous nuclear reactions occurring in metal at ultra low energies from electrolysis experiments [3] and gas-loading experiments [3-5]. These anomalous reaction rates cannot be explained using the conventional theory of nuclear reactions in free space, which predicts extremely low nuclear reaction rates at ultra low-energies (≤ 10 eV) due to the Gamow factor arising from the Coulomb repulsion between two charged nuclei undergoing nuclear-reaction process.

The theory is capable of not only explaining most of the experimental observations, but also provides theoretical predictions which can be tested experimentally for the confirmation of the theory. A detailed description of the theoretical explanation, based on the theory of Bose-Einstein condensation nuclear fusion is presented along with suggested experimental tests of predictions of the theory and a discussion of the scalability of the fusion rates based on the theory.

2. Anomalous experimental results

The conventional deuterium fusion in free space proceeds via the following nuclear reactions:

- {1} $D + D \rightarrow p (3.02 \text{ MeV}) + T (1.01 \text{ MeV})$;
- {2} $D + D \rightarrow n (2.45 \text{ MeV}) + {}^3\text{He} (0.82 \text{ MeV})$; and

{3} $D + D \rightarrow {}^4\text{He} + \gamma$ (23.8 MeV).

The cross-sections (or reaction rates) for reactions {1} and {2} have been measured by beam experiments at intermediate energies (≥ 10 keV). The cross-sections for reaction {1} – {3} are expected to be extremely small at low energies (≤ 10 eV) due to the Gamow factor arising from Coulomb barrier between two deuterons. The measured cross-sections have branching ratios: $(\sigma\{1\}, \sigma\{2\}, \sigma\{3\}) \approx (1, 1, 10^{-6})$.

From many experimental measurements by Fleischmann and Pons [2], and many others [3-5] over 20 years since then, the following experimental results have emerged. At ambient temperatures or low energies (≤ 10 eV), deuterium fusion in metal proceeds via the following reactions:

- {4} $D(m) + D(m) \rightarrow p(m) + T(m) + 4.03 \text{ MeV (m)}$;
- {5} $D(m) + D(m) \rightarrow n(m) + {}^3\text{He}(m) + 3.27 \text{ MeV (m)}$; and
- {6} $D(m) + D(m) \rightarrow {}^4\text{He}(m) + 23.85 \text{ MeV (m)}$,

where m represents a host metal lattice or metal particle. Reaction rate R for {6} is dominant over reaction rates for {4} and {5}, i.e., $R\{6\} \gg R\{4\}$ and $R\{6\} \gg R\{5\}$.

Experimental observations reported from electrolysis and gas-loading experiments are summarized below (not complete):

- [1] The Coulomb barrier between two deuterons are suppressed
- [2] Excess heat production (the amount of excess heat indicates its nuclear origin)
- [3] ${}^4\text{He}$ production commensurate with excess heat production, no 23.85 MeV γ ray
- [4] More tritium is produced than neutron $R\{4\} \gg R\{5\}$
- [5] Production of nuclear ashes with anomalous rates: $R\{4\} \ll R\{6\}$ and $R\{5\} \ll R\{6\}$
- [6] Production of hot spots and micro-scale craters on metal surface
- [7] Detection of radiations
- [8] “Heat-after-death”
- [9] Requirement of deuteron mobility ($D/Pd > \sim 0.9$, electric current, pressure gradient, etc.)
- [10] Requirement of deuterium purity ($H/D \ll 1$)

All of the above experimental observations are explained in terms of theory of Bose-Einstein condensation nuclear fusion (BECNF) in the previous publication [1] and this paper. In this paper, additional theoretical explanations are provided for the **observations** [1] through [4] in sections 5 and 6. Theoretical explanations of other observations such as “Heat-after-death” [6] have been described in [1].

3. Bose-Einstein condensation (BEC) of deuterons in metals

Development of Bose-Einstein condensate theory of deuteron fusion in metal is based upon a single hypothesis that deuterons in metal are mobile and hence are capable of forming Bose-Einstein condensates.

Experimental proof of proton (deuteron) mobility in metals was first demonstrated by Coehn in his hydrogen electro-migration experiment [7,8]. The significance of Coehn’s experimental results [7] is emphasized by Bartolomeo et al. [9]. A theoretical explanation of Coehn’s results [7] is given by Isenberg [10]. The Coehn’s experimental fact is not well known in review articles and textbooks. There are other experimental evidences [11-15] that heating and/or applying an electric field in a metal causes hydrogen or deuteron in a metal to become mobile, thus leading to a higher density for quasi-free mobile deuterons in a metal.

BEC condensate fraction $F(T) = N_{\text{BE}}/N$ of deuterons in a metal satisfying BEC condition can be estimated as a function of the temperature and using either Bose-Einstein or Maxwell-Boltzmann distribution function. N is the total number of deuterons and N_{BE} is the number of deuterons satisfying the BEC requirement $\lambda_c > d$ where λ_c is the de Broglie wavelength and d is the average distance between two deuterons. For $d = 2.5 \text{ \AA}$, we obtain $F(T=300^\circ \text{ K}) \approx 0.084$ (8.4 %), $F(T = 77.3^\circ \text{ K}) \approx 0.44$ (44%), and $F(T = 20.3^\circ \text{ K}) \approx 0.94$ (94%). At $T = 300^\circ \text{ K}$, $F = 0.084$ (8.4%) is not large enough to form BEC since motions of deuterons are limited to several lattice sites and the probability of their encounters are very small. On the other hand, at liquid nitrogen (77.3° K) and liquid hydrogen (20.3° K) temperatures, probability of forming BEC of deuterons is expected to be $\Omega \approx 1$. This suggests that experiments at these low temperatures can provide tests for enhancement of the reaction rate R_t , Eq. (4) described below, as predicted by BECNF theory.

4. Bose-Einstein condensation theory of deuteron fusion in metal

N-body Schroedinger equation for the system is given by

$$H\Psi = E\Psi \quad (1)$$

with the Hamiltonian H for the system given by

$$H = \frac{\hbar^2}{2m} \sum_{i=1}^N \Delta_i + \frac{1}{2} m \omega^2 \sum_{i=1}^N r_i^2 + \sum_{i < j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \quad (2)$$

where m is the rest mass of the nucleus. Only two-body interactions (Coulomb and nuclear forces) are considered since we expect that three-body interactions are expected to be much weaker than the two-body interactions.

The approximate ground-state solution of Eq. (1) with H given by Eq. (2) is obtained using the equivalent linear two-body method [16,17]. The use of an alternative method based on the mean-field theory for bosons yields the same result (see Appendix in [18]). Based on the optical theorem formulation of low energy nuclear reactions [19], the ground-state solution is used to derive the approximate theoretical formula for the deuteron-deuteron fusion rate in an ion trap (micro/nano-scale metal grain or particle). The detailed derivations are given elsewhere [18,20].

Our final theoretical formula for the nuclear fusion rate R_{trap} for a single trap containing N deuterons is given by [1]

$$R_{\text{trap}} = 4(3/4\pi)^{3/2} \Omega A \frac{N^2}{D_{\text{trap}}^3} \propto \Omega \frac{N^2}{D_{\text{trap}}^3} \quad (3)$$

where N is the average number of Bose nuclei in a trap/cluster, D_{trap} is the average diameter of the trap, $A = 2S r_B / (\pi \hbar)$, $r_B = \hbar^2 / (2\mu e^2)$, and S is the S-factor for the nuclear fusion reaction between two deuterons. For D(d,p)T and D(d,n)³He reactions, we have $S \approx 55$ keV-barn. We expect also $S \approx 55$ keV-barn or larger for reaction {6}. $A = S \times (1.4 \times 10^{-18}) \text{ cm}^3/\text{s}$ with S in units of keV-barn. $A = 0.77 \times 10^{-16} \text{ cm}^3/\text{s}$ for $S = 55$ keV-barn. Only one unknown parameter is the probability of the BEC ground state occupation, Ω .

The total fusion rate R_t is given by

$$R_t = N_{\text{trap}} R_{\text{trap}} = \frac{N_D}{N} R_{\text{trap}} \propto \Omega \frac{N}{D_{\text{trap}}^3} \quad (4)$$

where N_D is the total number of deuterons and $N_{\text{trap}} = N_D/N$ is the total number of traps.

Eq. (4) shows that the total fusion rates, R_t , are very large if $\Omega \approx 1$.

Eqs. (3) and (4) provide an important result that nuclear fusion rates R_{trap} and R_t do not depend on the Gamow factor in contrast to the conventional theory for nuclear fusion in free space. This could provide explanations for overcoming the Coulomb barrier and for the claimed anomalous effects for low-energy nuclear reactions in metals. This is consistent with the conjecture noted by Dirac [21] and used by Bogolubov [22] that boson creation and annihilation operators can be treated simply as numbers when the ground state occupation number is large. This implies that for large N each charged boson behaves as an independent particle in a common average background potential and the Coulomb interaction between two charged bosons is suppressed. This provides an explanation for the **observation** [1].

5. Theoretical explanation of anomalous ⁴He production (the observations [2] and [3])

For a single trap (or metal particle) containing N deuterons, the deuteron-deuteron fusion can proceed with the following two reaction channels:

$$\{6\} \quad \psi_{\text{BEC}} \{(N-2)D's + (D+D)\} \rightarrow \psi^* \{^4\text{He} + (N-2)D's\} \quad (Q = 23.85 \text{ MeV}), \quad (5)$$

and

$$\{7\} \quad \psi_{\text{BEC}} \{(N-2)D's + (D+D)\} \rightarrow \psi^* \{^4\text{He}^* + (N-2)D's\} \quad (Q = 3.64 \text{ MeV}) \quad (6)$$

where ψ_{BEC} is the Bose-Einstein condensate ground state (a coherent quantum state) with N deuterons and ψ^* are final excited continuum states. ^4He in Eq. (5) represents the ground state with spin-parity, 0^+ , while $^4\text{He}^*$ in Eq. (6) represents the 0^+ excited state at 20.21 MeV above the ^4He ground state [23]. Excess energy (Q value) is absorbed by the BEC state and shared by $(N-2)$ deuterons and reaction products in the final state. It is important to note that reactions {6} and {7}, described by Eqs. (5) and (6), cannot occur in free-space due to the momentum conservation.

For micro/nano-scale metal particles, the above consideration shows that excess energies (Q) lead to a micro/nano-scale fire-work type explosion, creating a crater/cavity and a hot spot with fire-work like star tracks. The size of a crater/cavity will depend on number of neighboring Pd nanoparticles participating in BEC fusion almost simultaneously. Hot spots and craters have been observed in experiments reported by Srinivasan et al. [24] and others.

We now consider the total momentum conservation for reaction {6} with the reaction channel Eq. (5). The initial total momentum of the initial BEC state with N deuterons (denoted as D^N) is given by $\vec{P}_{D^N} \approx 0$. Because of the total momentum conservation, the final total momenta for reaction {6} is given by

$$\{6\} \quad \vec{P}_{D^{N-2} \text{ } ^4\text{He}} \approx 0, \quad \langle T_D \rangle \approx \langle T_{^4\text{He}} \rangle \approx Q\{6\} / N$$

where T represents the kinetic energy.

For the reaction {6} with Eq. (5), the average kinetic energy for each deuteron is $T = Q\{6\}/N = 23.85 \text{ MeV}/N$. For the case of 5 nm Pd trap, the number of deuterons in the trap is $N = \sim 4450$, and $T \approx 5.36 \text{ keV}$. With this deuteron kinetic energy of $\sim 5.36 \text{ keV}$, a question arises whether the hot-fusion reactions {1} and {2} can occur as the secondary reactions to the primary reaction {6}. Since the secondary reactions {1} and {2} have not been observed, there have been speculations such as a hypothesis that the fusion energy of 23.85 MeV is transferred to lattice vibrations thus producing heat in metal. In the following, a more convincing alternative explanation is described to show that transfer of the fusion energy of 23.85 MeV to the metal can be accomplished by the energy loss of energetic (5.36 keV) deuteron due to the stopping power of the metal.

Experimental values of the conventional hot-fusion cross section $\sigma(E)$ for reaction {1} or {2} have been conventionally parameterized as [25]

$$\sigma(E) = \frac{S(E)}{E} \exp \left[- \left(E_G / E \right)^{1/2} \right], \quad (7)$$

where E_G is the “Gamow energy” given by $E_G = (2\pi\alpha Z_D Z_D)^2 \text{ MeV}^2 / 2$ or $E_G^{1/2} \approx 31.39(\text{keV})^{1/2}$ for the reduced mass $M \approx M_D/2$ for reactions {1} or {2}. The S factor, $S(E)$, is extracted from experimentally measured values [26] of the cross section $\sigma(E)$ for $E \geq 4 \text{ keV}$ and is nearly constant [27]; $S(E) \approx 52.9 \text{ keV} \cdot \text{b}$, for reactions {1} or {2}. The probability $P(E_i)$ for a deuteron to undergo the conventional hot-fusion reaction {1} or {2} while slowing down in the deuterated palladium metal can be written as [28]

$$\begin{aligned} P(E_i) &= 1 - \exp \left[- \int dx n_D \sigma(E_{DD}) \right] \approx \int dx n_D \sigma(E_{DD}) \\ &= n_D \int_0^{E_i} dE_D \frac{1}{|dE_D / dx|} \sigma(E_{DD}). \end{aligned} \quad (8)$$

The stopping power [29] for deuterium in PdD for $E_D \leq 20 \text{ keV}$ is given by [28]

$$\frac{dE_D}{dx} = 3.1 \times 10^5 \sqrt{E_D} \text{ keV} / \text{cm}, \quad (9)$$

for $n_{\text{Pd}} = 6.767 \times 10^{22} \text{ cm}^{-3}$ and $n_{\text{D}} = n_{\text{Pd}}$. If we use Eq. (9) and the conventional extrapolation formula for $\sigma(E)$ given by Eq. (7), the integration in Eq. (8) can be performed analytically to yield the following expression for Eq. (8)[27]:

$$P(E_i) = 1.04 \times 10^{-6} \exp\left(-44.40 / \sqrt{E_i}\right), \quad (10)$$

where E_i is in keV (LAB), for reactions {1} or {2} assuming equal branching ratios (50% each).

For the case of 5 nm diameter Pd particle containing ~ 4450 deuterons, $E_i = 5.36$ keV, and Eq. (10) yields $P(5.36 \text{ keV}) \approx 0.49 \times 10^{-14}$ per deuteron. Therefore, the total fusion probability for 4450 deuterons is $P_{\text{total}} \approx 2.2 \times 10^{-11}$, yielding a branching ratio of $R\{1\}/R\{6\} \approx R\{2\}/R\{6\} \approx 10^{-11}$. Tritium and neutron production from primary reactions $R\{1\}$ and $R\{2\}$ are shown to be both negligible due to a selection rule [1]. Even for the case of $E_i \approx 20$ keV with a 3.2 nm Pd particle containing ~ 1200 deuterons, $P(20 \text{ keV}) \approx 0.5 \times 10^{-10}$, and the total fusion probability is $P_{\text{total}}(20 \text{ keV}) \approx 0.6 \times 10^{-7}$. Therefore, the fusion energy of 23.85 MeV from {6} is transferred to the metal by the stopping power of the metal without appreciable production of T and n from secondary reactions {1} and {2}.

6. Theoretical explanation of anomalous tritium production (the observation [4])

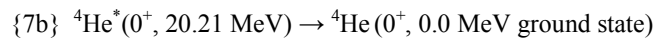
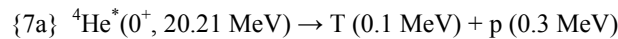
There have been many reports of anomalous tritium and neutron production in deuterated metal from electrolysis experiments [30-34] and gas/plasma loading experiments [24, 35-40]. The reported branching ratio of $R(T)/R(n)$ ranges from 10^8 to 10^9 in contrast to the conventional free-space reactions branching ratio of $R\{1\}/R\{2\} \approx 1$. In this section, we present a theoretical explanation of this anomalous tritium production based on the BECNF theory, using a new energy level scale which sets $E = 0$ for (D + D) state, and $E = -23.85 \text{ MeV}$ for the ^4He ground state. Q-value remains same since $Q = E_i - E_f$.

The reaction {7}, described by Eq. (6), can proceed via a sub-threshold resonance reaction [41,42]. The S-factor for the sub-threshold resonance reaction can be extracted from the cross-section given by Breit-Wigner expression [41,42], and given by

$$S(E) = \frac{\pi^2 \hbar^4}{4\mu^2 R_n^2} \frac{1}{K_1^2(x)} w \theta_0^2 \frac{\Gamma_2}{(E - E_R)^2 + (\Gamma/2)^2}, \quad (11)$$

where μ is the reduced mass in units of atomic mass unit (931.494 MeV), R_n is the nuclear radius, and w is the statistical factor. $K_1(x)$ is the modified Bessel function of order unity with argument $x = (8Z_1 Z_2 e^2 R_n \mu / \hbar^2)^{1/2}$. Γ_2 is a partial decay width and Γ is the total decay width to the final states. If E is measured from the threshold energy $E = 0$ of (D + D) state, we have $E_R = (20.21 \text{ MeV} - 23.85 \text{ MeV}) = -3.64 \text{ MeV}$. Eq. (11) shows that the $S(E)$ factor has a finite value at $E = 0$ and drops off rapidly with increasing energy E . θ_i^2 is the reduced width of a nuclear state, representing the probability of finding the excited state in the configuration i , and the sum of θ_i^2 over i is normalized to 1. The dimensionless number θ_i^2 is generally determined experimentally and contains the nuclear structure information.

For the entrance channel, $D + D \rightarrow ^4\text{He}^*(0^+, 20.21 \text{ MeV})$, there are two possible decay channels:



Once $S(E)$ factors are calculated from Eq. (11), it can be used in Eqs. (3) and (4) to obtain the total reaction rate. In the following, $S(E)$ factors are estimated for the decay channels, {7a} and {7b}, using Eq. (11).

For the decay channel {7a}, $\Gamma_2 = \Gamma_a = 0.5 \text{ MeV}$ [23]. When this value of Γ_2 is combining with other appropriate inputs in Eq. (11), the extracted S-factor for the decay channel {7a} is $S\{7a\} \approx 1.4 \times 10^2 \theta_0^2 \text{ keV} - b$ for $E \approx 0$. In reference [1], it was shown that $R\{5\} \ll R\{6\}$ due to a selection rule. Since ($^3\text{He} + n$) state at 20.58 MeV

is higher than ${}^4\text{He}^*$ state at 20.21 MeV, and $\Gamma_2 ({}^3\text{He} + n) = 0$ MeV [23], this value of $S\{7a\}$ may provide an explanation of the reported branching ratio of $R(T)/R(n) \approx 10^8 \sim 10^9$ [24, 30-40].

From section 5, we have theoretical prediction that $R\{2\}/R\{6\}$ or (i) $R(n)/R({}^4\text{He}) \approx 10^{-11}$. From this section, we have the above theoretical prediction of $R\{7a\}/R\{6\} \approx 2.6 \theta_0^2$ or (ii) $R(T)/R({}^4\text{He}) \approx 2.6 \theta_0^2$. Combining (i) and (ii), we have $R(T)/R(n) \approx 2.6 \times 10^{11} \theta_0^2$. If $\theta_0^2 \approx 10^{-4}$, we have $R(T)/R(n) \approx 10^7$ which is nearly consistent with reported values of $10^8 \sim 10^9$. If we assume $S\{6\} \approx 55$ keV-b (this could be much larger), we expect the branching ratio $R\{7a\}/R\{6\} = R(T)/R({}^4\text{He}) \approx 2.6 \theta_0^2 \approx 2.6 \times 10^{-4}$ if $\theta_0^2 \approx 10^{-4}$. Experimental measurements of $R(T)/R({}^4\text{He})$ are needed to determine θ_0^2 . If $S\{6\}$ ($=S({}^4\text{He})$) is determined to be larger from future experiments, $R(T)/R({}^4\text{He})$ is reduced accordingly.

For the decay channel $\{7b\}$ ($0^+ \rightarrow 0^+$ transition), γ -ray transition is forbidden. However, the transition can proceed via the internal e^+e^- pair conversion. The transition rate for the internal electron pair conversion is given by

$$\omega = \frac{1}{135\pi} \left(\frac{e^2}{\hbar c} \right)^2 \frac{\gamma^5}{\hbar^5 c^4} R_N^4, \quad R_N^2 = |\langle \psi_{\text{exc}}, \sum_i \mathbf{r}_i^2 \psi_{\text{norm}} \rangle|. \quad (12)$$

where γ is the transition energy. Eq. (12) was derived by Oppenheimer and Schwinger [43] in 1939 for their theoretical investigation of $0^+ \rightarrow 0^+$ transition in ${}^{16}\text{O}$. The rate for the internal electron conversion is much smaller by many order-of-magnitude.

For our case of $0^+ \rightarrow 0^+$ transition $\{7b\}$, we obtain $\omega \approx 0.79 \times 10^{13}/\text{sec}$, and $\Gamma_b = \hbar\omega \approx 0.52 \times 10^{-2}$ eV using appropriate inputs in Eq. (12). Using $\Gamma_2 = \Gamma_b = 0.52 \times 10^{-2}$ eV in Eq. (11), the extracted S-factor for decay channel $\{7b\}$ is obtained as $S\{7b\} \approx 1.5 \times 10^{-6} \theta_0^2$ keV - b for $E \approx 0$, which in turn yields a branching ratio, $R\{7b\}/R\{7a\} = S\{7b\}/S\{7a\} \approx 10^{-8}$. Experiments are needed for testing this predicted branching ratio.

7. Proposed experimental tests of theoretical predictions

7.1 Experimental test for metal particle size

The recent report of deuteron gas-loading experiment by Arata and Zhang [4] show positive results of observing excess heat and ${}^4\text{He}$ production using ~ 5 nm Pd particles imbedded in ZrO_2 and purified deuterium. The recent experimental results by Kitamura et al. [5] using ~ 10 nm Pd particles have confirmed the results of Arata Zhang [4], and also is consistent with one of theoretical predictions of the BECNF theory [1]. The theoretical prediction is that the reaction rate for smaller Palladium particles is expected to be greater than the reaction rate for larger Palladium particles, $R(\text{smaller Pd}) > R(\text{larger Pd})$. Their Fig. 3(a) and Fig. 3(c) confirm the above prediction. Their data in Fig. 3(c) are also consistent with the requirement of deuteron mobility in metal (the **observation [9]**).

7.2 Experimental test for anomalous tritium production

For experimental tests of the sub-threshold resonance reaction described in section 6, it is desirable to carry out high-sensitivity detection of weak signals (i) of Bremsstrahlung radiations from energetic electrons going through metal and (ii) of 0.51 MeV γ -rays from e^+e^- annihilation, as well as (iii) ${}^4\text{He}$ production during tritium production experiments to test the predicted branching ratio $R\{7b\}/R\{7a\} \approx 10^{-8}$, and also to determine the branching ratio $R\{7a\}/R\{6\}$ ($=R(T)/R({}^4\text{He})$) which in turn can provide information on θ_0^2 for $S\{7a\}$ and also $S(E)$ for $\{6\}$.

7.3 Experimental test for fusion-rate enhancement at low temperatures

As discussed in section 3, the BEC fraction and the probability Ω of the BEC ground-state occupation will increase at lower temperatures. This increase of Ω will enhance the total fusion rate R_t , Eq. (4). This prediction can

be tested by carrying out experiments at low temperatures. For an example, thermal cycling experiment [24] should be repeated with micro/nano-scale titanium particles.

7.4 Experimental test for fusion-rate enhancement at high pressures

High pressures will shorten the average distance between two deuterons in metal, thus enhancing the BEC fraction and hence Ω . This enhances the total fusion rates R_t , Eq. (4). This prediction can be tested by carrying out experiments at high pressures.

7.5 Experimental tests of Bose-Einstein condensation of deuterons in metal

BECNF theory is based on one single physical hypothesis that mobile deuterons in a metal/grain/particle form Bose-Einstein condensate. Therefore, it is important to explore experimental tests of this basic hypothesis.

One of the advantages of carrying out experiments for observing the BEC of deuterons in micro/nano-scale metal particles is that the modern nano-fabrication techniques allow us to fabricate them in multitude with a great precision in one-dimension, two-dimension, and three-dimension. This capability will allow us to produce the BEC of deuterons in metal (i) in a double-well potential trapping two Bose-Einstein condensates for studying the Josephson effect [44], and also (ii) in lower-dimensional traps to study the BEC in one-dimension and two-dimension.

8. Summary and conclusions

Based on a single physical concept of Bose-Einstein condensation of deuterons in metal, theory of Bose-Einstein condensation nuclear fusion (BECNF) is developed to explain deuteron-induced nuclear reactions observed in metal. It is shown that the BECNF theory is capable of explaining qualitatively or quantitatively almost all of ten experimental observations (listed in section 2) reported from electrolysis and gas-loading experiments.

It is shown that the fusion energy transfer to metal can be accomplished by the stopping power of metal without invoking hypothesis of fusion energy transfer to metal lattice vibrations. It is also shown that observed anomalous tritium production can be explained by incorporating a sub-threshold resonance reaction mechanism into the BECNF theory

The BECNF theory has also predictive powers as expected for a quantitatively predictive physical theory. Experimental tests of theoretical predictions are proposed and discussed, including tests of the basic hypothesis of Bose-Einstein condensation of deuterons in metal. Experimental tests are needed not only to test theoretical predictions, but also to improve and/or refine the theory, which are needed for designing reproducible experiments and for scaling up BECNF processes for potential practical applications.

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Anomalous Heat Generation in Charging of Pd Powders with High Density Hydrogen Isotopes, (II) Discussions on Experimental Results and Underlying Physics

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Abstract: By our D(H)-gas charging experiments using Pd/PdO/ZrO₂ powders, we obtained: 1) D-gas charge in the 1st phase (zero pressure interval) gave 20~90 % more excess heat than those for H-gas charge. 2) In the 2nd phase of pressure rise (finally up to 1MPa), significant excess heat (about 2 kJ/g-Pd) for D-gas charge was observed, while near zero level excess heat for H-gas charge was observed. We discuss the underlying surface and nano-particle physics in views of the enhanced surface adsorption potential by fractal sub-nano-scale trapping points on nano-Pd grain, the diffusion to inner shallower Bloch potential of regular Pd lattice, and the drastic mesoscopic and isotopic effect of surface and lattice rearrangement of nano-Pd particle by full D(H)-absorption to make deeper D(H) trapping potentials (about 2eV for D).

1. Introduction

The aim, experimental apparatus, experimental procedure and observed results of deuterium (and protium) gas charging experiments with various nano-fabricated Pd powders are written in our paper by Sasaki to this meeting¹. The observed results for Pd/PdO/ZrO₂ nano-composite samples (about 10 nm diameter Pd particles dispersed in about 7 micron size ZrO₂ flakes) provided us a confirmation-trial⁸ of Arata and Zhang experiment² and a very interesting performance of deuterium (D) and protium (H) absorption and exothermic energy generation.

The results by nano-Pd/ZrO₂ samples are very interesting since specific surface effects in adsorption and following absorption into inner “lattice” sites look taking place to result in anomalously large stoichiometry values ($x>1$) of PdD_x and deep trapping potential (or released energy). Compared with the results of 100nm Pd particle-powders, 10nm Pd particles dispersed in ZrO₂ are regarded to have shown the drastic mesoscopic effects with isotopic difference.

2. Trend of Heat-Power Evolution

The evolutions of heat and gas-pressure can be discussed for two different phases, the 1st phase and the second phase as we show typical data in ‘Fig.1’.

The 1st phase is defined as the time-interval where reaction chamber (cell) keeps nominal “zero” gas-pressure. This means almost all D(H)-gas charged was absorbed by nano-Pd powders. Heat-power evolution curve in the 1st phase may be regarded mostly by chemical reaction energy during the D(H)-gas absorption into nano-Pd powders, in the point of view of conventional chemistry. However, we may have a component of “nuclear” process that we discuss later. For determining a 1st phase interval for heat-power evolution, we need to take a time-delay (about 15 minutes or three times of calorimetry time constant 5 minutes) into account¹, while the evolution of pressure has quick response.

Trend of heat-power evolution in the second phase is very isotope dependent, as typical data is shown in ‘Fig.2’.

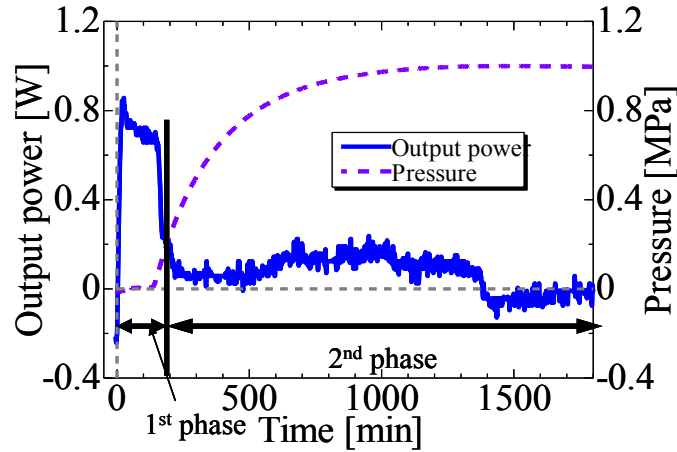


Fig. 1. - Typical heat -power evolution data with Pd/ZrO₂ nano-composite sample with D-gas charge (D-PZ1#1 run)

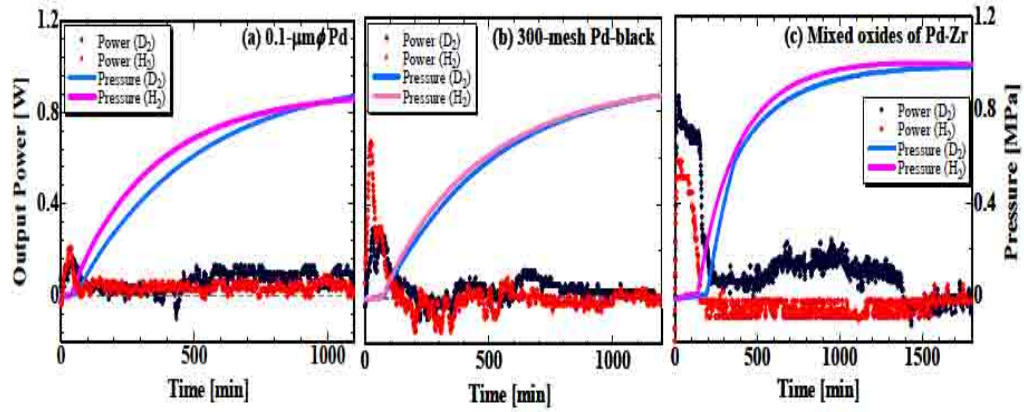


Fig. 2. - Typical “excess heat-power” evolution by D-charge for (c) Pd/ZrO₂ sample, net Pd weight = 3g (D-PZ1#1run), together with heat-power level by H-gas charge (H-PZ2#1 run), compared with (a) data by 100nm Pd powder, net Pd weight = 5g, and (b) data by Pd-black, net Pd weight = 3.2g (D) and 3.6g(H)

The H-gas charge has given “zero” power level (sometimes negative integrated values according to a possible zero-level drift of calorimetry or due to possible de-oxidation of PdO by D(H) charge). Obviously, the D-gas charge to the Pd/PdO/ZrO₂ nano-composite sample gave much more heat-power than that of the H-gas charge, for (c), which effect looks anomalously large compared to those by (a) and (b) and suggests a mesoscopic effect of Pd nano-particles on heat evolution, as discussed below.

3. Results and Discussions for 1st Phase Data

We summarized the integrated data of D(H)/Pd ratios, Heat per one-gram-Pd, Energy per D(H) atom absorption (E_{1st}) and gas-flow rates, and results are given in Table-1 of Reference-1 (see also Ref.8). First we discuss the data for 100nm Pd-particle powders (D-PP and H-PP runs in Table1 of Ref-1). Loading ratios, D(H)/Pd, are 0.43 and 0.44 respectively for deuterium (D) and protium (H) gas charging. Specific energies per absorbed D (or H) atom E_{1st} (or ΔH_s) values are 0.24eV/atom-D and 0.20eV/atom-H. When D(H) is absorbed in metal lattice, surface adsorption works on D(H) molecule (or atom) first and D(H)-atoms diffuse into inner lattice sites (O-sites of Pd, usually) gradually. ‘Figure 3’ illustrates typical form of surface trapping potential and inner periodical (Bloch) trapping potentials.

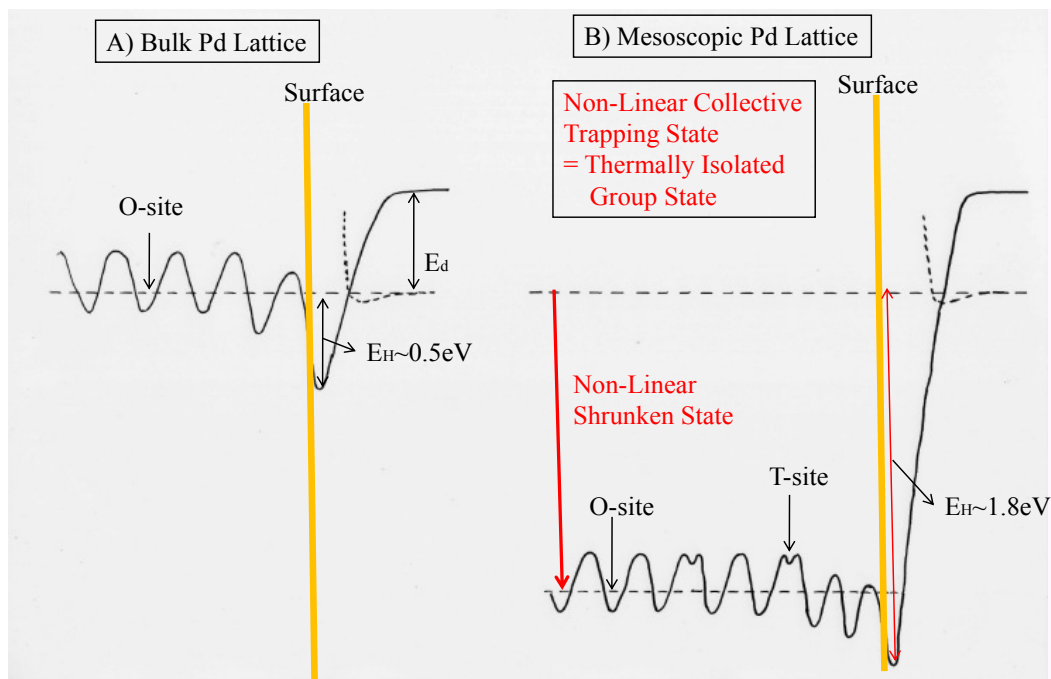


Fig. 3. - Image of D(H) trapping potentials at surface adsorption (depth E_H) and lattice absorption (depth E_{hydr}); trapped D(H) atom diffuses gradually into inner Bloch trapping potentials through the QM tunneling. After full loading ($x=1$ for $PdDx$), rearrangement of Pd lattice may happen to make shallower potentials for bulk Pd (left figure), while nano-Pd grain in ZrO_2 flake will have a specific mesoscopic potential (right figure) which reflects a non-linear combination of a deep collectively formed mesoscopic trapping potential (well-shape) and periodical Bloch potential of “local” $PdDx$ lattice.

For known values in text book³⁾, E_H is about 0.5eV and E_{hydr} is 0.23eV. The difference, $E_H - E_{hydr}$, is close to the energy released per D(H)-atom absorption in lattice and is about 0.25eV for bulk Pd lattice. Observed E_{1st} (ΔH_s) values for 100nm Pd particle powder are near to this value of bulk Pd metal. This means that 100nm Pd particle works as bulk-metal for D(H) absorption. We will see E_{1st} values for Pd-black and Pd/PdO/ ZrO_2 nano-composite samples will have given much larger energies (deeper trapping potentials) to show the drastic mesoscopic effects. For the definition of mesoscopic size, we consider a Pd grain having 2,000 to 20,000 of total number of atoms.

Next, we look integrated data for Pd-black samples (D-PB and H-PB runs) in Table-1 of Ref.1. E_{1st} values in averages of runs are 0.70 ± 0.15 eV/atom-D and 0.69 ± 0.10 eV/atom-H. These values are significantly higher than the bulk value about 0.25eV. For the virgin runs (#1 runs), significantly high loading as $PdD_{0.88}$ or $PdH_{0.79}$ were observed. However, for runs with used samples (#2, #3, #4 runs), loading ratios were as small as 0.23 in average. Nevertheless the specific E_{1st} values were observed as same as the virgin (#1) runs. This fact means that microscopic active adsorption sites on surface of used Pd-black are working in the same way as the virgin Pd-black sample, although effective area of active surface decreased to 1/3 or less.

Now we discuss the integrated data in the 1st phases for Pd/PdO/ ZrO_2 samples (D-PZ and H-PZ runs in Table1 of Ref.1). We observed heat-power levels were strongly dependent on the D(H) gas-flow rate. The larger gas-flow rate has trend to give the larger excess heat level in the 1st phase, but the 1st phase ends earlier than the case of smaller flow rate. This is understood as the faster gas-flow meets faster saturation of D(H) absorption in powders. Therefore, to compare specific values of E_{1st} (released energy per D(H)-atom), D(H)/Pd (loading ratio) and heat (in kJ) per g-Pd is more appropriate to understand the underlying physics.

Our first surprise is that all measured loading ratios, D(H)/Pd values for the 1st phases are greater than 1.0, namely overloading ($x=1.1$ in average for $PdD(H)x$ stoichiometry) in usual sense, even though the background gas pressure were nearly zero (near vacuum). This must be said as the drastic mesoscopic effect of D(H) absorption by the Pd nano-composite samples. For the known bulk Pd-metal, D(H) atoms are trapped in Bloch potentials (see Fig.3) at O-sites for $x < 1.0$. The observed anomalous data of $x > 1.0$ should show that the additional trappings at T-sites or surface happened by the mesoscopic effect (about 5,000 Pd atoms existing in a 5nm diameter particle).

The data for specific released energy E_{1st} values are also anomalously large and isotope (D or H)-dependent. These are 2.2-2.5eV/atom-D and 1.3-2.1eV/atom-H. Deuterium gives larger E_{1st} values. These released energy values are 5-10 times of the conventional value 0.25eV for bulk Pd metal. These values are however dependent on gas-flow rate, and we need further investigation so far. As PZ samples gave drastic mesoscopic effects, compared to the 100nm Pd powder we need further study by changing nano-Pd particle size.

In 'Fig.4' degassing data of Pd/ZrO₂ sample is shown compared with that of Pd-black, under baking procedures. Note that the vertical scale of pressure is logarithmic. Clearly, Pd/ZrO₂ sample can very highly retain D(H) atoms even after the evacuation. The desorption process of nano-Pd grain is speculated to be very unusual. The D(H) retention of Pd/ZrO₂ sample seems about 100-fold greater than that of Pd-black. This degassing results, showing peak at about 200°C, also suggest that the D(H) trapping potential of Pd/ZrO₂ nano-composite sample is much deeper than that of bulk Pd lattice.

4. Excess Heat for the Second Phase

As summarized in Table-1 of Ref-1, we observed positive excess heat in the 2nd phase of D-PZ series runs for virgin (#1 run) samples (we tried three pairs of samples for simultaneous runs with D-gas by A1 (A2 for D-PZ5) and H-gas by A2 (A1 for H-PZ6) cells). For the D-PZ5 run, D-gas cylinder dried out in the 2nd phase and gas-pressure decreased (we had leakage), so that excess heat phenomenon was not observed. For earlier two PZ runs, we observed clear excess heat, only for D-gas charging, 2.27 and 2.07kJ/g-Pd in the time interval of 1,600 minutes, respectively.

Now, we discuss about a possible chemical energy release by oxidation⁸ of charged D(H)-gas, as samples contained PdO and ZrO₂ components. Already 'Fig.4' shows clearly D(H)-gas was mostly absorbed by Pd-grains in PZ samples, since Pd-black gave the same pattern of degassing. We have to consider a reduction of PdO_x states followed by production of xD₂O (xH₂O) and PdD_y (PdH_y) states. The reaction energies Q_D and Q_H are evaluated to be $(162.6 \times x + 70.0 \times y)$ kJ and $(156.6 \times x + 58.0 \times y)$ kJ, respectively. For assumed values of $x = 1 \sim 0$ and $y = 0 \sim 1$, Q_D and Q_H are 0.84 ~ 0.73 eV/D and 0.81 ~ 0.60eV/H, respectively. These are too small to account for both the observed E_{1st} energies and the isotope effects. Consequently, the main component of heat for a 1st phase cannot be due to the formation of water (D₂O or H₂O) by the D(H)-gas charging to PdO nano-particles. A role of PdO surface layer of Pd-nano-partilce for making sub-nano-holes on surface under D(H)-chrage will be discussed in our future paper.

There might be an yet-unknown atomic/electronic process governing the phenomenon in the present mesoscopic system, or the concept of "atom clusters" might apply. However, it seems rather difficult to assume that such a large isotope effect is only in the electronic process of adsorption and/or hydride formation. Some nuclear process as suggested by the 4D/TSC model by Takahashi⁴⁻⁷ could be a candidate mechanism responsible for the phenomenon.

A speculation for the underlying physics of the atomic & molecular-level cluster formation by Coulombic interaction of deuterons and electrons in metal-hydride and the strong nuclear interaction of multi-body deuteron interaction is illustrated in 'Fig.5', viewing the aspect from a few body system to more complicated multi-body systems, namely, cluster, mesoscopic and bulk lattice systems. The 4D/TSC theory predicts a very rapid (in 1.4 fs) condensation⁵⁻⁷ of 4D-cluster keeping the tetrahedral symmetric configuration with time-dependent TSC trapping potential for a Coulombic interaction between four deuteron QM-waves and four electron QM-waves⁴⁻⁷.

A speculated deep potential trapping deuterons (or protons) into "local" Pd lattice inside the mesoscopic nano-particle grain is considered to be a combination of a collective deep well potential (resembling shape to the nuclear Woods-Saxon potential) and a "finite" Bloch potential of bulk Pd metal lattice. However the finite Bloch potential (locally periodical) is formed at the bottom of the collective deep well (See also 'Fig.3'). Particles (d or p) trapped in this "mesoscopic potential" will make a non-linear oscillation which magnifies the mobility (kinetic energy of trapped state) of deuterons (or protons) and enhances the cluster (especially 4D/TSC) formation probability under a collective dynamics. Possible formation of sub-nano-holes on surface of Pd-particle may arrange places for TSC formation.

The formation of collective deep well potential and more mobile particle motion inside it will enhance the speed of D(H) adsorption on surface and absorption into grain. The observed high retention of D(H) by Pd/ZrO₂ powder in vacuum will be also explained by such a mesoscopic potential. Nuclear strong interaction for simultaneous 3 and 4 deuterons in very condensed 4D/TSC is modeled⁴⁻⁷ based on the pion-exchange model (Hideki Yukawa) and potential (Hamada-Johnston). The pion exchange force for many body interaction has been scaled by the unit of PEF.

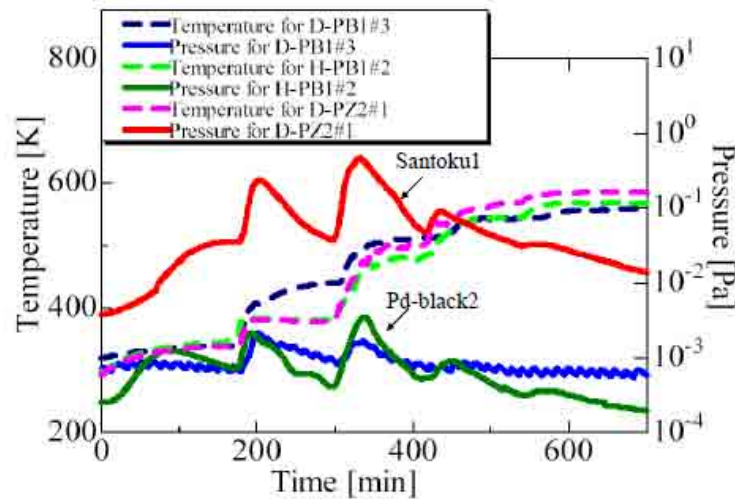


Fig. 4. - De-gassing data for Pd/ZrO₂(Santoku)-sample compared with that for Pd-black; Santoku-sample retains 100 times D(H)-atoms, presumably by its very deep trapping potentials of the mesoscopic effect of dispersed Pd-nano particles

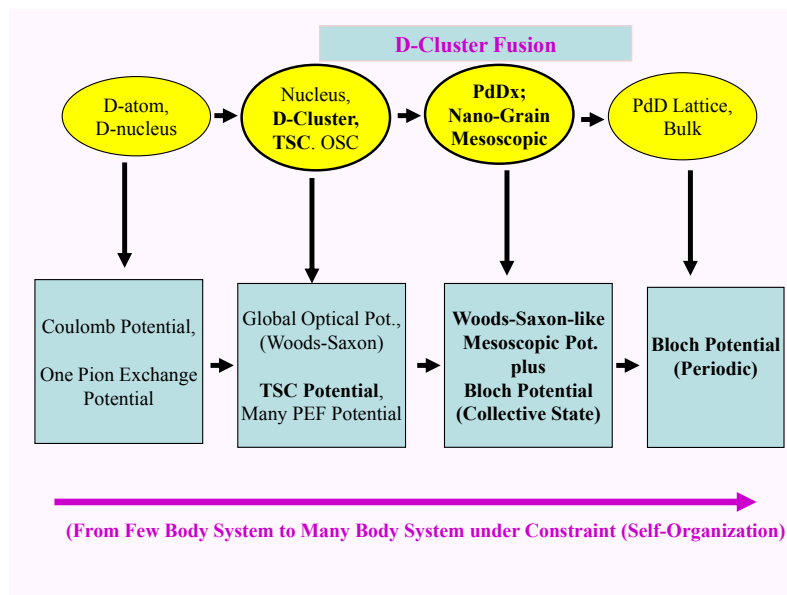


Fig. 5. - Speculation of potential change from a few body interaction to cluster, mesoscopic grain and bulk lattice of metal-deuterium (-protium) system, both for Coulombic and strong nuclear interaction. The proposed condensed cluster fusion is speculated to take place for the cluster, mesoscopic grain systems and near-surface of bulk metal as Pd.

5. Concluding Remarks

For Pd/PdO/ZrO₂ powders (Santoku-samples), we obtained results 1) through 4):

- 1) The D-gas charge in the 1st phase (zero pressure) gave 20-90% excess heat than the H-gas charge.
- 2) In the 2nd phase, significant excess heat (about 2 kJ/g-Pd) for the D-gas charge, while zero level for the H-gas charge, was observed.
- 3) No increase of neutron counts was seen, neither increase of gamma-rays over natural backgrounds.
- 4) D(H)/Pd ratios in the end of 1st phase was $x > 1.0$, namely over-loading ($x = 1.1$ in average). Flow rate dependence of x -values should be investigated further. Nano-Pd dispersed sample (Santoku, Pd/ZrO₂) retained 100 times more D(H) atoms after evacuation, than the Pd-black case.

We discussed that there may be a strong mesoscopic effect by Pd-nano-particle, namely surface and lattice rearrangement probably makes deep D(H) trapping potentials (1.0-2.5eV) by a nonlinearly coupled vibration states, of trapped D(H)-particles, between a deep collective trapping well potential and a periodical Bloch potential.

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Neutron Spectra in CMNS - Model Predictions and Past Data –

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Abstract: According to the recent SPAWAR claim on $^{12}\text{C}(\text{n},\text{n}')3\alpha$ detection due to 14 MeV neutrons by D-T reaction in a $\text{D}_2\text{O}/\text{Pd}$ co-deposition cell, we remind our old discussion on observed neutron spectra from CMNS/CF cells in the past. Structure or shape of neutron spectra should give important (decisive) evidences on underlying physical mechanisms on possible deuteron-related nuclear fusions in PdDx systems. This paper discusses plausible neutron spectra as consequences of major theoretical model predictions.

1. Introduction

According to the recent SPAWAR claim on $^{12}\text{C}(\text{n},\text{n}')3\alpha$ detection due to 14 MeV neutrons by D-T reaction in $\text{D}_2\text{O}/\text{Pd}$ co-deposition cell, we remind our old discussion on observed neutron spectra from CMNS/CF cells in the past. Structure or shape of neutron spectra should give important (decisive) evidences on underlying physical mechanisms on possible deuteron-related nuclear fusions in PdDx systems. This paper discusses plausible neutron spectra as consequences of major theoretical model predictions.

2. The SPAWAR Claim

Mosier-Boss et al. have observed triplet tracks in CR39 detectors used in their co-deposition $\text{Pd}/\text{D}_2\text{O}$ electrolysis type CMNS/CF experiments¹. They claimed the triplet tracks should be due to forward-peaked emission of three alpha-particles from $^{12}\text{C}(\text{n},\text{n}')3\alpha$ reactions by D+T fusion reactions as byproducts of D+D reactions in the co-deposition experiments. The $^{12}\text{C}(\text{n},\text{n}')3\alpha$ reaction has however threshold at 7.8MeV of incident neutron energy⁷. The author conceives that the explanation by secondary $\text{d} + \text{t}$ reactions after $\text{d} + \text{d}$ fusions is not plausible, because the yield of $\text{d} + \text{t}$ reactions by one 1MeV triton slowing down in PdDx matter is very small on the order of 10^{-5} , $\text{d} + \text{d} \rightarrow \text{p}(3.015\text{MeV}) + \text{t}(1.005\text{MeV}) + 4.02\text{MeV}$ for the conventionally known DD fusion. Estimation using available neutron cross sections (JEDL3 for instance)⁷, one $^{12}\text{C}(\text{n}, \text{n}')3\alpha$ event needs about 100 fluence of 14MeV neutrons getting into the used CR39 track detector by SPAWAR. This should correspond to 10^7 neutrons of 2.45MeV by the $\text{d} + \text{d}$ reactions. If we had 10^7 neutrons emitted from CF cells, we could detect very easily significant counting events and their recoil-proton-tracks of 2.45MeV neutrons. These can easily be detected, but has never been observed with so high 2.45 MeV neutron yield, by CR39 detectors. The author concerns that the conclusion of secondary D+T fusion by SPAWAR for triplet tracks is not plausible.

3. Model Prediction Case-1

[Case-1]: Some theoretical models⁸⁻¹¹ conceiving the $\text{d} + \text{d}$ to $^4\text{He} + \text{lattice energy}$ (23.8MeV) processes have been thought as possible explanation for the CMNS/CF phenomena since 1989, in spite of very negative view from the nuclear physics point of view¹².

If the “Dream” of the “**d+d to ^4He + lattice energy (23.8MeV)**”⁸⁻¹² were taking place, the doping tritons make “d + t to ^5He + lattice energy” reactions, in the same path and we shall have neutron emission by,



14 MeV neutrons are not major products in consequence of this theoretical model, but **low energy neutrons (0.716 MeV)** should be detected with the tritium doping of micro-Curie/cc-DTO; doping in experimental CMNS/CF cells. These “low” energy neutrons could not be detected by a CR39 detector because recoil-proton energies are too small to cause enough large ionization tracks. We shall use special neutron spectroscopy systems to detect and identify the 0.716 MeV neutrons.

4. Model Prediction Case-2

[Case-2]: Our **4D/TSC fusion model**¹³⁻¹⁵ predicts 23.8MeV/ ^4He energy deposit in PdDx lattice as main product by the major channel $4\text{D} \rightarrow ^4\text{He} + ^4\text{He} + 47.6\text{MeV}$ reactions. Minor branch products of triton and higher energy neutrons from 4D fusion are predicted as a product of symmetric fragmentation of $^8\text{Be}^*$ via excited state of $^4\text{He}^*(\text{Ex}=20.21\text{ MeV}$: first excited state) as shown in ‘Fig.1’.

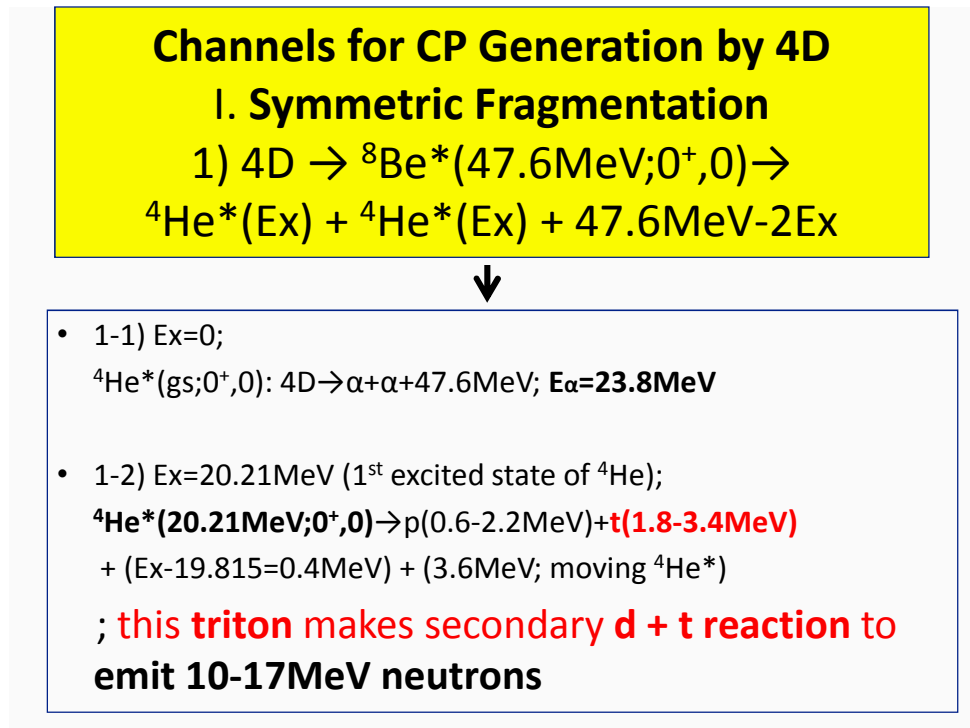
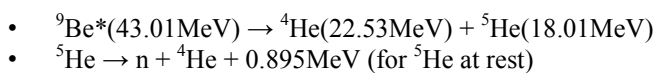


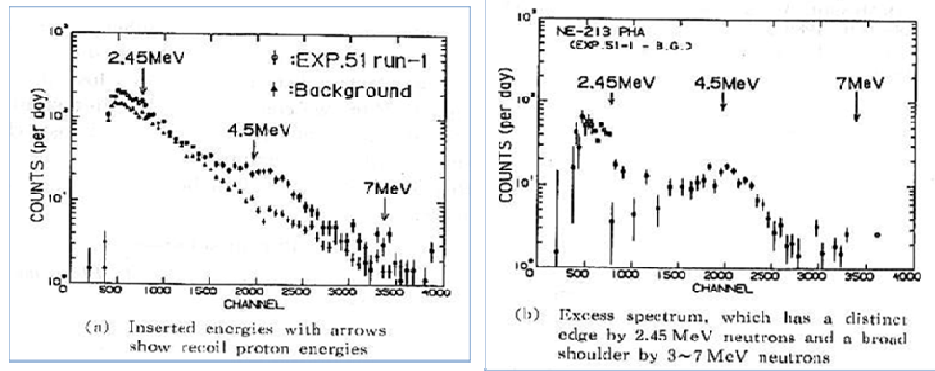
Fig.1 - Generation of triton by a symmetric fragmentation of $^8\text{Be}^*$ by 4D fusion and its secondary t + d reaction to emit high energy neutrons in a 10 – 17 MeV region which may correspond to the SPARWAR result.

Secondary t + d reactions, during the slowing down of thus produced tritons in PdDx matter, produce a 10-17MeV high energy component as observed by SPAWAR¹. In the symmetric fragmentation, higher excited states such as $\text{Ex}=21.01\text{MeV}(0^+,0)$, $21.84\text{MeV}(2^-,0)$, $22.33\text{MeV}(2^-,1)$, $23.04\text{MeV}(1^-,1)$, from which neutrons can be emitted, are forbidden by odd parity (spin-parity conservation – selection rule).

If we make a doping of tritium (on the level of micro Curie) in the process, (3D+T)/TSC makes $^9\text{Be}^*(43.01\text{MeV})$ intermediate compound state to break up as,



Neutron energy appears in 0.41 to 6.79 MeV (emitted from the break-up of moving ^5He of 18.01 MeV kinetic energy, as calculated by kinematics). We may predict the broad higher energy spectrum in 0.4 to 7 MeV region as major component (minor component in much higher energy region) by the tritium doping into on-going CMNS/CF cell experiments. This is the consequence of TSC model¹³⁻¹⁵. Obviously we can verify which theoretical model, Case-1 or Case-2 matches the observed phenomena of neutron emission in CMNS/CF experiments.



Two components: 2.45 MeV peak and 3-7 MeV Higher Energy Group

Fig. 2 - Two component neutron spectra observed by the past Pd/D₂O electrolysis experiments, copied from published paper²⁾

5. Our Past Data of Neutron Emission and Discussions

We refer now our past measurements²⁻⁶ of neutron spectra from CF-electrolysis experiments to be discussed under the above predictions. A typical result of measured neutron spectra from Pd/D₂O electrolysis cell² is copied in 'Fig.2'.

Fast neutron spectroscopy was done by measuring recoil-proton pulse height distribution of NE213 liquid scintillator with an n-gamma pulse shape separation technique⁴⁾. The background spectrum has "near-exponentially decreasing" recoil-proton pulse height distribution which was of spallation neutrons of cosmic-ray-origin showing similar spectrum as the fission-neutrons having a near Maxwellian distribution with a nuclear temperature 1.4 MeV. High energy protons by cosmic rays induce spallation reactions with nuclei in the matter surrounding the detector. The near Maxwellian spectrum has therefore a high energy tail in $E_n > 10$ MeV. The excess neutrons observed has two components in its energy spectrum: one is of 2.45 MeV neutrons, very probably by the D+D fusion reactions. The other broad component in the 3-7 MeV region (and we might expect higher energy- more than 7 MeV- tail to observe if statistics of experiment is improved) is unidentified origin (See Fig.2). In our past papers^{2,3,16}, we speculated that the higher energy component could be the product of the secondary high energy d + d reactions after the primary d + d + d three body fusion in PdDx-lattice; $D+D+D \rightarrow d(15.9\text{MeV}) + ^4\text{He}(7.9\text{MeV})$; In the slowing down process of 15.9 MeV deuterons, d + d reactions in PdDx produce higher energy component of neutrons seen in the 3-10 MeV region.

Now, we have to reconsider this explanation by referring our other past results shown in 'Fig.3'. In our reconsideration, the higher energy neutron component might have been the 0.4-7 MeV neutron emission by the (3D+T)/TSC 4-body fusion reaction in PdDx lattice dynamics (Case-2), because we had seen the significant accumulation of tritium atoms in the electrolyte (curve c) in Fig.2: This was already a kind of T-doped experiment which happened by chance. However, 4D fusions may emit much higher energy neutrons in the 10-17 MeV region, from minor out-going channels emitting tritons, as predicted in this paper. These high energy neutrons are considered to have caused the triplet tracks in CR39 detectors used in the SPAWAR experiments.

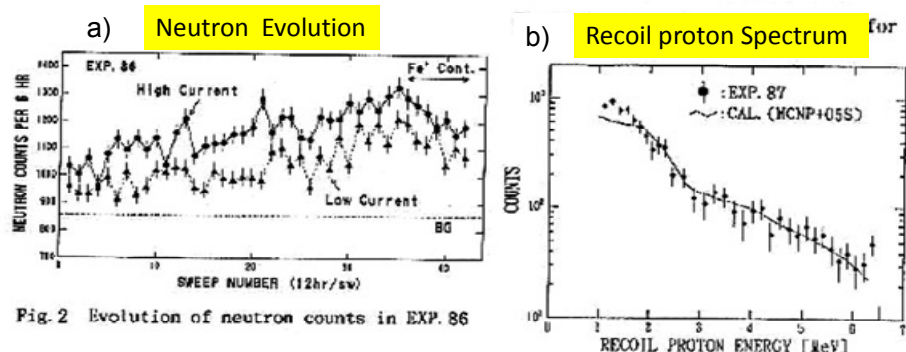


Fig. 2 Evolution of neutron counts in EXP. 86

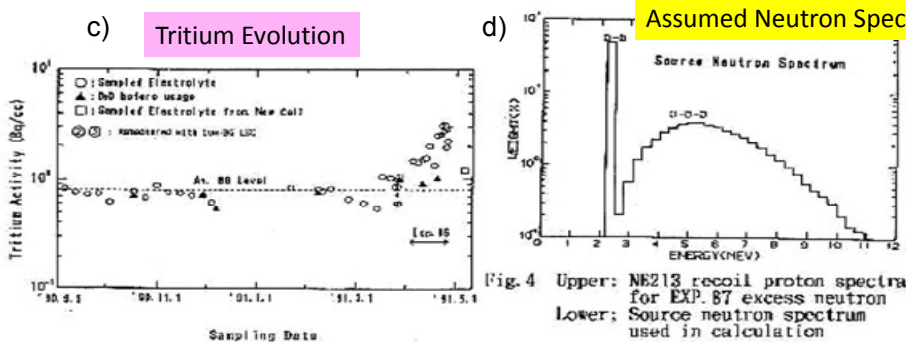


Fig. 5 Evolution of tritium level in electrolyte

Fig. 4 Upper: NE213 recoil proton spectra for EXP. 87 excess neutron Lower: Source neutron spectrum used in calculation

Or (3D+T)/TSC reaction

Fig. 3 - Our past data, copied from published prints^{3,16}, of neutron emission and evolution of tritium concentration in Pd/D₂O pulsed electrolysis experiments; a) evolution of excess neutron counts, b) recoil-proton pulse height spectra for excess neutrons, c) evolution of tritium concentration measured by LSC with sample electrolyte and d) assumed two component neutron spectrum for folding calculation of model.

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***SuperWaves™* as the Natural Origin of Excess Heat**

Irving I. Dardik, M.D.

Abstract. Energetics Technologies has had excellent reproducibility of its own experimental results on cold fusion; significantly, its work has been replicated at independent laboratories, at SRI and ENEA. We believe that one of the most important reasons for these results is the use of complex fractally nested current excitation. From this perspective, these results in replicating the production of excess heat are a further confirmation that natural phenomena, including the electrochemical processes for producing excess of heat, can be correctly described by these fractal dynamics. In this paper I describe basic concepts of the *SuperWaves™* theory, which is an original general approach to model and understand natural phenomena.

1. Introduction

According to our current understanding of Cold Fusion, we are faced with a paradox. On one hand, we get positive results for excess heat. But on the other hand, there is no theory to back it. The following is a short overview of *SuperWave™* Reality, which clarifies this issue on two fronts: it is a new understanding of nature, and therefore a new approach of how to go about understanding nature in the first place. The production of excess heat becomes not an anomaly but something expected and natural. This is because *SuperWaves™* reveals something new: an underlying truth about the details in science and in nature. It does not negate the findings of science but places them firmly in a new context. It is not an alternate view, but a way to imbue what we already know into an entirely new framework. It is the ultimate underlying reality of nature. And, it is exceedingly simple.

I derived this new understanding from life. Life is the most complex thing that we know of, and it offers vastly different insights from what is considered to be simple, *i.e.* the reductionist, scientific approach to understanding physical reality. I had dealt with the problems of disease and death as a vascular surgeon, and dealt with life, human performance, and health as founding Chairman of the United States Olympic Sports Medicine Council. While working in these capacities, I discovered an entirely new approach for understanding the dynamics of biological systems in terms of their *rhythms*.

First, we must understand that all motion and all processes in a living organism are rhythmic. Everything moves in waves: from the circadian rhythms of day and night to the behavioral cycles of exercise and recovery or anxiety and relaxation, to organ cycles such as the heart beating or the lungs breathing, to the cell cycle, to molecular oscillations and the metabolism. Everything in the human body is oscillatory. This simple, extraordinary discovery is that the heart beat itself cycles simultaneously within the exercise-recovery cycles of the entire organism --waves waving within waves. Thus, our familiar view of the heart rate, graphed as linear motion in an electrocardiogram, misrepresents nature. In nature, the heartbeat follows no line, but rather accelerates up and down, speeding/intensifying then slowing/relaxing, in synchrony with the whole body as it makes a larger cycle of exercise and recovery. That which we separate conceptually into two scales is inextricably joined in nature. The heart and blood vessels pulsate in cyclic patterns of waves of contraction and relaxation, which simultaneously nest as an inherent continuum within the exercise and recovery cycles of the organism as a whole. No boundaries separate the different modes of function – they merge into each other. I call this the HeartWave.

2. Fractal properties of natural phenomena

The concept of HeartWave incorporates many features of “fractal” dynamics. “Fractal” objects, in nature, are the same on different observation scales; in particular, properly fractal objects are the same if the scale changes are the same in all directions; intermediate fractal or “self-affine” objects are the same if the scale changes are different in each direction.

Fractal structure in the human body may be easily recognized by observing, for instance, the lungs and the circulatory system. A fractal motion shows similar patterns on different time scales, just as in the

case of the heartbeat. The heart beat is a complex motion, made of an extended set of oscillations, whose amplitudes vary continuously over the full frequency scale. The measurement of such a kind of motion with a standard instrument inevitably fails to give a complete description of it, due to the limitations of scale and sensitivity of the instrument. The right approach to measure / describe such a “complex” (*i.e.* fractal) motion, is to extract from the single measurements, each on a limited scale, the scale-invariant relationship embedded in them.

There are three major characteristics of the HeartWave, all properties of the inherent continuity of the cross-scalar relationships of waves waving:

1. Frequency and amplitude are a continuum across scales. The standard approach of treating waves using orthogonal dimensions including amplitude and frequency, allowing linear deconvolution via Fourier transforms, are practical means of working with waves that nonetheless fail to capture important ways in which waves interact. A shift of frequency in one scale simultaneously influences amplitude on the next scale, and vice versa, as an inherent continuum across all scales. Waves waving necessitates that these waves are ultimately not linear on any scale; waves waving are responsible for what science has been calling the ubiquity of non-linearity in nature
2. Since waves waving within waves occurs simultaneously across scales, we have what science calls non-locality or action-at-a-distance. The continuity of nested waves simultaneously affects each other across scales, top-down and bottom-up as they move forward, and change in time. They exhibit action-at-a-distance, at the same time that they change causally. I call this “simulcausality”.
3. This unremitting pattern of nested waves is an unbroken fractal phenomenon of order. The sharper the slope of the carrier wave, the faster the inner waves accelerate, which simultaneously increases frequency and amplitude of the inner waves, and thereby increases their density as they climb the carrier wave. Therefore, within the peak of the carrier wave is the highest density and motion, of inner waves – what we call attraction. Conversely, towards the trough, the waves slow down, flatten, and disperse – what we call repulsion. All of this arises from the cross-scale continuum of the fractal order of nature.

This powerfully constructive order of the HeartWave is present down through all levels of physiology, chemistry, and molecular biology, and in particular, what we call energy metabolism. The same three points outlined above: (1) frequency-amplitude as a continuum; (2) simulcausality; (3) the inherent fractal order of waves waving. The fractal order of the HeartWave explains why Brownian motion in a living organism exhibits highly elevated degree of order in its many levels of cybernetic feed-forward and feed-back loops [1]. This motion becomes enfolded and constrained within all the rhythms of the organism as a whole.

With the increased wave density and motion in the peak of exercise, the chemistry and metabolism exhibit an increase of heat. In contrast, there is a cool down in the troughs of recovery. Where there is motion, there is heat, therefore it can be understood that waves waving is the origin of temperature differences throughout nature.

In summation, the HeartWave encompasses the whole organism, the organs, cells, the molecular biology, and the metabolism. They all exhibit the same pattern of motion as waves waving within waves. If we take this down another level of scientific investigation, we reach the world of the atom and quantum physics. It is here that I concluded that all nature is, in reality, an inherent continuum of waves waving. This is in sharp contrast to our current thinking. The HeartWave, when followed down through all scales of nested oscillatory motion, tells us by logical extrapolation that the particle recognized by science as a wave packet (or wavicle) is not boundaried independently in space but is nested as an inherent continuum within a carrier wave.

Recently fractal waves have been involved in approaching and solving quantum mechanics problems. It has been demonstrated that fractal waves are fractal solution of the Shrodinger equation for a wide class of quantum problems, including the infinite potential well, harmonic oscillator, linear potential and free particle [1]. Fractal mathematics was also applied to other complex fields of physics, as, for instance, in investigating the fractal structure of the universe [2] and the fractal structure of surfaces. Fractal concepts apply also in chemistry, as for instance to the structure and chemistry of porous solids and to the growth of polymers and colloids. Fractal science is in progress and is extending across an increasing number of disciplines.

We extend such a concept to fractal modulated electric currents applied to electrochemical and glow discharge cells, since the signal can be traced back to a self similar shape. The signal is composed by several nested waves (SuperWaves™ see Fig.1) characterized by the same amplitude frequency ratio (the fractal dimension in this picture).

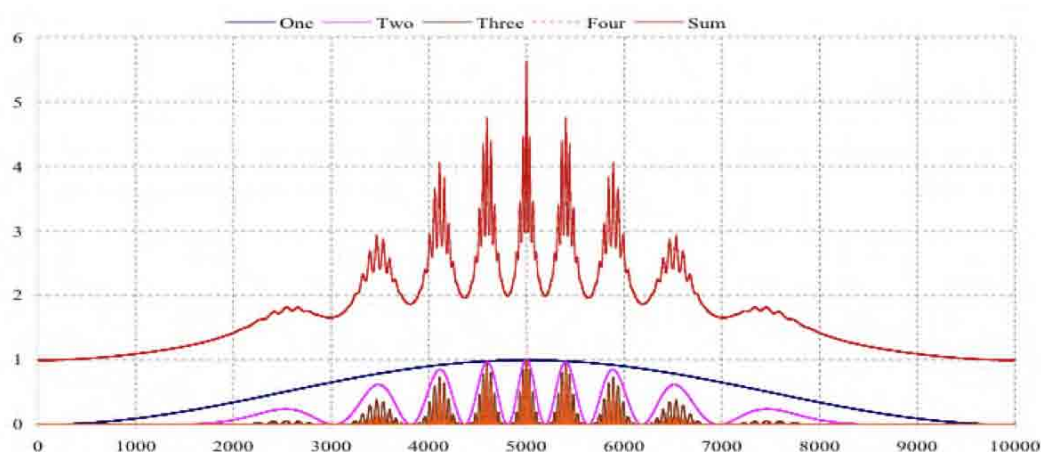


Fig. 1. - Showing nature and synthesis of fractally nested SuperWaves™.

The organization of fractal waves (*SuperWaves™*) in our electrochemical, glow discharge (and other) experiments were intended to bring this principle to bear by stimulating cyclic processes across scales. Peaking of *SuperWaves™* is the natural origin of what is termed excess heat. Clear evidence of the SW effect in controlling the excess of power production during electrochemical loading of palladium with deuterium is described in the appendix.

Acknowledgments

The author acknowledges significant contributions to the Appendix by Drs. V. Violante and M.C.H. McKubre.

SuperWaves is a trademark of Energetics Technologies, LLC.

3. Appendix

An example of one of the ways that *SuperWaves™* can contribute to enhancing LENR excess heat effects can be demonstrated from the advantage of pulsatile (rather than dc) current or pressure driven loading of hydrogen (and its isotopes) into metals that has been demonstrated to be a necessary condition for the occurrence of the effect.

The dissolution of hydrogen isotopes into a metal lattice is not only a problem of thermodynamic equilibrium between the hydrogen inside the lattice and the hydrogen in the external phase (gas or liquid) it is also a problem of dis-equilibrium produced by mass transfer. Both aspects of the phenomenon are correlated since the equilibrium concentration of the solute is achieved when the chemical potentials of the hydrogen in both phases are equal.

The chemical potential of the hydrogen in solid solution in a metal lattice is strongly influenced by all field force, like the stress field, modifying the free energy of the system [3]. Hydrogen isotopes dissolved into a metal (*i.e.* palladium) occupy interstitial positions causing lattice expansion. This process generates a stress field when remarkable concentration differences (strong gradients or coexistence of different phases) are created.

Therefore the loading process can be inhibited by an opposing stress gradient, particularly adjacent to the external surface. When a stress field is created is the hydrogen chemical potential into the metal lattice, increased by the product between the molar volume of the hydrogen in the lattice and the trace of the stress tensor.

$$\mu_s = \mu^* + V_s \sigma_h \quad [1]$$

Also the flux equation modify :

$$J = -D(\nabla C - \frac{C\bar{V}}{RT} \nabla \sigma) \quad [2]$$

Compared with Fick's law there is an additional term involving the stress gradient. Equation [2] shows that a zero flux condition may occur even if the concentration gradient has a non zero value (if the two terms into the brackets have the same value). A mass transfer equation has been obtained to describe the evolution of the hydrogen concentration profile during the loading of H into Pd [3]:

$$\frac{\partial \bar{c}}{\partial \tau} = \frac{\partial^2 \bar{c}}{\partial \bar{x}^2} - (1-\eta)b \frac{\bar{V}E}{RT} \left(\frac{\partial \bar{c}}{\partial \bar{x}} \right)^2 - (1-\eta)b \frac{\bar{V}E}{RT} \bar{c} \frac{\partial^2 \bar{c}}{\partial \bar{x}^2} \quad [3]$$

Appropriate metallurgical treatments may help in reducing the concentration gradients (*i.e.* the stress) in loading palladium with deuterium. In addition a proper loading dynamics can contribute to have a better loading.

We may explain this with an example. Figure A1 shows the H concentration profile evolution when the effective pressure is changing between two pressure levels arbitrarily labeled Hi and Low. When the pressure is high (Hi) a strong concentration gradient is created close to the surface of the sample to be loaded. A reduction of the pressure followed by a further increasing, destroys the gradient close the surface and move the region of high loading further into the sample, while relaxing the surface condition. If we again repeat the same operation using a new period that is comparable with the diffusion time required to move the hydrogen from the surface to the inside position where the gradient exists we may destroy the gradient again moving it into further inside, and so on.

The problem is that the real systems we are working with are made up of polycrystalline materials with distributed grain size. This requires many periods and amplitudes to make effective the process above described across the whole domain. A fractal wave (SW) can perform this task and provide a strong enhancement to both the loading and flux, both conditions that are known or believed to be important preconditions for LENR excess heat in the Fleischmann-Pons Effect. The experimental evidence of the effect of Super Waves on Deuterium loading is shown in Figure A2

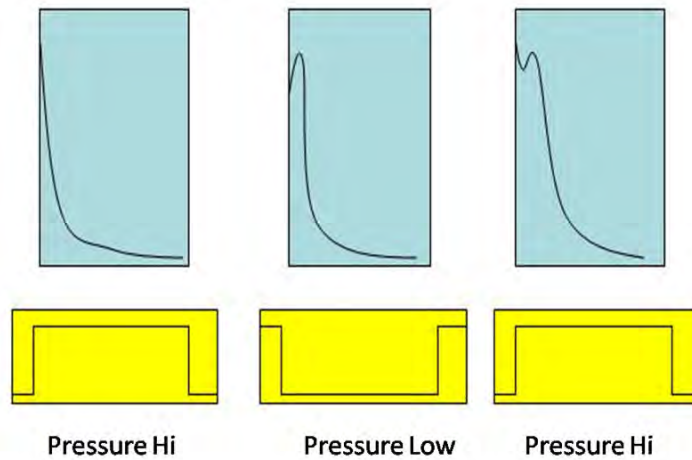


Fig. A1 - Concentration profile evolution under high-low pressure cycling

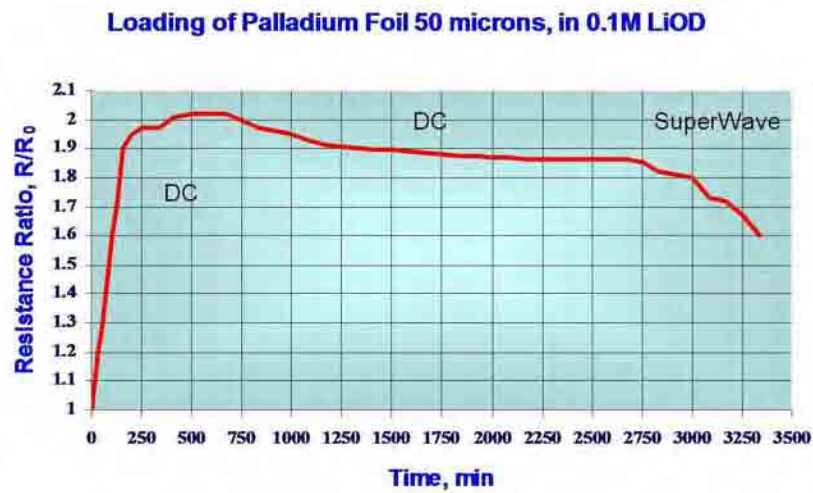


Fig. A2 - Experimental evidence of the SuperWave effect on loading.

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Theoretical Model Of The Probability of Fusion Between Deuterons within Deformed Crystalline Lattices with Micro-Cracks at Room Temperature

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Abstract. In this paper, we wish to demonstrate that the deformation of the crystalline lattice, at room temperature, can influence the process of fusion of the deuterons introduced into the lattice by deuterium loading. In fact, calculating the probability of deuteron-plasmon fusion within a micro-crack, showed, together with the enhancement of the tunnelling effect, an increase of at least 1-3 orders of magnitude compared to the probability of fusion on the surface of the lattice. These phenomena open the way to the theoretical hypothesis that a kind of chain reaction, catalysed by the micro-cracks produced in the structure as a result of deuterium loading, can favour the process.

1. Introduction

As a result of the numerical calculation performed for different metals, varying the temperature, the total energy and the concentration of impurities, it was possible to conclude that the probability of fusion was in effect substantially enhanced by increasing these parameters. In this paper, we wish to confirm the hypothesis regarding micro-cracks, by means of quantitative theoretical estimates of the coefficient of structural deformation of the perturbed² crystalline lattice independent of time, obtained for different temperature values in the range 100-300 K. In particular, we calculated the probability of fusion within a micro-crack, comparing it with that calculated on the surface, to evidence a possible enhancing effect.

Further, we also wish to observe, theoretically, any influence on the phenomenon produced by variation in temperature, which could favour the fusion of the deuterium nuclei as a consequence of the deformations and micro-cracks produced in the lattice. In fact these may be able to concentrate in their vicinity a relevant fraction of the deuterons present in the metal.

The phenomenon hypothesised above could possess characteristics analogous to the formation of the Cottrell atmosphere in metals², known for some time in solid state physics, which essentially consists of a redistribution of the impurities present in the metal around a dislocation of the ions making up the lattice.

In these cases, the interaction between the dislocation and the impurities present can significantly modify the electrical properties of the material; further, some particular reactions can occur, incorporating the impurities in the nucleus of the dislocations, as a result of the different arrangement of the atoms with respect to that of the unperturbed lattice. This type of process has been extensively studied in the literature for the case of crystalline semiconductors at high temperature² and for metals². In the latter, for example, it is found that the concentration of interstitial impurities around a linear dislocation, with a point component, depends on the temperature according to a law of the type:

$$c = c_0 \exp \left[\frac{\beta}{bkT} \right] \quad (1)$$

where c_0 is the concentration of impurities in the zone with zero internal pressure, $b^3 \simeq v_i$ the volume of the ions constituting the lattice, while β is proportional to the difference

$v_d - v_i$ between the volume of the atoms of the impurities and that of the lattice ions.

Our conjecture is that in a metal, such as Pd, a similar phenomena could occur between the atoms of deuterium penetrating the lattice as a result of deuterium loading and the micro-cracks produced by variations in temperature.

In this case, the parameter β of the previous expression would be *negative*, determining an increase in the concentration of deuterons in the vicinity of the micro-crack, which would then catalyse the phenomenon of fusion.

The procedures, such as deuterium loading within lattices³.

In effect, it is found that with the appearance of micro-cracks, in agreement with the “chain reaction” hypothesis proposed in reference¹, there is an increase in the rate of deuteron fusion within the lattice, obtained by evaluating the number of events per minute with a numerical simulation programme which employs the “WKB” method for the approximate solution of the wave equation. This calculation, which takes account of all the physical parameters, provides theoretical information, which we consider interesting, for “impure” metals at room temperature and for average deuteron energies.

2. Three-dimensional model of spherical symmetry

The numerical calculation, performed for three typical metals (Pd, Ti and Pt) on varying the temperature and total energy, in turn dependent within certain limits on the temperature, made it possible to conclude that the probability of fusion is in effect enhanced by increasing P , T and E .

The following table refers to the probability of fusion calculated on the surface of Palladium¹). It shows the trend of the probability of deuteron fusion in impure Pd ($J = 0.75\%$) on varying T and E (Tab.1 in reference¹). Palladium, which has CFC symmetry, shows higher values for the probability of fusion than Pt and Ti, for temperatures between 36.7 K and 63.7 K and energies between 140 eV and 240 eV.

T $\approx$	36.7 K	45.7 K	54.7 K	63.7 K
E $\approx$	P $\approx$	P $\approx$	P $\approx$	P $\approx$
140	10^{-60}	10^{-55}	10^{-59}	10^{-54}
160	10^{-52}	10^{-47}	10^{-50}	10^{-44}
180	10^{-45}	10^{-43}	10^{-42}	10^{-40}
200	10^{-42}	10^{-41}	10^{-39}	10^{-38}
220	10^{-40}	10^{-39}	10^{-37}	10^{-36}
240	10^{-37}	10^{-35}	10^{-35}	10^{-33}

An important effect on the reaction, due to the metal lattice, is represented by electronic screening. This effect, already studied by Rabinowitz et al.⁴, can be taken into account using a model in which the negative charge is distributed around the nucleon in a thin shell and can be schematised supposing the electric charge to be uniformly distributed with a thin spherical shell, with a radius $R \geq r_1$ equal to the effective range of the interaction between the nucleons, describable in terms of a “shifted⁴” Coulomb potential.

$$V = (kq^2) \left[\frac{1}{r} - \frac{1}{R} \right] \quad r_1 \leq r \leq R \quad (2)$$

where q is the charge of the deuton, r_1 is the nuclear radius, $k = 1 / 4\pi \varepsilon_0$. Then $V = 0$ for $r > R$. The solution for the semi-classic tunnelling factor Λ is⁴:

$$\Lambda = D \exp \left[-2\gamma(r_2) \right] \quad (3)$$

$$\gamma(r_2) = (\pi/2\hbar) \left[(2q^2/4\pi\epsilon_0) \mu r_2 \right]^{1/2} \quad (4)$$

In equations (3) and (4), D is a numerical constant of the order of unity, μ the effective reduced mass of the deuteron, r_2 the classic point of inversion, and $\hbar$ is the reduced Planck constant. To take account of the effect of the impurities present in the metal, we modify the constant D in (3) substituting the product $J\eta$, where J is the concentration of impurities and η a numerical constant, $\eta \cong 1$.

The function γ is proportional to the electrical charge of the nucleons and to the square root of the product μr_2 , where μ is the reduced mass of the mass centre system for an interaction of two bodies, and r_2 is the classic point of inversion.

Of the three metals considered, Palladium seems to be the most effective in catalysing fusion, as a result of its structural characteristics: This can be understood from a qualitative point of view, observing that the curve of interaction potential, within the metal, has a trend which requires a lower quantity of total energy.

The numerical calculation d-d in this case can be expressed as follows¹:

$$V(r) = k_0 \frac{q^2}{r} \cdot M_d \left(V(r)_M - \frac{JkTR}{r} \right) \quad (5)$$

where $V(r)_M$ is the Morse potential, $k_0 = 1/4\pi\epsilon_0$, q is the charge of the deuteron and therefore q^2/r is a potential, M_d the reduced mass of the deuterium nuclei, T the absolute temperature at which the metal is experimentally placed, J the concentration of impurities in the crystalline lattice and R is the nuclear radius.

3. Deformation in cubic lattices

In this section we wish to establish whether, and within what limits, the rate of fusion within a micro-crack in a generic cubic lattice subjected to deuterium loading can be conditioned or influenced, as well as by extensive lattice defects and by the other characteristics and thermodynamic conditions, also by any “deformations” produced in the crystalline lattice by variations in the temperature.

If this effectively occurs, it is not difficult to hypothesise that the energy produced by the micro-explosions within the micro-cracks present, could favour the creation of new fractures, which in turn would, by the same mechanism, capture other deuterons, and so on.

On the other hand, the formation of micro-cracks in Palladium electrodes produced by the energy released during long periods of electrolysis⁵ has already been observed experimentally for some time, but has until now been considered only a consequence of nuclear fusion. In fact, Heui Kyeong An, et al.⁶ an energy peak within micro-cracks during electrolysis.

Our hypothesis is that deuterons are injected into the micro-crack with force during loading and are therefore more likely to emit energy in micro-explosions, which in turn produce further micro-cracks. In this way the phenomenon observed could favour the process, enhancing the probability of fusion of the deuterons absorbed by the metal lattice.

We wish to study the internal perturbations which can take place in the lattice following D_2 loading and the consequent modifications in the properties of the metal. The loading does not, in fact, simply provide an increase in the percentage of deuterium present, with a resulting disequilibrium of the “d” band; rather this type of procedure also determines, according to our hypothesis, lattice deformations followed by dislocations which cause micro-cracks in the structure.

It can happen then that the interaction between the impurities present and the dislocations produced in the metal during deformation, significantly modify the electrical properties of the material. Some particular reactions can then take place which incorporate the impurities in the nucleus of the dislocations⁷, as a result of the different arrangement of the atoms with respect to that of the unperturbed lattice. An adequate theoretical description of the loading can therefore be obtained, in our opinion, only by treating it as a

perturbation independent of time.

We must also consider the fact that, under conditions far from those of saturation, the rate of fusion, within the metal depends on the number of deuterium nuclei absorbed in unit time, which could also depend on the deformation of the lattice. It is necessary therefore to study both phenomena.

It is known that in the presence of interaction between deuterium nuclei and collective plasmonic excitation in the metal, the number of fusions λ_f in a gas consisting of λ deuterons with density ρ is given by¹¹:

$$\lambda_f = \lambda \cdot \frac{4\pi \rho \hbar}{\mu_d} \cdot \left\langle \frac{1}{p} \right\rangle \quad (6)$$

where μ_d is the reduced mass of the deuterium nuclei, p is their impulse, and where the parentheses $\langle \rangle$ represent the thermal mean.

For simplicity we can now consider a cubic lattice structure subjected to deformations and calculate the probability of fusion within a micro-crack, Γ , on varying the temperature.

Indicating the volume of a single cell by $d\Omega$, the deformation of the entire lattice is given by:

$$\Psi \cong \left\{ \iiint_{\Omega} \eta \left(J \frac{\rho L^2 v b^2}{\alpha 2 h R} \chi \exp \left(- \frac{U_0}{kT} \right) \xi_{(r)} \right) d\Omega \right\} \quad (7)$$

where J is the concentration of impurities and η is a parameter which depends on the lattice and electronic structure of the metal under consideration.

In this study we have concentrated on the cubic structure of the lattice, in the specific case of Palladium, because it has an easily observable geometry and we have indicated by ρ the density of the mobile dislocation⁸ within the lattice at non constant lattice temperature, so that the thermodynamic stress of the deuterium nuclei per unit volume must be taken into consideration.

Further, demonstrate this, approximate calculations were made in which the lattice^{7,8,9} deformation and the micro-crack depth were taken into account.

Taking the centre of mass system as that of reference, the probability of fusion in a zone of the metal in which there is no micro-crack (e.g. on the surface) can be written¹ as:

$$|P|_{\text{int}}^2 = \exp \left(- 2 \int_0^a K(r)_{\text{int}} dr \right) \quad (8) \quad (12)$$

α is $0.15 \text{ \AA}$, $K(r)_{\text{int}}$ is given by:

$$K(r)_{\text{int}} = \sqrt{2\mu [E - V(r)] / \hbar^2} \quad (9) \quad (13)$$

E is the total initial energy, principally thermal in nature; μ is reduced mass of the deuteron ; $\hbar$ is Plank's constant.

Equations (8) and (9) refer to the process of fusion within the crystalline lattice.

The Coulomb potential $V(r)$, containing the temperature contribution, is given by the expression (5) :

The symbols adopted here are the same as those used in (5). In (14), the Morse potential $V(r)_M$ is given by:

$$V(r)_M = (J/\zeta) \{ \exp(-2\varphi(r-r_0)) - 2\exp(-\varphi(r-r_0)) \} \quad (10) \quad (15)$$

Here, J indicates the concentration of impurities present in the metal, while the parameters φ and r_0 depend on the dynamic conditions of the system.

ζ is a parameter depending on the structural characteristics of the lattice, the number of “d” band electrons

and the type of lattice symmetry, and variable between 0.015 and 0.025.

If we divide (8) by (6) and multiply by (7), it follows that:

$$\Gamma \approx \frac{\exp\left(-2 \int_0^a K(r)_{int} dr\right)}{\lambda \cdot \frac{4\pi \rho \hbar}{\mu_d} \cdot \left\langle \frac{1}{p} \right\rangle} \cdot \Psi \quad (11) \quad (16)$$

Expression (11) represents the probability of deuteron fusion within a micro-crack: it is directly proportional to the number of deuterons absorbed by the metal until the target is saturated, thereafter the probability of fusion will be inversely proportional to the number of nuclei absorbed by the metal. In the context of the approximations made, the probability of fusion calculated in this way is equal to the edge deformation coefficient per unit of total deformation of the whole lattice.

From (11), with $K(r)_{int}$ calculated adopting the Morse potential, a numerical simulation programme employing the “WKB” method was used to determine the probability of fusion, normalised to the number of events per minute.

The results of Tab.1 can be compared with those of Tab.2, where the potential (5) was substituted by a “shell” potential of the (2) type, modified as followed:

$$V = (kq^2) \left((1/r) - \frac{KT}{J\varepsilon R} \right) \cdot r_1 \leq r \leq R \quad (12)$$

where KT is the mean kinetic energy of the gas, ε is the vibrational energy which is typically of the order of some eV for the quantum states under consideration and q is the charge of a deuteron.

Table 1. – For “impure” metals ($J \approx 0.75\%$), adopting the Morse potential, the probability of fusion Γ was calculated for Pd within a micro-crack, in the presence of D_2 loading, normalised to number of events per minute, for different values of temperature (100 ÷ 300 K) and energy (150 ÷ 250 eV). It can be seen that the probability generally increases with T and E, and is systematically greater by some orders of magnitude than the probability of fusion P on the surface.

Palladium $J \approx 0.75\%$ T - range $\approx 100 - 300$ K $\alpha \approx 34 \text{ \AA}$ $\lambda_f = 1.38 \cdot 10^{-3} \text{ eV/min}$ $M_{Pd} / \mu g$												
T $\approx$	100 K		140 K		180 K		220 K		260 K		300 K	
E $\approx$	$\Gamma \approx$	P $\approx$	$\Gamma \approx$	P $\approx$	$\Gamma \approx$	P $\approx$	$\Gamma \approx$	P $\approx$	$\Gamma \approx$	P $\approx$	$\Gamma \approx$	P $\approx$
150	10^{-75}	10^{-77}	10^{-66}	10^{-69}	10^{-67}	10^{-68}	10^{-63}	10^{-64}	10^{-64}	10^{-66}	10^{-60}	10^{-68}
160	10^{-73}	10^{-75}	10^{-65}	10^{-68}	10^{-64}	10^{-67}	10^{-61}	10^{-63}	10^{-63}	10^{-65}	10^{-58}	10^{-65}
170	10^{-70}	10^{-73}	10^{-63}	10^{-65}	10^{-62}	10^{-65}	10^{-59}	10^{-62}	10^{-60}	10^{-64}	10^{-56}	10^{-62}
180	10^{-69}	10^{-72}	10^{-58}	10^{-62}	10^{-60}	10^{-64}	10^{-57}	10^{-61}	10^{-58}	10^{-63}	10^{-55}	10^{-60}
190	10^{-67}	10^{-71}	10^{-56}	10^{-60}	10^{-59}	10^{-63}	10^{-55}	10^{-60}	10^{-56}	10^{-62}	10^{-50}	10^{-58}
200	10^{-65}	10^{-70}	10^{-55}	10^{-59}	10^{-57}	10^{-62}	10^{-54}	10^{-59}	10^{-53}	10^{-61}	10^{-47}	10^{-54}
210	10^{-64}	10^{-69}	10^{-54}	10^{-58}	10^{-56}	10^{-61}	10^{-53}	10^{-57}	10^{-52}	10^{-60}	10^{-44}	10^{-51}
220	10^{-62}	10^{-67}	10^{-52}	10^{-57}	10^{-54}	10^{-60}	10^{-52}	10^{-56}	10^{-51}	10^{-59}	10^{-40}	10^{-47}
230	10^{-60}	10^{-66}	10^{-51}	10^{-56}	10^{-53}	10^{-59}	10^{-50}	10^{-55}	10^{-50}	10^{-58}	10^{-32}	10^{-40}
240	10^{-59}	10^{-65}	10^{-50}	10^{-55}	10^{-52}	10^{-58}	10^{-49}	10^{-54}	10^{-49}	10^{-57}	10^{-27}	10^{-34}
250	10^{-58}	10^{-63}	10^{-49}	10^{-53}	10^{-51}	10^{-56}	10^{-48}	10^{-51}	10^{-48}	10^{-53}	10^{-21}	10^{-25}

Table 2.- For “pure” metals ($J \approx 0.25\%$), adopting the “shell” potential, the probability of fusion Γ was calculated for Pd within a micro-crack, in the presence of D_2 loading, normalised to number of events per second, under the same dynamic conditions as Tab.1. Also here Γ is systematically higher by some orders of magnitude compared to the probability of fusion P on the surface, but the values are systematically lower than those of the previous case.

Palladium $J \approx 0.25\%$ T -range ≈ 100 - 300 K $\alpha \approx .34 \text{ \AA}$ $\lambda_f = 1.38 \cdot 10^{-3} \text{ eV/min}$ $M_{Pd} / \mu g$

T $\approx$	100 K		140 K		180 K		220 K		260 K		300 K	
E $\approx$	Γ $\approx$	P $\approx$	Γ $\approx$	P $\approx$	Γ $\approx$	P $\approx$	Γ $\approx$	P $\approx$	Γ $\approx$	P $\approx$	Γ $\approx$	P $\approx$
150	10^{-75}	10^{-81}	10^{-76}	10^{-85}	10^{-73}	10^{-78}	10^{-69}	10^{-75}	10^{-66}	10^{-76}	10^{-65}	10^{-71}
160	10^{-74}	10^{-79}	10^{-78}	10^{-83}	10^{-70}	10^{-77}	10^{-68}	10^{-74}	10^{-65}	10^{-75}	10^{-63}	10^{-70}
170	10^{-73}	10^{-76}	10^{-76}	10^{-81}	10^{-69}	10^{-76}	10^{-67}	10^{-73}	10^{-63}	10^{-74}	10^{-59}	10^{-66}
180	10^{-71}	10^{-75}	10^{-75}	10^{-80}	10^{-68}	10^{-75}	10^{-65}	10^{-72}	10^{-62}	10^{-73}	10^{-55}	10^{-65}
190	10^{-69}	10^{-73}	10^{-73}	10^{-78}	10^{-67}	10^{-74}	10^{-64}	10^{-70}	10^{-60}	10^{-72}	10^{-53}	10^{-64}
200	10^{-67}	10^{-72}	10^{-72}	10^{-75}	10^{-65}	10^{-73}	10^{-62}	10^{-69}	10^{-58}	10^{-71}	10^{-49}	10^{-62}
210	10^{-65}	10^{-70}	10^{-70}	10^{-74}	10^{-64}	10^{-72}	10^{-60}	10^{-68}	10^{-56}	10^{-68}	10^{-46}	10^{-59}
220	10^{-64}	10^{-67}	10^{-68}	10^{-73}	10^{-63}	10^{-70}	10^{-59}	10^{-67}	10^{-54}	10^{-67}	10^{-43}	10^{-55}
230	10^{-63}	10^{-65}	10^{-66}	10^{-71}	10^{-61}	10^{-69}	10^{-57}	10^{-66}	10^{-52}	10^{-65}	10^{-41}	10^{-52}
240	10^{-61}	10^{-63}	10^{-64}	10^{-70}	10^{-60}	10^{-68}	10^{-55}	10^{-64}	10^{-51}	10^{-61}	10^{-38}	10^{-50}
250	10^{-60}	10^{-61}	10^{-63}	10^{-68}	10^{-58}	10^{-64}	10^{-54}	10^{-62}	10^{-49}	10^{-56}	10^{-35}	10^{-47}

To confirm qualitatively the effect of enhancing the probability of fusion, the trend of the potential curve was obtained on varying the temperature¹² in the range 100 - 300 K, in the case of Palladium. It can be seen that both the height and the thickness of the potential barrier are less in the impure metal ($J \approx 0.75\%$). Fig.1 shows an example of the potential curves obtained.

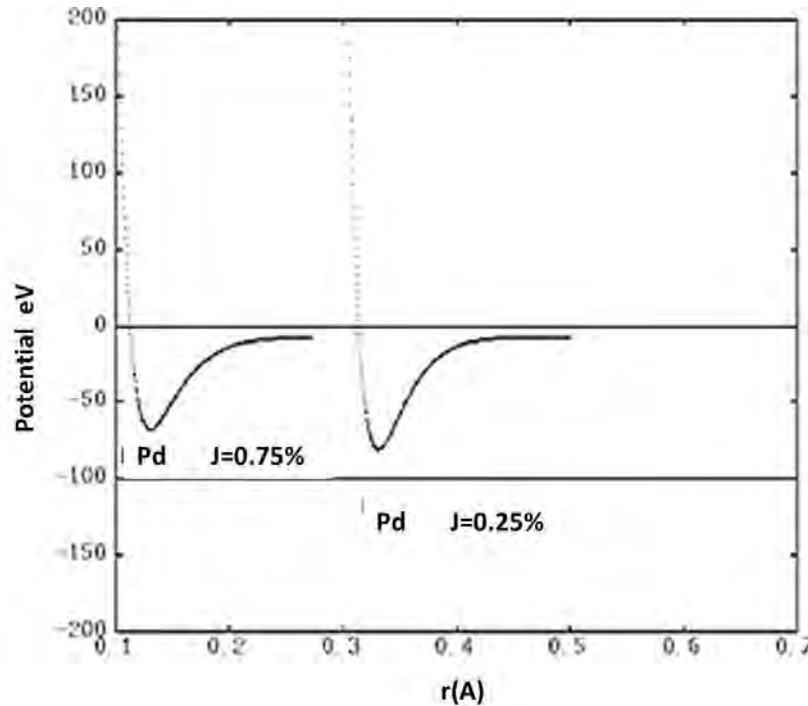


Fig.1. - Comparison between the potentials (14) and (17), in the presence of D_2 for $J \approx 0.75\%$ and $J \approx 0.25\%$, respectively, at temperature $T = 290 \text{ K}$. In the first case, both the height and the thickness of the potential barrier are reduced.

4. Conclusions

The present study was to demonstrate if and how the deformation of the crystalline lattice and the formation of a micro-crack could influence the process of fusion at room temperature. More precisely, we calculated numerically the probability of fusion within a micro-crack, comparing it with that calculated on the surface to evidence a possible enhancement effect. The factors which most catalyse the fusion reactions remain however, in the three-dimensional case, the percentage of impurities J , the deformation of the lattice and the consequent formation of micro-cracks, as can be seen by comparing Tab.1 and 2. Further, tunnelling in the presence of deuterium loading was analysed, observing that, from the *theoretical* point of view, the phenomenon can be treated as an internal perturbation of the lattice. As shown in Fig. 1, it was found that in the presence of loading, the tunnelling appears enhanced due to the reduction¹, in both height and thickness, of the barrier “K”. The loading seems therefore to be an important factor conditioning the phenomenon of fusion. One of these mechanisms essentially “consists” of a kind of chain reaction between deuterons and plasmons, catalysed by the deformations and micro-cracks which arise in the structure as a result of variations in the thermodynamic conditions and other causes, such as deuterium loading.

This was hypothesised in the present paper and constitutes one of the principal motives of its inspiration. It is however possible to confirm that the initial results obtained so far validate the hypothesis presented here.

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Usefulness of Quasi-Particle Ion Band States in Modeling LENR Processes

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Abstract. The density of atoms with 3 or more electrons is determined by Pauli exclusion. Conduction electrons in a metal and reactant deuterium atoms are in Bloch function form, in which corresponding positions in a lattice are equivalent. 2-dimensional symmetry D-atoms are thin, flat, and have reduced Coulomb repulsion between pairs. Fusion takes place inside an interface between an ionic crystal and an epitaxy metal layer. 2-dimensional and 3-dimensional systems are different. Both are real, benefit from shock stimulation, and are Bloch systems; but they require different environments.

1. Introduction

Low Energy Nuclear Reaction (LENR) processes are new types of catalyzed reactions. They depend on causing potential reactants to assume non-classical geometric configurations. Nature does this sort of thing when it creates a metal. But we are now so familiar with a metal's non-classical geometry that we accept it as a routine part of the Quantum Mechanics of solids and liquids. When electrons become part of the electron medium of a metal that carries electricity, we call them quasiparticles. Their charge is "coherently partitioned". They have adopted a many-centers¹ geometry modeled by Felix Bloch. Bloch function physics explains how a solid with a density greater than that of insulators like salt can be a good conductor of electricity.

LENR processes are those in which a laboratory chemical process can cause some sort of nuclear reaction to occur.

LENR processes that produce measurable heat or measurable quantities of transmutation products are of primary interest. There are secondary LENR processes that can occur when an overvoltage main stream process produces a 2-dimensional symmetry product and the process is disturbed or interrupted. The result can be rare side-effects like those that cause MeV nuclear particles to be produced. These strange quantum processes when reproducible have important diagnostic value.

There is no single road to identifiable LENR products

This paper considers 3 classes of process:

Production of heat in electrochemical systems

Production of heat in gas loading systems

Production of MeV particles resulting from overvoltage electrolysis LENR

We first consider the physics by which heat is produced in gas loading systems.

2. Quasiparticle Physics

Quantum Mechanics textbooks typically start off with solving problems like the behavior of an electron in a harmonic potential well, an electron in an inverse square potential (hydrogen atom), or a particle-in-a-box. In these problems there is an identifiable center-of-mass. Bloch asked the question, what happens when the electron is in lattice electric field that extends in 3 directions in space and repeats and repeats forever? In this problem there is no identifiable center-of-mass. Such electrons are called quasiparticles. Corresponding positions in each unit cell of the lattice are equivalent. The charge in each unit cell is its partition fraction. This idealized picture is clearly unphysical and has no boundaries, but the solutions to

Bloch's lattice potential proved effective in describing the observed behavior of electrons in a real metal to within a few layers of the metal's surface. Most of a metal's electrons are not involved in conducting electricity and are permanently part of the metal's atom lattice. Only the quasiparticle electrons carry the electric current. LENR physics is quasiparticle physics applied to deuterons, and in some cases to other ions like protons and Li^+ ions.

Reaction rate modeling of deuteron quasiparticle systems can be studied using time-dependent Schrodinger wave equations, or it can be studied using stationary state wave equations plus time dependent perturbation theory to connect "initial" and "final" states. When one is using stationary state wave equations, one has the option of representing them in terms of a sum over Wannier functions. Wannier functions portray quasiparticles as a sum of random snapshots of collapsed many-centers wave functions. I think it is easier to understand the physics if one avoids the Wannier function approach. I also adopt the view that a complete fusion reaction may occur in successive steps in which the final state of step 1 is the initial state of step 2. In this picture, a sequence of metastable states plays a major role in LENR fusion events. Each transition delivers heat to the adjoining metal lattice.

3. 2-Dimensional Symmetry Reactions

We start our study by focusing on 2-dimensional symmetry LENR. 2-dimensional DD-fusion reactions are examined because they are the easiest to picture. They are called DD reactions rather than dd reactions, because the deuterons are always neutralized by an electron. D designates a D atom. A D atom is a D^+ ion plus its accompanying electron. Neutralization occurs because it is required by equilibrium chemistry, which insists on minimizing system Gibbs free energy. By an electron I mean a quantum of electron charge. In our initial simplified picture we ignore a requirement for imposing coordinate exchange symmetry on an entangled 2-body system, but recognize that the electron is a fermion with spin 1/2. We also recognize that the K-shell of an atom is an entangled spin-zero electron pair.

4. Permeation Transport

It is important to recognize that conduction by quasiparticles is not the only form of D transport. In permeation studies, D quasiparticle conduction competes with D-atom diffusion. D diffusion is driven by the local negative gradient of the interstitial D concentration. D quasiparticle conduction is driven by a difference in D concentration at entry and exit boundaries of a discrete finite volume of ordered lattice.

5. Gas Loading Reactions with ZrO_2 + NanoPd Catalyst

Arata and Zhang (A-Z) made major progress toward production of DD fusion heat when they first used ZrO_2 + NanoPd Catalyst.² In switching from Pd black they introduced a highly stable ionic solid into their composite catalyst. ZrO_2 has a large negative Gibbs free energy, which means its crystalline structure is not easily influenced by adjacent layers of metal. The metal is a much more malleable lattice component.

A-Z made a second major step when they switched from using electrolysis to gas loading as their means of adding deuterium to the nanoPd employed.³ Iwamura had previously made a similar discovery when he discovered that measurable heat could be produced by diffusion of deuterium through a plate with embedded CaO.⁴ CaO also has a highly negative Gibbs free energy. These developments suggested that the interface between stable oxides and Pd metal is a likely site for deuteron quasiparticle transport and DD fusion reactions.

6. Essential Role of Pauli Exclusion

Pauli exclusion as applied as an axiom in Quantum Mechanics includes two features. The primary feature is that there is a limit to the number of electrons that can occupy a cell in quantum phase space. Quantum phase space is a 6-dimensional theory space in which occupiable cells are designated by position

coordinates x, y, z and momentum coordinates p_x, p_y, p_z . Adding a spin phase space dimension doubles the density of a solid. Pauli exclusion as applied to electrons largely determines the density of atoms having atomic number greater than helium. The electrons largely determine the density of condensed matter because condensed matter is nothing more than an assembly of contacting atoms. In contrast, protons, neutrons, and nuclei play almost no role in determining the density of atoms and solids. This is an enormously important aspect of quantum physics. It also applies to white dwarf stars,⁵ and is confirmed by their difference from neutrons stars. White dwarf stars are supported by a completely degenerate electron phase-space lattice. Neutron stars are dwarfs that have lost their electron-based structure by inverse beta decay. White dwarfs have the mass of the sun in a volume equal to that of the earth. Neutron stars have the mass of the sun in a volume whose diameter is that of Washington, DC.

7. Interface between Perfect Crystal Surface and Epitaxy Metal Layer

ZrO₂ crystals appear to be able to provide flat faces on which there are areas with perfect lattice order. Imperfect Pd metal seems able to configure itself so as to form an epitaxy fit to this layer.⁶ When a diffusing D encounters the interface volume containing an area of lattice with perfect order, it switches to quasiparticle form. The D atom suddenly becomes a superthin flat atom, as shown in Fig. (1).

If the perfect area exceeds 1000, or maybe 10,000 contacting lattice atoms, additional important physics occurs. The superthin flat atoms have at thickness of 0.001 or maybe 0.0001 times the thickness of a normal metal layer. It then becomes possible for two flat atoms to occupy the same volume of space. Their joint occupancy is no longer prevented by Coulomb repulsion. The required area of perfect lattice order for hosting double flat atoms has been calculated based on a requirement for system energy minimization..

The double flat D atom is a form of flat ⁴He. Successive momentum transfers deliver released nuclear energy to quasiparticle electrons in the adjoining bulk Pd metal lattice.

Flat ⁴He extends to a boundary of the perfect order region. At the boundary the flat ⁴He converts to spherical atom form. This conversion to spherical form completes the primary fusion process.

8. Reduction of Coulomb Repulsion

Fig. 2 shows pictorially why the large area occupied by a super-thin geometry of individual D quasiparticles reduces the Coulomb repulsion between two parallel D atoms. The partition fraction local charge associated with the area next to one of the ionic crystal atoms is repulsed by the same segment area of local charge in its neighbor. Adding up all these neighbor-neighbor repulsions leads to a segment-segment repulsion of $1/N_{\text{cell}}$, where a segment area roughly that of a normal spherical D atom cross section. See Eq. (1). The means that the larger the area of perfect order on the ZrO₂ face, the lower the energy of the fusion product ⁴He. It also means that system energy is lowered if the flat atom can move so as to expand its area.

For a pair of flat atoms at small separation distance d ,
the Coulomb force F_{Coul} is:

$$F_{\text{Coul}} = \sum_1^{N_{\text{cell}}} \left(\frac{e}{N_{\text{cell}}} \right)^2 \left(\frac{1}{d} \right)^2$$

As $N_{\text{cell}} \rightarrow \infty$, $F_{\text{Coul}} \rightarrow 0$

Eq. (1)

The same process that allows flat D atoms to form ⁴He allows flat ⁴He atoms to form flat ⁸Be and flat ¹²C. These entities are seen as the players in Mossier-Boss's CR39 studies.⁷

Spherical Atom Change into Flat Atom

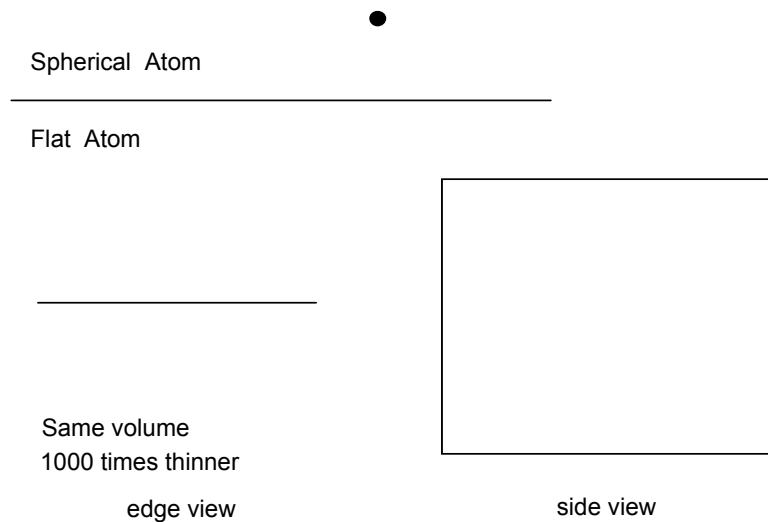


Fig. 1 - A normal spherical atom changes into a flat atom. Its volume is preserved but it becomes much thinner. If the area covers a 1000 atom array, the atom's thickness is reduced by a factor of 1000.

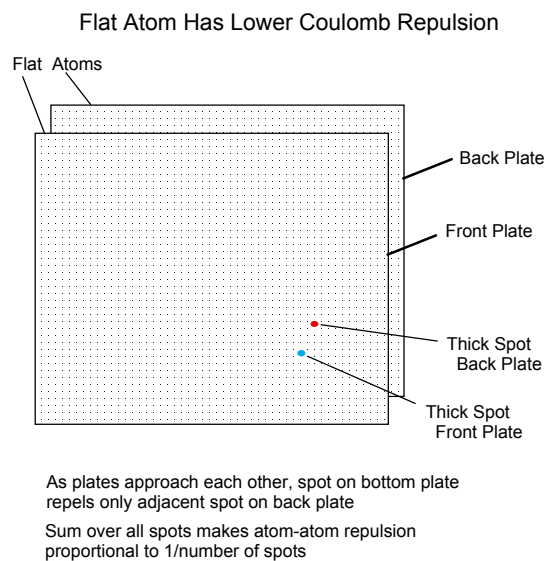


Fig. 2 - Flat deuterium atoms have an array of relatively thick spots. When two flat D approach each other and are separated by nuclear scale distance, a thick spot on the one is repelled only by the corresponding thick spot on the other. Summing over the repulsion potentials shows that the atom-atom repulsion is reduced by the number of thick spots in the array, designated N_{cell} . Each atoms is said to be coherently partitioned into N_{cell} equivalent spots. See Eq.(1).

Apparently similar flat atoms are produced from flat Li atoms fusing with flat D and H atoms in Oriani's CR39 studies.⁸ In some of the Oriani experiments the stable ionic crystal involved could be NiO, but in Mossier-Boss's case it may be that the crystalline plastic container used to house the electrolysis cell could be the ordering crystal. In both cases the crystal that imposes lattice order may be an ionic crystal formed by oxidation of an impurity in the electrolyte employed, or on the containment vessel.

9. Interruption of Fusion Cascade

Mossier-Boss and Oriani have observed MeV-energy particle tracks that start and end inside CR39 plastic detectors. The source of these tracks is believed to be the breakup of a metastable ^8Be or ^{12}C flat nucleus accompanying its transition to normal atom form. The flat nuclei are stable when residing in their birthing interface. When a flat atom is released from its birthing interface, it can temporarily adopt an independent existence. When electrolytic loading is employed, flat are nuclei probably rare side products of overvoltage electrolysis. Also, it may be that on some occasions the energy transfer cascade that leads to a flat ^8Be and ^{12}C atom can be interrupted prior to its transition to its ground state. It is predicted, but not certain, that no CR39 double or triple tracks will be observed in gas loading experiments because of nearly reversible chemistry.

10. 3-Dimensional Symmetry Fusion

The discovery of cold fusion by Fleischmann and Pons appears to be the result of the fusion of 3-dimensional symmetry D quasiparticles in electrolytically loaded PdD_x where $x > 0.85$. 2-dimensional and 3-dimensional systems are different. Both are real, benefit from shock stimulation, and are Bloch systems; but they require different environments.

To explain 3-dimensional cold fusion it is helpful to examine the behavior of atoms in optical lattices.⁹ An optical lattice is an array of potential wells separated by barriers created by interfering laser beams. Bose atoms show different behavior when the barriers between potential wells are high than when they are low. When high, the atoms behave as "particles"; when low, they behave as quasiparticles. When high, but not too high, the center of each potential well is occupied by a "particle", while the periphery is occupied by the partition-fraction of a shared quasiparticle. In PdD_x with x near 1, the periphery of the octahedral sites of Pd metal plus the centers of the 2 tetrahedral sites constitute a communication network of shallow potential wells. This network can become occupied by D quasiparticles in the same manner that the interface volume in a 2-dimensional fusion system becomes occupied. Therefore, paired 3-dimensional quasiparticles are subject to the same reduction in Coulomb repulsion between overlapping partners as occurs with 2-dimensional quasiparticles.¹⁰

11. A Historic Experiment

Oriani and Fisher have described an experiment in which they constructed an electrolysis cell in which they placed paired CR39 detector detectors facing each other in the gas space above the cell's mixed H_2 and O_2 offgas. They observed a shower of MeV particles from a source that moved during the detector exposure interval. They wrote, "It is clear from Fig. 3 that the shower of charged particles that created the tracks originated somewhere in the region above the lower left corner of the chip. One can also infer that the source of the particles was not stationary during the duration of the burst because of the absence of circular symmetry in the density distribution. The intersection of these surfaces occurs approximately 2 mm from the chip surface (Fig. 5B). ¶ This suggests that a fairly compact source of energetic particles moved away from the chip surface as it rosewe estimate that the burst produced about 250,000 charged particles ¶ One might expect that a shower of particles near one chip would have affected the other; indeed this is the case"

Based on this description I concluded that Oriani-Fisher showers were caused by clusters of very thin "flake" atoms.¹¹ It seems to me that for an entity to be suspended in a slowly rising gas stream such as produced by electrolysis requires that the entity be incomparably less dense than any previously known macroscopic material. The flat ^8Be atoms described in this paper would seem to fit this requirement

12. Don't Be Too Pure

It is probably desirable that the hydrogen gas that is used to chemically reduce $\text{ZrO}_2 + \text{nanoPd}$ catalyst during its preparation should not be too pure. The creation of an epitaxy layer on an ionic crystal requires

an assembly of Pd fragments, as described by Barcaro et al.⁶. Having both interstitial H and D atoms within the Pd metal should be helpful.

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Evaluation of d/d Reaction Rates in Metallic Lattices as a Function of the Deuteron Energy. A Phenomenological Model of Nuclear Fusion in Solids

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Abstract. Recently, unexplained enhancements of d/d reaction rates in solids were observed. This enhancement is lower than a factor of 10 at low energies of the deuteron (a few keV) and as high as a factor of 10^{18} for extremely low energies (0.025 eV). Based on the calculation of d/d reaction rates in a lattice, a phenomenological model is proposed to infer the enhancement that can be expected for deuterons of energies in between these two extremes. A potentially interesting zone (between 500 and 2000 eV) has been identified.

1. Introduction

Recently, experiments on d/d reactions were run, in 2 zones of the reacting deuteron energy: the zone of low energy (3 to 20 keV) [1] and the zone of extremely low deuteron energy (eV level, SPAWAR heavy water electrolysis experiments [2]). In [1], the cross sections of the d/d reactions were measured using a high energy proton (deuteron) generator. In [2], track-etching detectors (CR 39 chips) were used to record tracks of high energy charged particles. The number of tracks recorded gives an estimation of the reaction rates (assuming these tracks come from d/d fusion products). In [1] and [2] an enhancement is observed compared to the calculated reaction probabilities. The enhancement factor is 2 to 10 in [1] and many orders of magnitude (10^{18}) in [2]. This was in both cases attributed to the screening effect of the electrons of the metallic lattice where the reactions take place.

In [3], the contribution to the d/d reaction rate enhancement, of an attractive Yukawa type of potential, acting between nucleons, was evaluated. Its effect was shown to be of the same order of magnitude as the screening of the lattice electrons for deuteron energies of a few keV [1]. Nevertheless, the combined effect of this potential and of the screening of the lattice electrons (150 to 300 V) was shown not to be sufficient to explain the whole enhancement [1,3]. Under SPAWAR electrolysis experimental conditions, the effect of the Yukawa potential was found to be negligible compared to the screening effect of the lattice electrons, which in turn fails by a many orders of magnitude to explain the enhancement observed [3].

A coupling between the deuterons in the target with the incident deuteron beam was thus suggested [3] to explain the enhancement observed, by fusion reactions taking place between the deuterons already trapped in the target. The consequences of this hypothesis on d/d reaction rates are examined, for energies of the incident deuteron beam varying from 2 to some 100 000 eV.

2. Evaluation of d/d reaction rates as a function of the reacting deuteron energy

Using the model developed in [3], the reaction rates and the power production resulting from the interaction of a 1 W beam of deuterons with a metallic target (palladium) loaded with deuterium (1 mmole, loading ratio 0.7), was evaluated as a function of the incident deuteron energy. For a thick target, the reaction rate r is: $r(cm^{-3}s^{-1}) = \sigma(cm^2)\phi(cm^{-2}s^{-1})N_0(cm^{-3})$, with $\sigma(cm^2)$ being the reaction cross-section, $\phi(cm^{-2}s^{-1})$ the deuteron flux and $N_0(cm^{-3})$ the deuteron concentration in the target. From [3], the reaction cross section is: $\sigma = \sigma_{geom.}P(E_d)$ with $\sigma_{geom.}$ being the geometrical cross section of the target deuteron (≈ 0.5 barn) and $P(E_d)$ the probability for the deuteron of energy E_d , to tunnel through the potential barrier of the target deuterons, calculated from [3]. The probability $P_{S+Y}(E_d)$ of tunneling through the screened Coulomb potential under the influence of the Yukawa potential is $P_{S+Y}(E_d) = F_{S+Y}P_B(E_d)$, the probability of tunneling through

the bare Coulomb potential being $P_B(E_d)$ (corresponding to a rate r_B) and F_{S+Y} being the enhancement factor due to the screening of the electrons and the action of the Yukawa potential. Hence, $r_{S+Y} = F_{S+Y} r_B$. The deuterons concentration n_0 (cm^{-3}) outside the target, corresponding to a deuteron flux (mass m and energy E_d (J)), depositing 1W on the target is:

$$n_0 = \frac{1}{100E_d} \sqrt{\frac{m}{2E_d}}, (\text{cm}^{-3}) \text{ corresponding to a flux: } \varphi = \frac{1}{E_d} (\text{cm}^{-2}\text{s}^{-1})$$

For 1 mmole of deuterium (d) loaded in a palladium target with loading ratio 0.7:

$$N_0 = 4.74 * 10^{22} (\text{cm}^{-3}, \text{palladium thickness: } 127\mu\text{m})$$

For an incident deuteron flux of 1 Wcm^{-2} and for 1 mmole of deuterium in the target, the power produced from the fusion reactions is (after correction for the target thickness):

$$W_{S+Y} = r_{S+Y} \frac{Q}{2} = 1.6 \cdot 10^{-13} * 0.0127 = 7.39 r_{S+Y} \cdot 10^{-15} (\text{J.s}^{-1}.\text{cm}^{-2}.\text{mmole}^{-1})$$

$Q = 1 + 3 + 0.83 + 2.44 = 7.27 \text{ MeV}$ is the total energy of the two main d/d fusion channels.

3. Effect of electron screening and Yukawa potential on reaction rates and energy production

The reaction rates r and the power produced W , were evaluated, for the incident deuteron energy varying from 2 to 100 000 eV. Calculations were run in two situations: bare Coulomb potential (r_B and W_B) and screened (screening energy 150 V) Coulomb and Yukawa potential (r_{S+Y} and W_{S+Y}). Results are summarized in Fig. 1 and Fig. 2

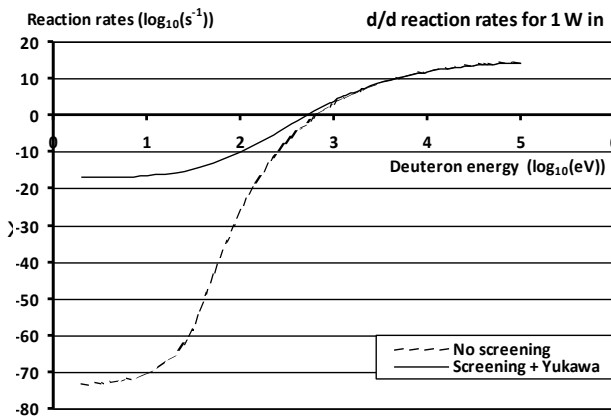


Fig. 1 – d/d reaction rates for 1W in.

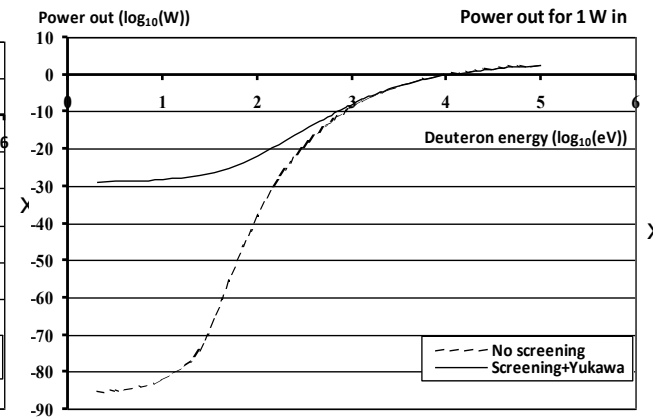


Fig. 2 – Power out for 1W in.

It can be seen from Fig. 1, that for deuteron of energy 0,025 eV, the reaction rates r without screening, are extremely low ($1.32 * 10^{-74}$ reactions per second), corresponding to a very small amount of produced power W ($1.9 * 10^{-88}$ W). Taking into account the screening effect of the electrons acting on the combined repulsive Coulomb potential and the attractive Yukawa one, considerably increases the reaction rates r_{S+Y} ($7 * 10^{-18}$ reactions per second) and the power production W_{S+Y} (some $1.1 * 10^{-31}$ W). At these extremely low energies, the contribution of the Yukawa potential and of the energy of the deuteron (up to 2 to 3 eV), are negligible compared to the screening of the electrons. Anyhow, the reaction rates are still very much lower than what is observed in SPAWAR experiments (which can be estimated to be round 10^{-1} reactions per second ($\approx 7 * 10^4$ in 1 week), assuming that the charged particles observed in SPAWAR experiments are the signature of d/d reactions. At energies of the deuteron round 2 to 3 keV, the effects of the screening of the electrons and of the Yukawa potential are of the same order of magnitude, but their combined effects do not account for the totality of the enhancement factor observed at these energies. In [3] it was thus proposed that the incoming deuteron could

couple with the deuterons already present in the lattice, inducing additional fusion reactions between them. A phenomenological model based on these ideas is proposed.

4. The resonant coupling phenomenological model

4.1 The concepts that back the phenomenological model

A plasma is a globally neutral collection of free charged particles, with the same concentrations: 10^{20} m^{-3} ($T \approx 10 \text{ keV}$) in nuclear fusion and 10^{29} m^{-3} ($T \approx 3 \text{ keV}$) in dense astrophysical plasmas. In both cases, nuclear fusion reactions occur at a high rate, only because the high thermal energy of the hydrogen isotopes ions allows significant tunneling through their Coulomb potential barrier.

In order to measure the d/d nuclear fusion reactions rates, use is made of a deuteron gun that projects deuterons on a target loaded with deuterium, under vacuum and with a controlled energy. Recently it has been experimentally observed [1], that at low energy (3 to 20 keV) of the impinging deuteron, the reaction cross sections are increased by a factor that can reach 2 to 10 compared to what is expected from the Gamow factor at these low energies. This was attributed [1], to the screening effect of the electrons of the target. The corresponding potential was experimentally found to be as high as 500 V. It is only 150 V when evaluated from the Thomas Fermi approximation (low temperature of the deuterons) and some 300 V when considering the Debye-Hückel one (high temperature $>$ tens of keV of the deuterons). Similar screening effect is invoked when considering the calculation of alpha disintegration constants from the tunneling of the alpha particle through the Coulomb barrier of the daughter nucleus of the decaying atom [1,4].

A screened potential naturally arises for the conduction electrons in a metal. The screening acts on the pseudo potential that the electrons of the conduction band experience from the cations in the lattice. In first approximation, this unscreened pseudo-potential is taken equal to zero for distances lower than a distance in the order of the Bohr radius and equal to the Coulomb one for distances higher. This is a semi-empirical way to simplify, in a representative way, the wave functions of the electrons in the conduction band of the metal, which mostly ignore the cations of the metal, (hence the empty lattice name of the method) [5].

The interactions of charged particles with a metallic lattice, are understood in two extreme situations:

- Extremely low energy charged particle: metallic hydrides can be viewed as the typical interaction. They have a metallic character (electrical conduction). The protons (deuterons) in the lattice are very mobile: their diffusion coefficients are very high and they move under the influence of an electrical field. In that respect, metallic hydrides can be viewed as a plasma of protons (deuterons) and electrons embedded in the lattice of the host metal. But contrary to electrons, protons (deuterons) in a lattice experience the screened full Coulomb potential of the lattice ions and not the screened pseudo-potential, resulting in potential wells at tetrahedral or octahedral sites, where the hydrogen isotopes find a stable equilibrium position. So they are not completely free to move, but the potential wells have a depth E_A (activation energy of the diffusion process) in the order of a few tenths of eV. They are thus easy to activate (acquiring an energy higher than E_A) and can thus move more or less freely.

- High energy charged particle. This is typically the interactions of an alpha particle (a few MeV energy) impinging a metallic lattice (in that case the interaction would be similar with a non metallic lattice) the alpha loses most of its energy through inelastic collisions with the electrons of the lattice (ionization, resulting in the range of the alpha measured by nuclear physicists) and rarely with the nuclei of the lattice.

- A situation much less explored, is that of a metallic lattice loaded with deuterium, submitted to a flux of deuterons of energy between say a few eV to 15 000 eV. In that case, the impinging deuteron will mainly exchange energy with the loaded deuterons, through very efficient elastic collisions (same mass). A non equilibrium situation is created where the hotter part of the deuterons partition could activate the main deuteron population, inducing movements of the deuterons in the lattice beyond the diffusion rates observed at thermodynamic equilibrium and yielding an increase of the fusion reaction rates (note that hot spots, even macroscopic, have been observed in certain experiments). Moreover, the possible focusing action of the periodic potential of the embedding metallic lattice ("conduction band" of the activated deuterons) could result in increasing the apparent geometric cross sections determining the fusion reactions rates.

4.2 Proposed phenomenological model

So far, no model exists describing this hypothetical mechanism. It is reasonable to think that it is more and more efficient as the de Broglie wavelength of the impinging deuteron increases with the decrease of its energy E_d (2 eV = 15 000 fm, 10 000 eV = 200 fm). It is thus proposed to describe this interaction by a phenomenological model: a resonant coupling enhancement factor F_C , which adds its effects to the already observed enhancements

due to the electron screening (and to the Yukawa potential for low energies used in [1]). The reaction rates are given by $r_{S+Y+C} = F_C F_{S+Y} r_B = F_C r_{S+Y}$. In this concept, F_C is a function of the energy of the impinging activating deuteron. The Fermi energy E_f of the metal is likely to play a role in this mechanism. The maximum of F_C is thus hypothesized to occur at this energy. The deuteron plasma activation mechanism is rather clear in the case of deuteron gun experiments. It requires some additional hypothesis in the case of electrolysis and more generally of extremely low energy experiments. Modifications of surface and bulk conditions (cracks) of the cathode during electrolysis, conditions of preparation of the cathode (metallurgy and pretreatment, size and morphology of the small metal particles when supported on a porous dielectric material etc...) forced diffusion of deuterons through the embedding metal, could provide explanations for the formation of a hot population of deuterons of energy E_d of a few eV.

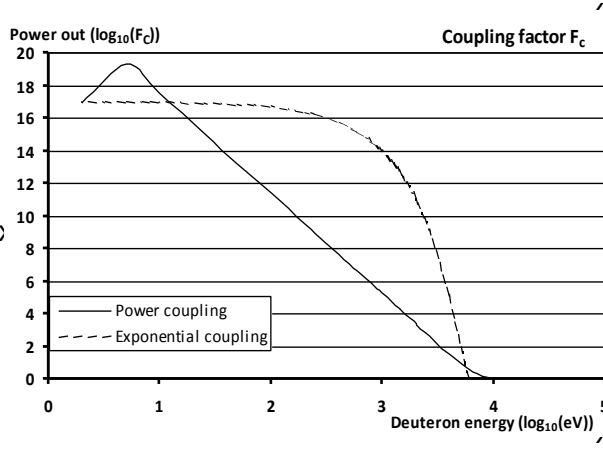


Fig. 3 – Coupling factor F_C .

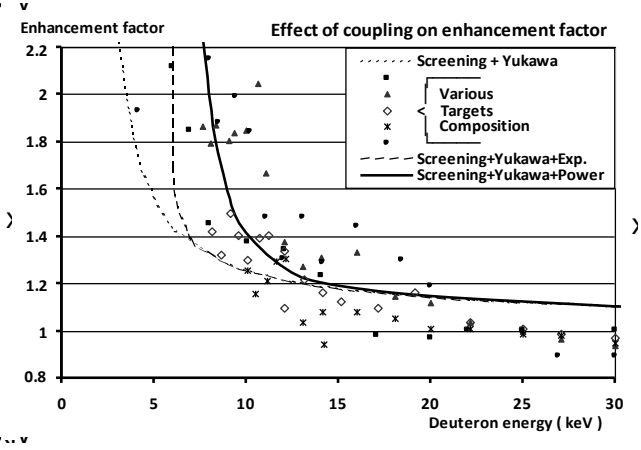


Fig. 4 – Effect of coupling on enhancement factor.

The coupling invoked in [3] could thus be a general phenomenon, extending from extremely low energies (a few eV) to low energies (a few keV) of the deuteron. To define the coefficients of the resonance coupling curve, use is made of the experimental results given by [1] and [2]. In the case of [1], an additional enhancement factor (F_C) of 6 is required for $E_d = 5500$ eV (see Fig. 4). From the experimental results of [2], a reaction rate of 10^{-1} s^{-1} can be inferred. In that case, the energy of the activating deuterons is supposed to be 2 eV. The corresponding calculated (screened) reaction rate $r_{S+Y} = F_{S+Y} r_B$ is $1.3 \cdot 10^{-17}$ [2], requiring for F_C a value $F_C(2) = 8.14 \cdot 10^{16}$, giving $r_{S+Y+C} = F_{S+Y+C} r_B = 0.1 \text{ s}^{-1}$. Two coupling laws have been examined: a power law and an exponential one.

4.3 Determination of the coupling factor F_C as a function of E_d

4.3.1 Power coupling: in that case, $F_C = 1 + \lambda (E_d/E_f)^{\pm n}$, + for $E_d \leq E_f$ and - for $E_d > E_f$

$\lambda (2.24 \cdot 10^{19})$ is determined by the condition $F_C(2) = 8.14 \cdot 10^{16}$ and $n (6.13)$ by the condition $F_C(5500) = 6$.

4.3.2 Exponential coupling: in that case: $F_C = 1 + \lambda' \exp(-n'(|E_d - E_f|/E_f))$

$\lambda' (8.31 \cdot 10^{16})$ is determined by the condition $F_C(2) = 8.14 \cdot 10^{16}$ and $n' (0.034)$ by the condition $F_C(5500) = 6$. The two laws are shown on Fig. 3

5. Effect of the coupling on reaction rates r_{S+Y+C} and power production W_{S+Y+C}

Fig. 5 and 6 give the result of the calculation of r_{S+Y+C} and W_{S+Y+C} , for both coupling laws.

The parameters of both laws have been computed to fit the experimental data at extremely low (2 eV) and low (5500 eV) energy of the deuteron. As can be seen in Fig. 4 the fitting is not very good, for the exponential law at low energy of the deuteron (5500 eV). The power fitting is better (Fig. 4). This could be a consequence of the non thermodynamic equilibrium of the populations of deuterons in the lattice. The objective of the phenomenological model is to infer the behavior of the deuterons in the lattice for all energies E_d , from the 2 extreme and experimentally known situations ($E_d = 2$ eV and 5500 eV). Fig. 5 shows that the reaction rates

r_{S+Y+C} are significantly increased by the power coupling when compared to the “Screened + Yukawa” reaction rates r_{S+Y} . Values as high as 10^5 to 10^{10} s^{-1} are predicted, for E_d between 500 and 1000 eV, whereas in this zone, r_{S+Y} vary from 1 to 10^5 s^{-1} . It is thought that this energy window could be used in a research program, to optimize the target characteristics. From results presented in [1] it can be seen that the enhancement factor varies very much with the target used. These variations are of much bigger amplitudes than the standard deviations presented in [1]. They can be attributed to the exact characteristics of the target used, hence opening the possibility for optimization. This optimization could be done, by using as an optimizing criterion the neutron emission of the studied targets. This emission is predicted to be significantly higher than the background against which the optimization would be done, the calculated r_{S+Y} emission rate. This optimization could result in a very significant increase of the enhancement factor.

Fig. 6 shows that the reaction rates r_{S+Y+C} are considerably increased by the exponential coupling. From Fig. 3, it can be seen that this type of coupling is not representative for energies E_d of the deuteron higher than some 3 keV. It cannot be excluded that with the decrease of the energy, the exponential coupling becomes more and more representative (less departure from thermodynamic equilibrium) and that the true coupling is in between power and exponential for lower values of E_d .

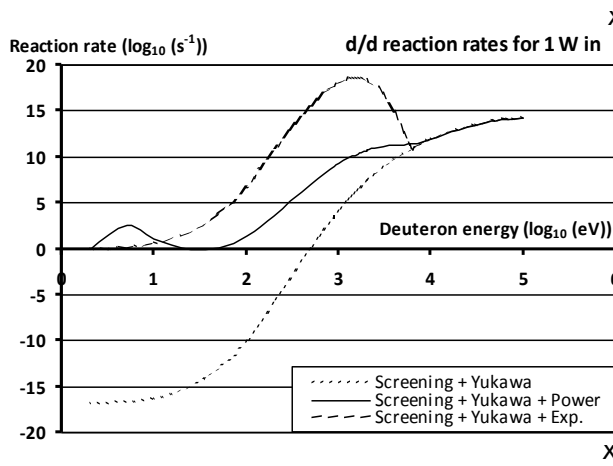


Fig. 5 – d/d reaction rates for 1 W in.

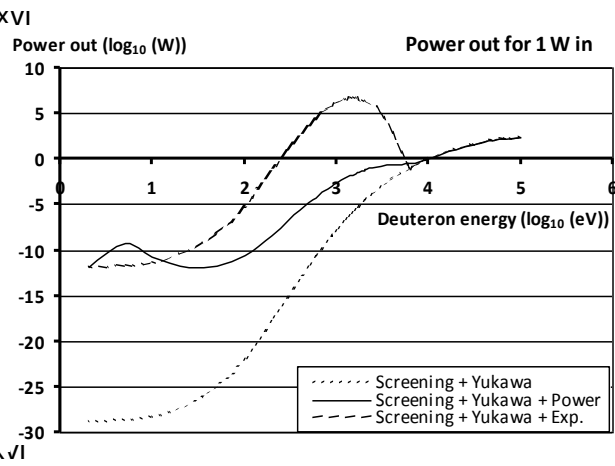


Fig. 6 – Power out for 1 W in.

6. Conclusion

Because of the development of surface treatment and electronic industries, ion generators of several kW power are now available on the market. They can produce ion (proton, deuteron) beams of high intensity (several A), with ion energies in the range 100 to 4000 eV and are thus able to work in the 500 to 1000 eV energy window. Technological devices can be imagined, to generate energy by bombarding appropriate targets with such ion beams.

It is thought that much of the work done in the field (on the cathodes physico-chemical characteristics), could be used to test the possibility of this hypothetical coupling. Such materials could be good candidates as targets for this last approach. A prototype has been built in the lab, using a two steps glow discharge to generate the ions and able to produce currents up to some tens of μA [6]. The energy of the ions is in the order of hundreds eV and the hydrogen (deuterium) pressure at the level of the target is 3 to 4 Pa. A neutron detector (helium 3) monitors the fusion reactions that are expected. Experiments will be run to define precisely the requirements for a lab scale ion generator based on a μwave discharge. Finally, more insight could also be gained on what happens in the extremely low energy region ($<2 \text{ eV}$).

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Role of cluster formation in the LENR process

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Abstract. Presence and absence of expected radiation, occurrence of nuclear reactions having only one apparent product, and transmutation reactions involving addition of more than one deuteron all indicate involvement of large clusters of deuterons in the LENR process. These clusters are proposed to hide their Coulomb barrier and to react with isolated deuterons to produce fusion and to react with larger nuclei to produce transmutation. Members of the cluster not directly involved in the nuclear reaction might be scattered by the released energy, thereby allowing momentum to be conserved and the resulting energy to produce particles having energy too small to be easily detected or to cause easily detectable secondary reactions. Justification of this model is discussed. This proposed model is consistent with most observations, but raises additional questions about the nature of such super-clusters and other ways the energy may be communicated directly to the lattice that will be addressed in future papers.

1. Introduction

Many attempts have been published in an attempt to explain how fusion and transmutation are possible at or near ambient conditions in solid materials. A successful theory must show how the Coulomb barrier is lowered and how the resulting energy is dissipated into the environment. This dissipation process can be imagined to take two forms: emission of energetic radiation or dissipation of energy directly into the environment. If radiation carries the energy, the amount detected should be consistent with the amount of heat produced. Some radiation has been detected but not enough to account for the energy being generated as heat. Consequently, either several processes dissipate the energy or most emitted radiation is absorbed before it reaches the detector. In addition, the energy of emitted particles must be too low to produce secondary reactions that should be easy to detect. This paper will explore one possible mechanism for production of energetic particles fitting these requirements.

The cold fusion process can release a large amount of energy from very energetic nuclear reactions. This aspect of the phenomenon has been demonstrated by too many studies, as reviewed by Storms,[1] to cite here and needs to be accepted as an important characteristic of cold fusion. Conventional nuclear reactions release energy either promptly as radiation, consisting of energetic particles and/or gamma emission, or slowly as radioactive decay. The only known example of direct coupling of nuclear energy to an atomic lattice is the Mossbauer Effect. However, the energy involved in this process is much smaller than that produced by the nuclear reactions associated with cold fusion, which makes this mechanism hard to relate to the cold fusion process. If radiation has sufficient energy, secondary reactions will be detected, which can reveal more information about the process. Absence of such secondary radiation limits the possible energy of the primary energetic particle. Nevertheless, a variety of particle and X-ray energies are reported, which demonstrate that not all energy is being directly deposited in the lattice. In addition, a model must explain the observed complex collection of emission energies and types of detected radiation.

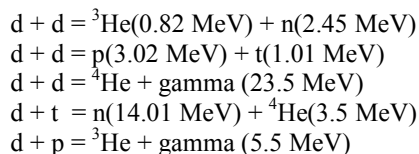
Most models focus on the periodic structure that exists in solid PdD as being the location of the nuclear active environment (NAE). In contrast, this proposal draws attention to the surface of nanoparticles where large clusters of deuterium are thought to form. These clusters are proposed to be involved in the initiation of the fusion and transmutation reactions as well as allowing at least some energy to be released into the environment as energetic particles without producing easily detectable radiation. Logic requires the clusters to contain many more deuterons than has been considered in the past, so called super-clusters.

Although the cluster concept is not new, the full extent of their involvement, their proposed large size, and the location of their formation have not been published before. This paper shows the logical connection between this concept and observed behavior.

2. Discussion

Table 1 summarizes some of the possible fusion reactions. In each case, two products are formed and observed to result when high energy is applied. Two products allow momentum to be conserved while depositing the energy into the environment. If only one product is observed, a different type of reaction must be proposed to achieve the same result.

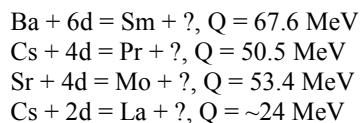
Table 1. Reactions resulting from fusion involving deuterons.



For example, many studies have shown that helium results when extra heat is produced.¹ Because the expected gamma of 23.5 MeV is absent, the reaction cannot occur as written in Table 1. A more complex process must take place. Takahashi[2, 3] proposed that four deuterons came together as a cluster to form two helium nuclei each of which carry away 23.8 MeV and the necessary momentum. Such a reaction conflicts with the absence of significant neutron radiation resulting from the well-known (α , n) reaction, mainly involving lithium, that such high-energy alpha will initiate. Consequently, a small cluster, the members of which completely fuse, is not consistent with observation, even if a plausible process, such as formation of a Bose-Einstein Condensate [4], could create the cluster. While many models have been proposed to avoid some of these issues, each has limitations that encourage a new approach.

Creation of isotopes and elements not present in the initial environment by addition of deuterons to the nucleus of certain elements has been frequently reported.[1] While some elements or isotopes might have been present as contamination, this argument has not been applied successfully to all the observed reactions. Two studies stand out in showing the role of clusters in such transmutation reactions. For the first, Iwamura et al. [5-9] in a series of papers claimed to detect the reactions shown in Table 2. Clusters containing as many as 6 deuterons are required to enter the nucleus as a unit. However, a problem remains to explain how the significant energy released by the process is communicated to the environment. Clearly, something must be emitted that is not detected, as indicated by the question mark.

Table 2. Observed transmutation reactions reported by Iwamura et al.



The second study involves the work of Miley et al.[10, 11]. His results, based on use of SIMS, AES, EDX and NAA for analysis, is summarized in Fig. 1². The work is based on the use of thin films of nickel and/or palladium with a small amount of platinum as an impurity from the anode and perhaps a little sulfur as an impurity from the electrolyte, which contained Li_2SO_4 in H_2O . Elemental analysis was made before and after electrolytic action. The general pattern shows the following: regions of atoms having high concentration are found from about mass 106 (Pd) to mass 130; from mass 195 (Pt) to mass 210; and from about mass 25 (S?) to mass 32. The region around nickel (58) shows elements on both the high mass and

¹ This work has been previously evaluated1. Storms, E.K., *The science of low energy nuclear reaction*. 2007, Singapore: World Scientific. 312. and is too extensive to cite here.

² Although of poor quality, this is the only representation of the summary that is available.

the low mass sides. The question is, “What process can explain these general observations”? Transmutation requires a target nucleus to which something is added. The possible addition of neutrons, protons or deuterons to Pd is explored next.

Figure 2 shows the position of the stable isotopes near palladium with respect to their atomic number and atomic weight. If neutrons are added to palladium, the resulting isotopes would follow a horizontal line on the figure and eventually produce beta emitters. These have half-lives that decrease from minutes to milliseconds as more neutrons are added. To produce the observed elements near the upper limit of the Miley data, a series of decays from parent to daughter would have to take place over a significant length of time as each isotope decayed to another radioactive isotope with gradually increasing atomic number. In addition, the radioactivity is not detected even though this would be an easy measurement. Therefore, transmutation does not result from neutron addition from any source. If protons were added to palladium, the resulting isotopes would follow a line parallel to the one shown on the figure for protons.

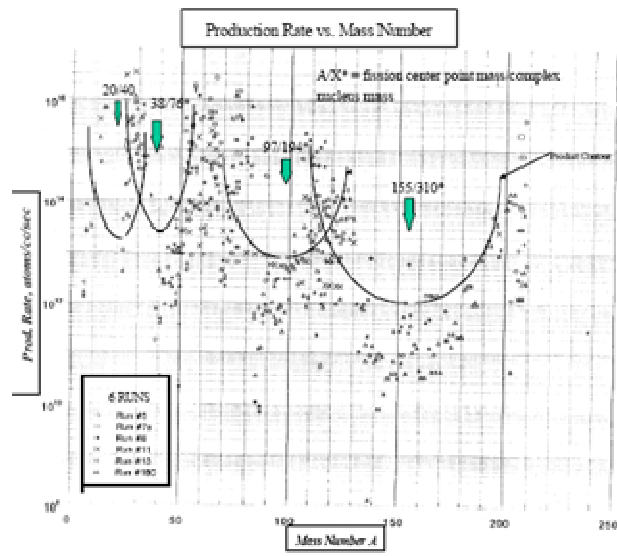


Fig. 1 - Log rate of production vs mass number of elements produced in thin films by electrolysis in $\text{H}_2\text{O} + \text{Li}_2\text{SO}_4$.

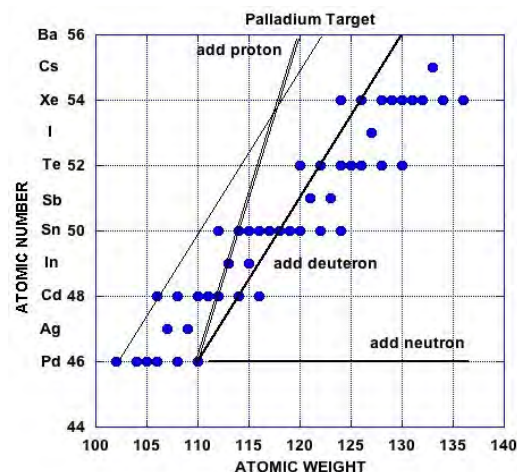


Fig. 2 - Stable elements as a function of atomic weight and atomic number near palladium.

Radioactive isotopes are produced above mass 114, which is not high enough to explain the full range of reported data. Only addition of deuterons results in the full range of observed stable isotopes. This same process can be applied to nickel, platinum and sulfur to give the same conclusion in spite of normal water being in the electrolyte. Apparently, deuterons, regardless of their concentration, produce active clusters

and most transmutation. In the case of elements having a mass lower than nickel, these cannot result from a reaction with deuterons or any other particle. These elements might result from fission of nuclei after addition of deuterons to palladium, as has been suggested by several authors. Because the resulting nuclei are at and near iron, additional energy can be released by formation of these very stable nuclei. Consequently, a certain fraction of nuclei resulting from addition of deuterons to Pd split into two parts during the transmutation process and may account for the frequent reported presence of iron on the palladium cathode of electrolytic cells. These two studies, as well as many others, suggest a role for clusters containing at least 8 deuterons in the transmutation process. Where are these clusters formed?

The only universal feature found in all successful cold fusion experiments are nanoparticles. These form slowly on the surface of electrolytic cathodes, they form as a result of gas discharge, and they are known to be active when certain such materials are exposed to deuterium gas.[12, 13] Consequently, a feature associated with such a structure can be assumed to initiate all of the observed cold fusion reactions.

The difficulty in producing cold fusion indicates a special condition is required before the nuclear reaction can occur, presumably after nanoparticles are formed. This special condition is hard to create, occurs only in small and variable amounts, and presently is produced largely by accidental conditions within the apparatus. Where is this special condition located?

McKubre et al. used the following equation to describe excess power (EP) obtained from wire cathodes in a Fleischmann-Pons cell. [14, 15]

$$EP = M(x-x_0)^2(i-i_0)\delta x/\delta t, \text{ where } x_0=\text{critical average D/Pd of the bulk cathode, } i_0=\text{critical average I/cm}^2$$

We can expand this equation by adding the equation:

$$M = n * [nae], \text{ where } [nae] \text{ is the amount of NAE having 'n' efficiency.}$$

Consequently, the heat producing reaction favors locations where the deuterium concentration is greatest. This location exists at the surface of the cathode in an electrolytic cell and on the surface of nanoparticles.[16-18] The deuterium concentration becomes especially great on the surface of a cathode as the bulk composition approaches unity and on the surface of nanoparticles as they become smaller. This analysis reveals the bulk composition is only important because it affects the surface composition where the nuclear reactions actually occur.

3. Conclusion

The goal of this paper is to show a logical connection between selected observations and a proposed mechanism involving energetic particle emission and super-clusters without describing exactly how the mechanism works. In addition, the proposed mechanism is not likely to be the only one operating. The nature of the proposed super-cluster and its manner of formation will be subjects of future papers.

A mechanism must dispose of energy resulting from a nuclear reaction in a manner consistent with observation and known laws of nature. The same mechanism is expected to operate regardless of the energy source, whether it is fusion or transmutation. The absence of detectable gamma radiation when helium is produced means the energy is either being directly absorbed by the lattice[19-21] or particles are being emitted by an unconventional process and these are absorbed before most can reach a detector. The fact that some particles do reach a detector[22-24] puts greater emphasis on the role of energetic particles and the need to find the unusual mechanism for their creation. Indeed, the nature of these particles and the mechanism of their formation is the unique challenge facing any theory of cold fusion. One solution to this challenge involves clusters, but in a way that has not been suggested before.

Clusters of deuterons are clearly involved in transmutation reactions. Apparently, a variety of new elements are made based on the number of deuterons in an active clusters and availability of suitable targets. Various rules must determine how many d can enter at the same time to avoid producing radioactive products, which are rarely found. We next assume the same mechanism is operating to cause fusion between deuterons.

The fusion rate will depend on the number of active clusters and the concentration of deuteron targets. Consequently, the fusion rate will be more sensitive to the deuterium concentration than is transmutation. Because clusters are made from deuterium and form where the deuterium concentration is

greatest, fusion as expected to occur close to where clusters form. Transmutation, on the other hand, is expected to occur at a distance from the site of cluster formation, as has been observed.

For any nuclear reaction to occur, the clusters must hide their nuclear charge. Fusion would require less reduction in charge than does transmutation, hence would involve smaller³ hence more numerous clusters. However, the charge-hiding process requires a critical number of deuterons to be in a cluster before it becomes active. Even though small clusters are more numerous, they are not able to initiate a nuclear reaction until a critical number of deuterons are combined. This charge-reduction process is an essential feature of this model, but will not be addressed here.

Once a cluster reacts to produce a nuclear reaction, energy is dissipated. While this process might involve direct coupling of some energy to the atomic lattice, this paper focuses only on a method for particle production. If the cluster contains more deuterons than actually enter the nucleus during transmutation or are involved in the fusion reaction, these extra deuterons are proposed to dissipate the energy as energetic deuterons. However, the energy of these particles must be low enough not to produce secondary reactions, such as fusion with other deuterons the emitted deuterons might encounter. Consequently, the majority of clusters involved in the fusion reaction would need to contain nearly 50 deuterons and even more when transmutation occurs if all energy is dissipated this way. However, active clusters would not all have the same size, resulting in a spectrum of sizes. The complex variety of observed particle energies would result from clusters of various sizes being involved in a nuclear reaction. For example, Karabut et al.[25] detected a spectrum of individual peaks corresponding to energies from about 1 MeV to 18.5 MeV that they identified as alpha emission. This emission occurred immediately after glow discharge in D₂. This observation is similar to the radiation spectrum of individual peaks reported by Storms and Scanlan[26] during glow discharge that they attributed to deuterons. This behavior can be explained by energy being shared between a different number of deuterons. Smaller, less abundant clusters would produce a few very energetic emissions that could produce secondary radiation. This rare energetic primary radiation might be detected occasionally as periodic but low intensity secondary neutron emission. Meanwhile, most deuterons would have energy too low to be easily detected and too low to produce secondary reactions. While the large cluster size required by this logic seems implausible, the proposed process should be explored, perhaps in relationship to other dissipation processes.

These clusters of deuterons are proposed to form by an exothermic reaction requiring a catalyst or template. Once formed, an active cluster is small enough, thanks to its unusual structure, to diffuse through the PdD lattice and react with targets of opportunity. This catalyst is rare so that cold fusion occurs infrequently only when and near where this catalyst is present. This rarity results because the catalyst is proposed to be a complex combination of certain atoms that seldom combine in the required formation. Several different combinations of several different elements are probably active, all in the form of nanoparticles. Consequently, the NAE is located on the surface of nanoparticles that are formed on a surface or present after having been placed in the apparatus fully formed. Naturally, not all such particles will be active. As a result, the amount of power produced by a cell will be highly variable, as is observed. The challenge is to identify the nature of the active nanoparticle and to make these in large amounts. Only then can the effect be made reproducible and a source of significant power.

Depending on their size, these clusters react with deuterons where the deuterium concentration is highest to produce d-d fusion and with other atoms to generate transmutation products at a lesser rate. The environment in which this occurs is very inhomogeneous and complex, resulting in a wide variation in reaction rates including no detectable rate. The process can be detected by measuring short-range particle emission, low-energy X-rays, He⁴, and extra heat. Tritium may be produced by clusters having a critical number of deuterons, hence is a rare product.

The proposed model is still very incomplete and ignores many observations. Nevertheless, the logic suggests a new way to look at the problem that might be helpful in the development of more complete models. While many questions remain, the approach has many ways it can be tested and suggests how the cold fusion effect might be increased.

³ Smaller means fewer deuterons. The actual dimension is proposed to become smaller as the number of deuterons increases in a cluster as a result of an increased number of bonding states.

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Tunneling beneath the ${}^4\text{He}^*$ fragmentation energy

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Abstract. The repulsive Coulomb barrier between deuterium nuclei is reduced in length and height by a catalytic mechanism involving optical phonons and electric fields in a lattice. If the mechanism induces the formation of $\text{D}^- \text{D}^+$ pairs, the tightly-bound and energetic electron pair (in the D^- ion) becomes a binding force between the nuclei. The lattice constraints and **slow** collision processes, force the ions into a near 1-D configuration that deepens the electron ground-state potential well. This permits the electron pair to remain closely bound to one deuteron and to do work in bringing the $\text{D}^- \text{D}^+$ pair together. These tightly-bound electrons may remain as a pair, attached to a single deuteron, during the fusion process. In reducing the Coulomb repulsion of the nuclear protons, these electrons bring down the total energy of the fusing $\text{D}^- \text{D}^+$ pair and raise the fragmentation energy level. This process accounts for the observations in CMNS of excess heat (in both p-p and d-d reactions) and for the differing observations (or their absence) of tritium, ${}^3\text{He}$, neutrons, and ${}^4\text{He}$ in the d-d reaction. Thus, all major observed CMNS processes are explained.

1. Introduction

At ICCF-14, we presented the means whereby the repulsive Coulomb barrier between hydrogen (deuterium) nuclei is reduced in length, perhaps by orders of magnitude [1]. This mechanism, involving optical phonons and electric fields (internally or externally generated) in a lattice that induce the formation of $\text{D}^- \text{D}^+$ pairs, increases the tunneling probability by more than 100 orders of magnitude [2]. It has additional major consequences described below.

In brief: the lattice constraints and collision processes force the interstitial deuterium ions into a temporary, but cyclic, nearly one-dimensional (1-D) configuration that greatly deepens the D-D and electron ground-state potential well. The proposed tightly-bound and energetic-electron pair (a local-charged Boson - the lochon) results in sub-lattice $\text{D}^- \text{D}^+$ pairs and becomes more than strong screening; it becomes a binding force between the nuclei [3]. Thus, the Coulomb-barrier height is reduced as well as its length. With this greatly enhanced barrier-penetration probability, the energy level of nuclei with reasonable tunneling probability drops from the multi-100 keV range down into the eV range.

In this earlier version of our model (only concerned with the barrier-penetration problem), normal tunneling is into resonant states above the fragmentation levels [4]. Thus, even if the Coulomb barrier is overcome by the tightly-bound electron pair and fusion is possible, the major observations of LENR (e.g. more heat than neutrons) are not accounted for. This requirement of tunneling into states above fragmentation is dictated by the mass deficit [5] between the two colliding D atoms and the resultant ${}^4\text{He}$ atom ($2\text{D} - {}^4\text{He} = Q = 23.8 \text{ MeV}$). Therefore, even with zero incident energy, a deuteron pair will have too much energy to tunnel beneath the fragmentation levels at 20.6 and 19.8 MeV above the ${}^4\text{He}$ ground state. Nevertheless, the model was successful in providing a mechanism to overcome a major argument against LENR. The present work shows how its extension also explains most of the experimental results observed in the field.

2. Extended Lochon Model

In a more detailed study of the model, new and unexpected effects are found. Just as slow-motion photography can reveal unsuspected processes, low-energy collisions (i. e., eV compared to MeV) have

provided some surprises. It is the non-equilibrium conditions of a “slow” $D^- D^+$ collision in a linear sub-lattice that provides an answer to the “nuclear ash” problem of CMNS. The deuteron motion is slow; but, the bound-electron motion is not. This distinction allows us to separate the actions and use the Born-Oppenheimer approximation [6] (common in quantum chemistry) to solve for the electron quasi-steady-state parameters, step-by-step, as the $D^- D^+$ pair approach each other over the PdD lattice barrier separating them.

As the nuclear potential well deepens while a D_2 molecule is being confined to 2 dimensions, so does the electron potential well. A deepening of the electron potential wells does not necessarily mean that the electrons go deeper into the well; they must lose total energy to do that (although they gain kinetic energy as they move into the well, they lose it again on the way back out). However, being in a ground state ($l = 0$), they cannot directly radiate photons or induce phonon excitation. Nevertheless, in a critical concept provided online by Tom Barnard, a mechanism is provided whereby they may dissipate energy as the separation of the electron and $D^- D^+$ pairs is reduced. Since work is done by the electrons during this motion (they transfer energy to the deuterons), they fall deeper into the deuteron’s Coulomb potential well. Being deeper in the well means that neither of the paired electrons is likely to transfer to the potential well of the other deuteron during this process. **This is a critical assumption of the model.**ⁱ Since this electron pairing is a possible state, quantum mechanics can calculate the probability of a 2-electron deuterium sub-lattice state relative to that of zero or single-electron occupancy. However, the probability depends on the energy of the electron pair and the local Fermi levels, and those depend on the recent history of the $D^- D^+$ pair.

Collisions in nuclear physics experiments are so fast that, except for the electrons directly involved, equilibrium electron-energy levels do not have time to change before the event is over. On the other hand, during the critical portion of the $D^- D^+$ interaction in a lattice, the “slow” motion of the converging deuterons allows the electrons to orbit hundreds of time during each increment of deuteron closing and therefore allows the electrons to experience and respond to the changing fields - and to do work. As the electrons move deeper into the D^- Coulomb potential well, the cancellation of electric fields (electron and proton) reduces the total field energy (potential energy) and therefore (initially very slightly) the mass of the particles. Since energy is conserved, part of this loss in field energy goes into the increased kinetic energy of the electrons (T_e), part into the increased kinetic energy of the deuterons (T_d), and part into increasing the e-e and d-d electric field strengths as the like-charge particles move closer together. (Just as the electrons do work in bringing the deuterons together, the deuterons and electrons have work done on them to move them closer together.) The net result of this 4-body interaction is that the paired, tightly-bound, energetic, electrons (e^*) remain at nearly constant total energy (more KE and deeper in Coulomb well), the D^+ gains some total energy, and the D^- loses total energy.

As the colliding deuterons move still closer together (and climb the barrier between the deuteron sites), the screening from the lattice electrons and the residual barrier between the deuterons becomes smaller. The $D^- D^+$ Coulomb potential grows and the collapse of the $D^- D^+$ pair is accelerated. However, the energy expended in overcoming the lattice barrier keeps the $D^- D^+$ pair moving slowly until the pair gets very close (~ 1 picometer). As the pair gets even closer together, the $D^- D^+$ potential dominates the lattice barrier and the closing velocity increases.

The electron’s kinetic-energy increase and its movement deeper into the Coulomb well about the deuteron causes the electron orbit to “shrink.” Its deBroglie wavelength decreases with increased velocity and, as it spirals in, its field energy is further “cancelled” and concentrated by that of the proton (within the deuteron). With an increase in energy from the $T_e = 10$ eV range of the electron in the “free” deuterium atoms to a 1 keV of a bound electron as it approaches the deuteron, the deBroglie wavelength is reduced by an order of magnitude. As the energy of this “shrinking-orbit” electron, e^* , increases to the 100 keV range, its wavelength drops by 10x again and approaches that of an electron’s Compton wavelength. However, by this time, the electron field (and therefore the electron center of “mass”) has shifted to within 10s of Fermi of the nucleus. The e^* may no longer be a separate entity. The e^* -proton pair has become a relativistic rotating dipole field (quadrupole field, if two bound electrons are present). The cancelled charge-field energy has been transformed to electromagnetic and relativistic-mass energy.

ⁱ The existence of $D^- D^+$ pairs in a lattice is accepted physics ([2] and references therein). Their existence in a PdD lattice must still be verified.

3. Nuclear Interactions

The reduced Coulomb repulsion between the protons (resulting from the shrunken e^* or lochon orbits) increases the total nuclear attraction between them relative to that of normal ${}^4\text{He}$. Thus, the nucleons spend more time closer together and therefore more time in the nuclear-potential well. This increases the effective “depth” of the well and decreases the energy of the excited states of the ${}^2\text{He}^*$ or ${}^4\text{He}^*$ structures formed. There are other reasons why the nucleus might shrink even further. Both the closer binding of the nucleons and the deeper potential well reduces the probability of fragmentation.

Examining the traditional D-D to ${}^4\text{He}^*$ transition (Fig. 1), we see the broad transition region > 23.8 MeV above the ${}^4\text{He}$ ground state. This is the energy difference that corresponds to the mass difference between the deuterium pair and ${}^4\text{He}$. Even with tunneling from zero kinetic energy states (i.e., $E_k = 0$), the excess mass of the deuterium atoms would put the deuterons into this high level. This excited ${}^4\text{He}^*$ state is above the fragmentation levels at ~ 20.6 and ~ 19.8 MeV. While fragments from both levels have been observed in LENR experiments, the radiation levels are not nearly high enough to explain the excess heat observed. Furthermore, the levels of ${}^4\text{He}$ measured have been orders of magnitude higher than would be expected and, in some cases, have been high enough to account for the observed heat. How does this happen? Conventional physics sees the overcoming of the Coulomb barrier at low temperatures/energies, the distortion of the normal fragmentation ratio ($p:n = 50:50$ from $E > 22$ MeV), the high levels of ${}^4\text{He}$, and, more recently, transmutation of elements as reasons for considering the Cold Fusion results as impossible.

Since the observed data is not possible within the known framework of nuclear physics, something else must be going on. We have shown how the Coulomb barrier problem is solved and laid a foundation for the D-D nuclear interaction with the help of tightly-bound, high-kinetic-energy electrons. Now we put the parts together.

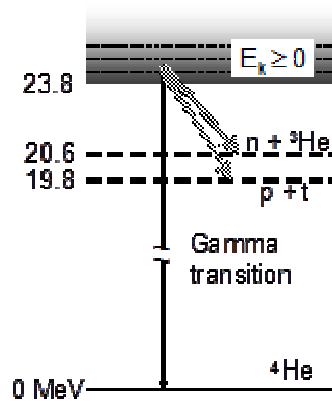


Fig. 1 - Energy levels and decay branches associated with conventional D-D to ${}^4\text{He}^*$ fusion reactions.

4. Reduced Energy ${}^4\text{He}^*$

With the ability of deuterons to tunnel from an appropriate PdD lattice site through the nuclear Coulomb barrier of an adjacent **reduced-energy** ($E_t = T + V$) nucleus of a D^+ ion, the possibility of a low-energy excited compound nuclei becomes real. If, with the lochon, the excited (but neutralized) helium-4 nucleus does not have sufficient energy to fragment, and gamma decay is highly forbidden, how does it shed the excess energy to get to its ground state? It is proposed that this condition and the subsequent decay process is the basis for the experimental observations of CMNS.

To see how this “new” process can occur, we must take a closer look at Fig. 1. There are no energy levels below the ${}^3\text{H} + p$ (or $t + p$) fragmentation level. In a d-d interaction, if fusion were to take place, it would be resonance tunneling into one of the many levels above the region at 23.8 MeV. Decay from these excited states would almost always give nearly equal probabilities of fragmenting into the p or n channels. If a state existed below ~ 20 (or 19) MeV, then n (and p)-channel fragmentation would become unlikely. Unsuccessful attempts have been made specifically to find such an excited state. We propose a non-fragmentation mechanism that does not rely on a new state below 19.8 MeV. It shifts some of the existing states down below that level and it demonstrates how the fragmentation levels are shifted up in energy.

The key to the mechanism is the lochon, which during the collision process attains significant energy (keV to MeV range); but, remaining in an $l = 0$ ground state, it does not radiate. If it survives the final tunneling process of the d^+ through the thin, residual, D^- Coulomb barrier, it may have attained multiple MeV energies from the work done at the expense of the D^- Coulomb potential energy. Thus, it is very-tightly and closely bound and both the lochon and the D^- nucleus have lost electric-field mass. Since the lochon mass and orbital radius is now so small, even in a circular orbit, the orbital angular momentum is less than $\hbar/2$. Therefore, there is little possibility of photonic radiation.

5. The new ${}^4\text{He}^*$

Once the D^+ is inside the D^- nuclear-Coulomb barrier, the situation is different from that of the normal d-d scattering problem. The nuclear potential is greatly different, because the Coulomb barrier between the protons is much reduced. Thus, they can be much closer together. Since most of the normal nucleon wavefunction is outside the d-d nuclear well, the depth of the nuclear potential well with which the nucleons are bound is increased by both the loss of Coulomb repulsion and the gain in nucleon time spent in the well (increased wavefunction overlap). As a consequence, the effective depth of the nuclear well is increased; the excited nuclear-state energies become lower; and the energy required to break apart (fragment) the excited nucleus is higher.

If the new ${}^4\text{He}^*$ energy, is too low to fragment and it has an e^* or two spending much of their time inside the nuclear region, it cannot form a stable nuclear state (even if one existed in the normal ${}^4\text{He}^*$ nucleus). The continual and extreme proximity of the highly-excited deuterons to these electrons (in the femtometer range) allows resonance transfer of energy between them, via near-field EM coupling, at a frequency associated with, or below that of, soft x-rays. Thus, the nuclear energy is able to be transferred to the shrunken-orbital electron(s) and from there it is radiatively transferred to the lattice, since the e^* is also close-coupled (in the nanometer range) to the bound Pd electrons. If the average radiated x-ray energy is in the keV range, it takes little time for most of the nuclear energy to be dissipated. However, as decay progresses, the rate of energy transfer and dissipation decreases, giving more time for the electron(s) to be ejected from the nuclear region ($e^* \Rightarrow e^-$) with the remaining energy. Since e^* is deep in the nuclear Coulomb potential this ejection is not as an energetic electron, but as a gradually slowing (and expanding-orbit) electron being driven out of the well by energy from the proton-generated EM field.

This extended fusion / radiation process lasts:

- a) until the neutral entity (${}^2\text{He}^*$ or ${}^4\text{He}^*$) drifts into a neighboring nucleus, resulting in a transmutation process;
- b) until one (or more) of the energetic shrunken electrons combines with a proton ($p + e^* \Rightarrow n + \nu$, via the $p-e^*-p$, $p-2e^*-p$, $d-e^*-d$, or $d-2e^*-d$ reaction); or,
- c) until diproton fragmentation or the ${}^4\text{He}$ ground state is reached, on ejection of the electron(s).

6. Conclusion

Depending on the actual energy of the excited (compound) nuclei and the number of e^* still present (0, 1, or 2) after the nuclear Coulomb barrier has been penetrated, the decay process could include fragmentation, or not. This accounts for the observations in CMNS of excess heat, in both p-p and d-d reactions, and the observations (or absence) of tritium, ${}^3\text{He}$, neutrons, and ${}^4\text{He}$ in the d-d reaction. The ability of the lochon to alter the nuclear potential well and fragmentation energies permits radiation-free decay to the ${}^2\text{H}$ or the ${}^4\text{He}$ ground state and transmutation. This variation (apparent unpredictability) of results, heretofore the stumbling block to acceptability of LENR, is now perhaps the greatest validation of its existence. Thus, all major observed CMNS processes are explained, but not necessarily the best means of, or materials for, producing them. That comes next.

Acknowledgments

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Bose-Einstein type D-cluster Electrode Development

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Abstract. Our recent research has developed a technique for imbedding ultra high density deuterium “clusters” (D cluster) in Palladium (Pd) thin film. Experiments have shown that in Pd these condensed matter state clusters approach metallic conditions, exhibiting super conducting properties. Using Temperature Programmed Desorption TPD system, the local concentration of hydrogen in the dislocation core is found to be $[H]/[Pd] \sim 1.8$. At near 70 °K Pd foil with abundant D clusters also show class II superconductivity, indicating the trapped hydrogen condensed into a metallic-like phase. Room temperature cluster formation is found to be adequate for the desired “nuclear reactive” sites. By careful calculation and experimentation, it is found the D cluster has a Bose Einstein Condensation state when a high deuteron diffusion flux is triggered. The resulting momentum transfer initiates reactions. The trigger can be electrochemical, giving LENR reactions. Thus this configuration can provide a small LENR power cell. Currently, we are searching for new methods to improve the volume density of dislocations. These methods mainly involve modifying Pd thin film with multi-layer structure.

1. Introduction

Recent SQUID measurement has shown ultra-dense states of deuterons with many more than 100 deuterons within a crystal defect in a palladium crystal are possible, and a superconductive state of these clusters was demonstrated in these experiments [1, 2]. Similar ultra-dense state of deuterons was seen at surface defects of iron oxide resulted in ion energies of 630 eV through Mass spectrometry measurements [3]. It may well be assumed that both cluster states are of the same nature though the states are concentrated at the surface in the iron oxide case due to the catalytic generation in contrast to the Pd samples with localization in the bulk volume [2]. In both cases their existence was confirmed by the LENR process [4] which likewise should be valid including when an inverted Rydberg state is present. Based on the excess heat measurements, local power densities exceeding a kW/cc are possible, promising very high energy density power units. Since the radiations emitted (protons, alphas, and x-rays) are not very penetrating (do not escape the cell structure) and no long lived radioactive reaction products are observed, LENR power units would be a remarkable “~~gen~~” nuclear technology.

2. Earlier work on LENR at University of Illinois

There are a wide variety of fusion nuclear reactions. As illustrated in Figure 1, the original Pons-Fleishmann (P-F) reaction involved DD Fusion. But, instead of the normal reaction where the channel passes through deactivation of the He4 by transferring energy to the lattice which ultimately appears as heat, a number of researchers have reported transmutation reactions that involve interaction between deuterium/hydrogen and atoms in the host lattice, typically heavy metals. This branch is commonly termed Low Energy Nuclear Reactions (LENRs), although recently there has been a move to include DD reactions as LENRs as well. In this review we concentrate on host atom reactions.

<u>D-D Reactions</u>		
		% branching
	<i>hot fusion</i>	<i>“P-F” type</i>
$D-D \rightarrow T + p$	50	< 0.1
$D-D \rightarrow He-3 + n$	50	< 10^{-6}
$D-D \rightarrow He-4 + \gamma$	< 10^{-5}	99+
<u>LENRs</u>		
$p + metal \rightarrow \text{products or “fission” product array}$		

Fig. 1 - Comparison LENR reactions and the DD reactions.

Transmutation reactions can be broadly classified according to their products. Some experiments have observed a large array of reaction products with mass numbers ranging across the periodic table. These reactions are traced to multi-body events leading to a heavy compound nucleus, which can both decay, and fission into an array of elements [5]. The other set of experiments lead to one or few distinct isolated products [6]. These reactions may or may not involve multi-bodies but the net result is direct formation of the reaction products as opposed to the disintegration of a compound nucleus. Earlier works on transmutation reactions involved thin films on microspheres, while our recent studies at the U of I have converted it to thin films coated on a flat alumina substrate as illustrated conceptually in Figure 2. In this design, a double-layer Pd/Ni thin film, at 8000 Å and 1000 Å respectively, sputtered on ceramic Al₂O₃ substrate at rate 0.41 Å, was used as a cathode. The electrical current flow is parallel to the thin film surface so that a high current density and high proton flow rate are obtained along with a high deuterium density [7].

The possible heat evolution during electrolysis runs was detected by a high sensitivity open-type calorimeter in a fixed temperature of 28.0 ± 0.05 °C. [8] To check actual performance during Foreground electrolysis runs (with Alumina/Pd-Ni samples), including heat convection, bubbling, electrode's geometry, and positioning, as well as H₂+O₂ recombination, smooth Pt sheets were used as cathodes in Reference runs, since Pt does not produce excess heat in the light water electrolysis [9]. The performance of this runs at various current (50 ~ 600 mA) is defined by the calorimeter “heat recovery” value $R = P_{th}/I(U-U_0)$, where, P_{th} is the thermal power measured in calorimeter by thermistors; $I(U-U_0)$ is Joule heating P^* , in which I and U are the electrolysis current and voltage, respectively; U_0 is an effective water dissociation potential (WDP) (2.01 V for Pt/Pt pair and 2.06 V for Pd-Ni/Pt pair) [10]. A constant electrolysis current ranging from $I = 100 \sim 600$ mA ($j = 8.5 \sim 50.0$ mA/cm²) corresponding to a cell voltage U 3.5 ~ 5.5 V were applied to Alumina/Pd-Ni cathodes Typical kinetics of the heat measurement (P_{th} vs. elapsed time t) are presented in Fig. 3.

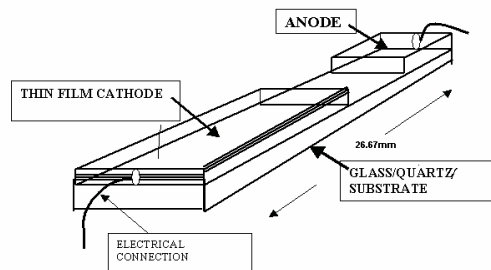


Fig. 2 - Recent Work Uses a Unique Integrated Thin film Plate-Type Electrode.

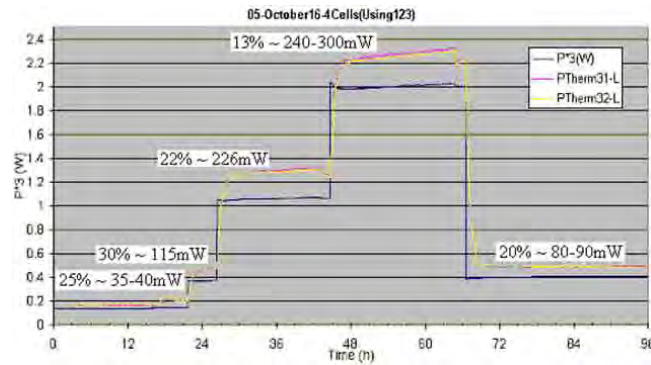


Fig. 3 - Heat measurement for two layers electrode: 8000Å Pd and 1000Å Ni on Alumina. Correlation between Transmutation Products and Excess Heat

As seen, shortly after stating the run, the thermal yield P_{th} exceeds Joule heating P^* . The current was run in “jumps” purposely to examine changes as a function of input power. The maximal heat recovery R of 135 % occurs at electrolysis current $I=100$ mA ($j = 8.0$ mA/cm²), while the corresponding absolute value of excess heat production is $W_{ex} = 60 \pm 28$ mW. Increasing the current density to 48 mA/cm² leads to decrease in heat recovery R from 135 to 115 %. In typical cases the excesses heat evolution from the cathode at $I = 200$ mA continues for ~ 15 days. The decrease in R during a long Foreground run is accompanied by an increase in cell voltage. The last process indicates an increase in the cell inner resistance due to defects and micro-cracks generation in Pd/Ni cathode. The cathode samples survive, i.e. they do not detach the Alumina substrate during these long runs. Thermistor calibration runs repeated immediately after this Foreground run show that calorimeter parameters, (including temperature change vs. input power) did not change during the time of operation with Alumina/Pd-Ni sample (15 days). This gives a proof of stability of the calorimetry system and indicates that our measurements of excess heat production were actually correct.

Although good progress has been made on direct correlating He-4 production and excess heat, supporting the D-D reaction hypothesis, the correlation between the transmutation and excess heat production, as well as the product measurements, still leave open a fairly large error band. Earlier, we have observed a variety of reaction products (isotopes) with masses both higher and lower than that of the host electrode material in thin film electrodes, [11][12][13], suggesting the existence of proton-metal initiated reactions in such LENR cells. Later, we discussed evidence that the production of these reaction products is correlated with the excess heat described above [14]. Such a correlation for LENR reactions would be equivalent, in principle, to the correlation of He-4 with excess heat that is reported for heavy water-Pd experiments where a D-D reaction is postulated.

A characteristic result, shown in Fig. 4, indicates that a variety of reaction products occur with masses lying well below and above that of the base electrode metal (Ni and Pd in Fig. 4, of cf. numbers defined in the references). A striking pattern consistently observed in these measurements is that the high-yield reaction products occur in four mass ranges, roughly $A = 20-30$, $50-80$, $110-130$, and $190-210$ [12] [13]. The high-yield products ($> 10^{13}$ atoms/cc-sec in Fig. 4) are well above background impurity limits, but some uncertainties due to possible impurities, especially in the electrolyte, still plague measurements of the lower yield products ($< 10^{13}$ atoms/cc-sec in Fig. 4). Interestingly, a recent study by Widom and Larsen claimed that the theoretical transmutation calculations reasonably well match the Miley & Patterson result (see fig. 3 in [15]).

Two other points should be stressed. First, no neutrons have been observed in these experiments despite repeated attempts with sensitive detectors Likewise, no tritium has been observed in electrolyte analysis after runs. [Note: some LENR experiments run other quite different conditions have reported neutrons and tritium production. Thus, depending on the experimental design, there appear to be different branches to the LENR reactions]. Second, as noted in Miley and Patterson [11], long exposure of photographic films to electrodes removed after extensive runs indicate low levels of soft x-ray and/or beta particle emission.

This is consistent with the recent theoretical models where the fission-like process occurring in the transmutations has little excess energy. Thus, unlike uranium fission where the intermediate compound nucleus is highly excited, this energetically “soft” type fission leads to many products that are stable and others only slightly unstable [15] [16]. This process then avoids energetic gamma emission and the production of highly radioactive nuclear waste encountered in uranium fission systems. These remarkable results are basic to this new field of LENR nuclear physics and the unique processes that can be created by causing nuclear reactions in condensed matter. Please note that the “production rates” shown represent a time average over the experiment run-time since it was only possible to take samples at the beginning and end of a run. Likewise, the excess heat reported represents an average over the run, so that a comparison of these two results is consistent. Thus, to test a possible correlation between transmutation products and excess heat, the measured product yields are used along with their respective binding energies to compute a theoretical “excess power”, W_{ex} , as shown in Fig. 5a. The computation is straightforward but tedious due to the large number of reaction products produced. Basically, W_{ex} is computed by taking the product of all the isotope yield rates times their binding energies and subtracting the corresponding product for the “fuel”. A key point is the determination of the amount of original material that is consumed or “burned up.” This calculation is done by first allotting the maximum number of reaction product nucleons to the metal nucleons. Then, any remaining nucleons are attributed to the protons, allowing for a variable proton/metal atom ratio to retain generality. This balance rests on the assumption that the protons plus the electrode metal (e.g. Ni in this case) are the reactants in LENR cells. This follows because protons in the light water electrolyte cannot react with themselves. The ‘salt’ employed in the electrolyte, e.g. Li_2SO_4 , should not be involved in the reaction either, because various workers have used different salts while still obtaining similar reaction products.

Product yield results from three runs (run numbers refer to experiments described in Miley and Patterson (1996) where adequate information was available for this type of evaluation are summarized in Fig. 5b. Although one has a mean measured value that is a factor of two larger than the calculated value, two of the results show quite close agreement. While these results are not definitive, in view of the many uncertainties in both of the calculated values (due to uncertainties in the yield measurements) and in the calorimetry, the agreement obtained strongly suggests a relation between products and excess heat. The situation where heavy water is used instead of light water, as reported in some other LENR studies (see [17]), is less clear but again appears to involve proton-metal reactions. In that case, p-metal reactions could occur simultaneously with D-D reactions. More study is needed to resolve possible reactions involved this important regime.

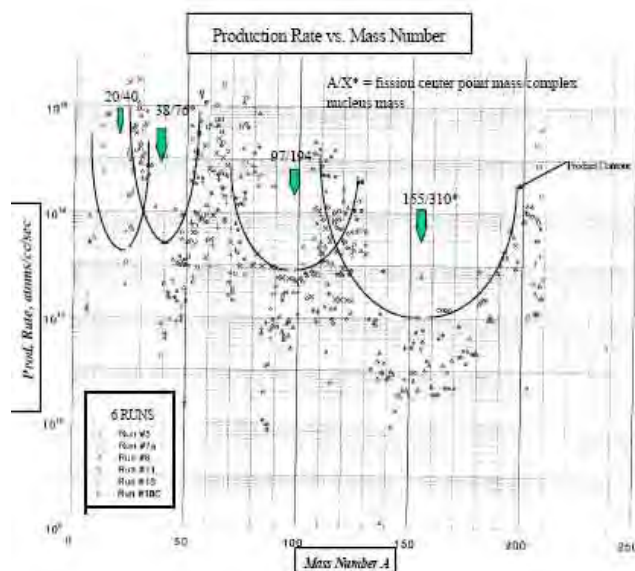


Fig. 4 - Reaction Product Yield vs. Mass Curve.

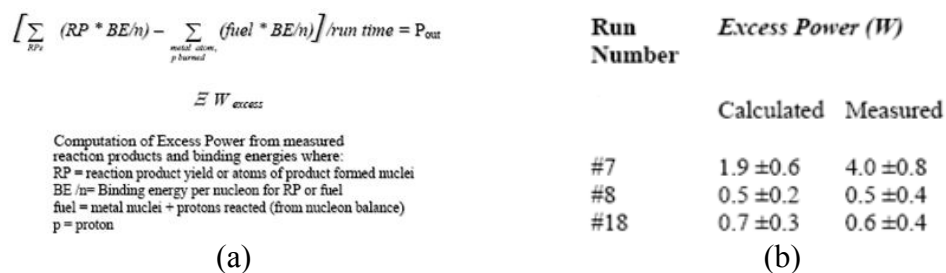


Fig. 5 - (a) Computation of excess power from reaction n product measurements. (b) Results from Energy Balance Calculations for Three earlier Thin-Film experiments. All experiments used Li₂SO₄ in H₂O for the electrolyte and thin-film Ni coated cathodes.

Another way of viewing these data is to calculate the energy released (the observed excess heat times the run time) and divide by the number of Ni atoms reacted (based again on the number of nucleons associated with the measured quantities of reaction products observed). Then, for the runs referred in Fig. 5b, an energy release of order of 150 keV/Ni atom reacted is obtained. This value is consistent with nuclear as opposed to chemical processes. It is several orders of magnitude less than the energy released in neutron-induced fission, but is roughly in the range of “soft” fission releases predicted for LENR conditions [16].

These results also bear on an issue that is often raised about the LENR experiments: how can a positive excess power occur since the base metal involved, such as Ni, has a binding energy per nucleon near the peak of the binding energy-mass curve? In the present analysis this can be explained by noting that the “fuel” i.e. the reactants, are a mixture of protons and metal. Then the average binding energy of the reactants (p + metal) is reduced below that of the metal alone. As a result, there is an expanded range of reaction product masses laying around the mass of the base metal that offer a positive energy release, i.e. a positive Q-value for the reaction. Still, the fact that some reaction products lie outside of this range might seem to infer that reactions occur despite a negative Q-value, but then a very large input energy would be needed to drive the reactions. This dilemma is overcome, however, if the reaction occurs through multi-step excitation and/or formation of a compound nucleus which can split up or fission into a variety of reaction products of different masses [11] [16]. The energy balance requirement is that the formation energy of the compound nucleus must be supplied. Subsequently, the break-up energy is, in effect, shared among products.

In order to obtain further proof for nuclear reactions in the thin-film cathodes [18], the detection of nuclear radiation accompanying the electrochemical loading of those cathodes is strongly desirable. Although the studies of long-range alpha emission have been done after the electrochemical loading of Pd with deuterium/hydrogen [19], it was a great interest to expand the experiments on charged particle detection to in-situ measurements during the electrolysis process. Unfortunately, it is hard to apply electronic SSB and X-ray detectors directly to the cathode during electrolysis experiment. Thus, a technique using non-electronic detectors (CR-39 and thermal luminescence detector (TLD)) was employed to allow in-situ measurement of energetic charged particles and X-rays during the electrochemical loading of the flat-plate Pd-thin film cathodes.

In the electrolysis experiments the freshly opened CR-39 detector chips or TLD crystal were attached either to the Pd thin-film cathode (Foreground) or to the substrate side or/and immersed in electrolyte in the cell (Background). The charged particle and x-ray detection were carried out simultaneously with excess heat measurements in open type calorimeter. The electrolysis current and duration during one Foreground run were normally varied in the range of 50-400 mA and 2-30 days, respectively.

Fig. 6 and insets show the Foreground and Background CR-39 reading for both alpha particles and protons. The count rates of protons and alphas after Background subtracting are statistically significant with Background level being close to zero. In the control experiment with CR-39 detector attached to the thin film NiO_x (obtained by annealing of Alumina/Ni(4000A) sample in air atmosphere), where despite of the high voltage applied (U~10.0 V), the electrolysis current in the cell was very low (I~1.0 mA), and no tracks with d < 7.8 μm were detected.

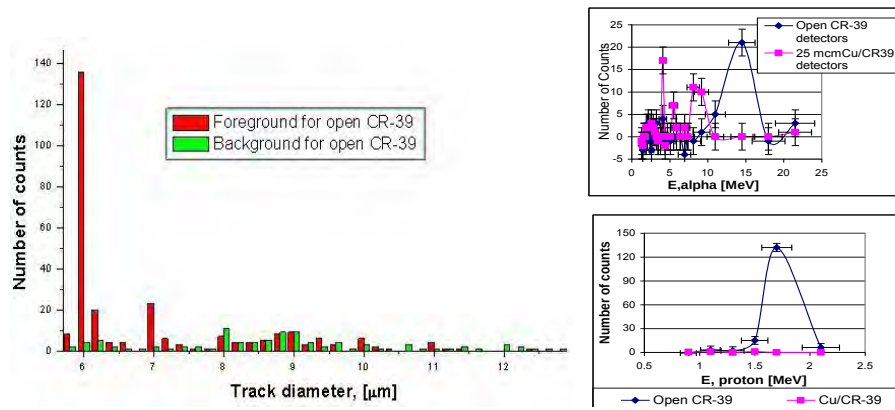


Fig. 6 - Electrochemical loading of Pd thin film cathodes on dielectric substrates unambiguously produced high-energy charged particles: 1.5-1.7 MeV protons and 11-16 MeV alphas. Insets: Alpha-tracks energy distribution and Proton energy distribution after background subtracting.

In contrast to charged particle detection results, the statistical significant level and reproducibility of X-ray emission was not satisfied. Some result (e.g. Pd/Glass sample with LIF TLD) showed consistency between the emitted X-ray fluency and absorbed dose but others (e.g. other cathode with $\text{Al}_2\text{O}_3\text{:C}$ TLD) did not show statistically significant results due to higher initial background level (~ 10 mrad) of these TLD compared to that for LiF. The X-ray measurement results indicate the absence of massive nuclear reactions caused by nuclear transmutation in Pd [18]. However, these results could not rule out the possibility of a weak X-ray emission as a result of the charged particle generation or Pd thin film fracture or detachment from the dielectric substrate.

In summary, the observation of MeV particle emission, combined with the transmutations and excess heat measurements, provide extremely strong evidence for nuclear reactions occurring in the thin films during electrolysis. There results, combined with recent observations of localized sites (“clusters”, discussed next) have lead us to consider the new approach to power producing LENR cells described here.

3. Ultra High Density Deuterium Cluster Electrode Fabrication

The SQUID magnetic measurements described in Lipson *et al.* [1] show “clusters” have characteristics of a type- II superconductor. Cluster regions can have hydrogen densities approaching $10^{24}/\text{cc}$ (See Fig. 7). Dislocation loop cluster type electrodes are fabricated by cyclic loading-unloading, hence being named “Dislocation Loops by Repetitive Loading-DeLoading (DLRLD)” electrodes. These DLRLD electrodes are based on studies where high loadings in dislocation loops in treated Pd have exhibited properties associated with a superconducting phase termed a “cluster”.

After several loading-unloading cyclings, the Pd/PdO:H_x was annealed at 300°C for 2 hr to remove all the weakly bond hydrogen or deuterium. Then, a high-vacuum thermal desorption technique is used to estimate residual hydrogen concentration in the Pd/PdO:H_x samples (Fig. 7C). The samples were heated in a high vacuum (10^{-8} Torr) chamber with a quadruple mass-spectrometer. The hydrogen desorption peak area and the temperature of its maximum were found by analyzing the desorption species and comparing their yields to background data from the Pd/PdO : H_x or Pd/PdO .

By using Garlic-Gibson kinetics model, the activation energy of desorption is found to be approximately 0.65 ± 0.10 eV, which is consistent with the result of Kirchheim for hydrogen trapping at dislocation core sites in cycle Pd. This indicates that the hydrogen is solely bound inside the deepest core sites [approximately one Burgers vector ($2.75 \text{ \AA}$)], meaning that all residual hydrogen is localized inside the dislocation loops (in the direction of Pd) determined by Burgers vector $b [101] = 2.75 \text{ \AA}$. Then, the dislocation density calculation give x_{eff} is ~ 1.8 , suggesting superstoichiometric hydride formation in the deep dislocation cores.

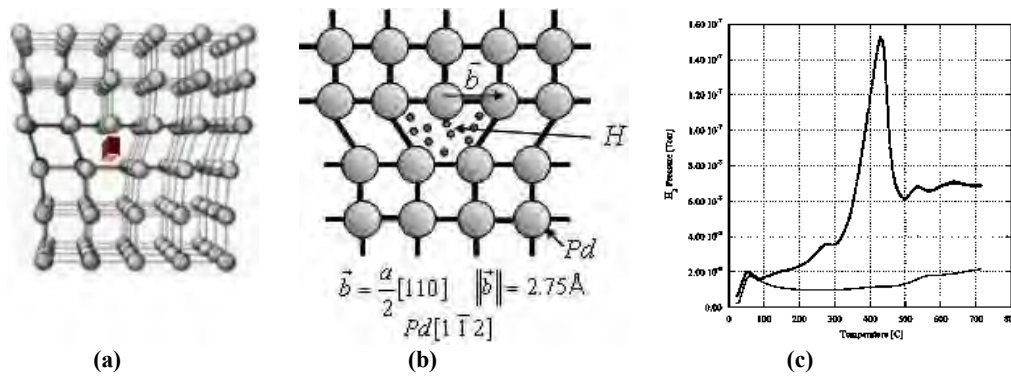


Fig. 7 - SQUID magnetic measurements show clusters have characteristics of a type-II superconductor. Cluster regions can have hydrogen densities approaching $10^{24}/\text{cc}$. (a) 3D scheme of typical edge dislocation core (see orange bar) in the Pd crystal. (b) Cross-section of A. (c) Thermal desorption measurements of Pd/PdO : Hx (thick solid line) and Pd/PdO (thin solid line).

4. Other Ultra-High-Density Deuterium Cluster – Rydberg Matter

Encouraged about the result [1, 2] that SQUID measurements confirmed the localization of more than 100 nuclei of hydrogen in a crystal defect within a palladium crystal, an estimation was given [20] how many such defects may be generated in a crystal. A density of such defects in crystals may well be more than 10^{19} cm^{-3} before the crystal is breaking. This is the experience from the property in silicon crystals where such densities of doped atoms are well known. Similar density of defects with voids has been produced in silicon too by very intense electron bombardment. [21, 22, 23, 24] If these voids are then in an average distance of 10 atoms in the crystals for laser fusion targets based on LiH or similar crystals at room temperature, the targets with a density of fusion fuel of 1000 times solid state density may be possible [b].

A necessary condition, however, is that the clusters in the crystal volume should have the density of 10^{24} cm^{-3} . These densities have been confirmed [3] from clusters which were produced in crystal defects at the surface of iron oxide by catalytic processes of inverted Rydberg states. These densities were proved from the Coulomb repulsion energy of deuterons in such states as time-of-flight measurements showed 630 eV w. This corresponds to a distance of the deuterons of 2.3 pm within the inverted Rydberg clusters. The repulsion process is given, when laser irradiation of 546 nm wave length removes the neutralizing electrons between the deuterons [3].

The mechanism of the electron emission by the laser radiation has been analyzed by inclusion of the correspondence principle of electromagnetic interaction [25]. A virtual quiver motion of the electrons in the quantum state in the inverted Rydberg cluster arrives at a quiver elongation of 2.3 pm at a laser intensity of $1.01 \times 10^{10} \text{ W/cm}^2$. This intensity was just measured as the lowest threshold [3] for the measurement of the 630 eV deuterons.

A further conclusion of this analysis is that the state of the deuterons in these clusters represents an effective Bose-Einstein condensation at room temperature. [26] A further result is for a hydrogen atom, the virtual quiver motion of the electron within the laser field with an elongation of the Bohr radius corresponds to the well known ionization energy of 13.6 eV. This energy has the unique value of $\alpha^2 mc^2/2$ expressed by the fine structure constant α and the rest mass energy of the electrons mc^2 with the electron mass m and the vacuum speed of light c .

5. Conclusion

This paper makes a strong case that condensed matter deuterium cluster formed in dislocation loops are one way to achieve nuclear reactive sites in LENR electrodes. The problem to date has been that the volumetric density of such sites, which is highly reactive, have a low density of sites per unit volume.

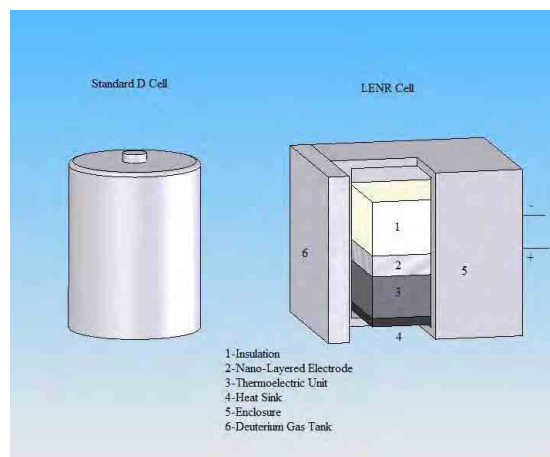


Fig. 8 - Small LENR Battery -- design based on present experimental data base

Possible methods to achieve a high volumetric density of sites (i.e. achieve a massive cluster electrode (MCE) that are under study are briefly outlined. This is thought to offer an orderly 'roadmap' for moving on to very unique future power cells for both space and commercial use. Such cells would employ nuclear reactions for energy but enjoy no neutron release and a minimal radioactive product buildup. These characteristics are based on the experimental observations cited here where any neutron levels were below detection limits; MeV particles, while observed, had very low emission rates; and the reaction (transmutation) products created are generally close to stable, with only soft x-ray or beta emission being observed.

Based on the excess heat measurements, local power densities exceeding a kW/cc are possible, promising very high energy density power units. Since the radiations emitted (protons, alphas, and x-rays) are not very penetrating (do not escape the cell structure) and no long lived radioactive reaction products are observed, LENR power units would be a remarkable "green" nuclear technology. A sketch of a small D-cell equivalent LENR battery is shown in Fig. 8. The cell shown has a deuterium gas tank attached.

Gas loading is used rather than electrolysis for compactness. Heat flow is directed to the outer casing through a thermoelectric element using an insulation and heat sink design. Modular sections connected in series allow a 1.5 V output at 0.1 A. This type of battery must be used in devices where natural convection air cooling or other heat flow dissipates heat from the battery casing. The battery run time is determined by the amount of deuterium stored refilling the depleted tank is provided by pump down and gas injection through a filtered line connected to a "filling station". The unit shown is designed for 1000 Ahr per gas fill. The main technological step needed before construction of this battery is to finish development of the nano-layered electrode structure described earlier.

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Quantum Mechanical Study of the Fleischmann-Pons Effect

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Abstract. Resonances in deuterium-deuterium fusion were examined by calculating the transmission behavior of a single deuteron through a deuterium atom, or through a system comprising two or three deuterium atoms, using transfer matrix methodology. Many unit-transmission resonance peaks were observed in the results of the calculations, even at incoming deuteron energies of a few electron volts, but resonance peak widths were found to be very narrow at low energies, so that the probabilities of fusion would be small.

1. Introduction

The Fleischmann-Pons Effect (FPE) was swiftly rejected when first published in 1989, yet many researchers have since reported energy gains in similar experiments [1]. The body of evidence suggests that the energy gains are real, even though the heat production powers are small and often difficult to replicate. Fleischmann and Pons suggested that these gains are the result of “cold fusion”, or low energy nuclear reactions, where energy is released from a deuterium-deuterium (D-D) fusion. However, the probability of D-D fusion under the conditions of an FPE cell is vanishingly small as currently understood. As stated by Pons, et al., “It is necessary to reconsider the quantum mechanics of electrons and deuterons in such host lattices” [2].

The current work undertook a simple study of resonance bands that may exist for quantum-mechanical deuterium particles to penetrate through the nucleus of a deuterium atom. Solutions to Schrödinger’s equation were developed first for a single-atom system, and then for multi-atom systems using the transfer matrix methodology. The effect of energy perturbations on the atom potentials was also examined.

1.1 Time-Independent Schrödinger’s Equation in One Dimension

Phenomena of interest were examined using the simplified, one-dimensional and time-independent Schrödinger’s equation for quantum mechanics. This equation can be written

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) = (E - V(x)) \cdot \psi(x) \quad (1)$$

where m is the particle mass, E the particle energy, x the spatial variable, and $V(x)$ is the background potential energy of the system encountered by the particle. The general solution of this equation is the wave equation,

$$\psi(x) = Ae^{ikx} + Be^{-ikx} \quad (2)$$

where A and B are wave magnitudes and $k = \frac{\sqrt{2m}}{\hbar} \sqrt{E - V}$ is the wave number of the particle at position x .

1.2 One-Dimensional Transfer Matrices

The above wave solution can be drafted in matrix notation as

$$\psi(x) = \begin{pmatrix} e^{ikx} & e^{-ikx} \end{pmatrix} \cdot \begin{pmatrix} A \\ B \end{pmatrix} \quad (3)$$

From this it can be observed that the wave can be “propagated” to the left or right by a distance a via the straightforward matrix operation

$$\begin{pmatrix} A \\ B \end{pmatrix}_{x=a} = \begin{pmatrix} e^{ikx} & 0 \\ 0 & e^{-ikx} \end{pmatrix} \cdot \begin{pmatrix} A \\ B \end{pmatrix}_{x=0} \equiv \mathbf{P}(V, a) \cdot \begin{pmatrix} A \\ B \end{pmatrix}_{x=0} \quad (4)$$

Likewise, the background potential can be changed discontinuously from V_1 to V_2 via the “discontinuity matrix” at the origin

$$\mathbf{D}(V_1, V_2)_{x=0} = \begin{pmatrix} 1 + \frac{k_1}{k_2} & 1 - \frac{k_1}{k_2} \\ 1 - \frac{k_1}{k_2} & 1 + \frac{k_1}{k_2} \end{pmatrix} \quad (5)$$

where the subscripts indicate wave numbers at the respective potentials. A similar discontinuity can be applied at $x = a$ using a combination of the above discontinuity matrix and suitable backward and forward propagation matrices,

$$\mathbf{D}(V_1, V_2)_{x=a} = \mathbf{P}(v_2, -a) \cdot \mathbf{D}(v_1, v_2) \cdot \mathbf{P}(v_1, a) \equiv \mathbf{t}_{total} \quad (6)$$

Finally, the transmission through a system comprising multiple discontinuities, all contained within a system transfer matrix $\mathbf{t}_{total}$, can be calculated using the formula

$$T = 1 - \frac{|\mathbf{t}_{total21}|^2}{|\mathbf{t}_{total11}|^2} \quad (7)$$

where the subscripts indicate particular matrix elements by row and column. [3]

2. Methodology

2.1 Basic Atom

A single deuterium atom was represented by stepped discontinuities in potential energy.

The most basic atom comprised only a hard core potential at 100 MeV and a potential well at -50 MeV. These values were chosen as representative of the energies in a real atom, but were not meant to be precise duplicates of real potentials. As was discovered in developing the results documented below, a choice of different values of these potentials did affect the locations of the resonance bands found, but did not change the overall resonance structure of the systems in question. Plots of the potential energies for this atom are shown in Fig. 1. The radius chosen for the hard core potential was 0.34 femtometers [4], and a radius of 7.24 femtometers was chosen for the Yukawa well; this is the radius at which a simple Yukawa attractive potential would adopt a value of -50 MeV [adapted from equations in reference 5].

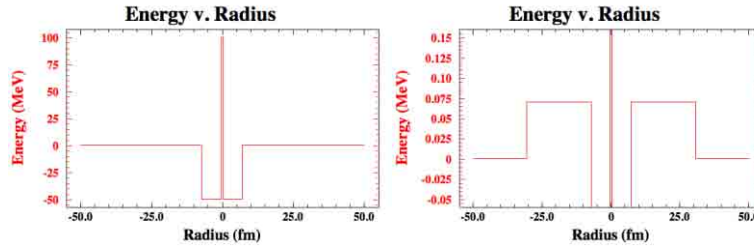


Fig. 1 – Basic atom potentials, including first coulomb potential.

More complicated atoms included additional potentials, which were used to represent the coulomb attraction experienced by a deuteron near a deuterium atom. These included a 70-keV potential from the edge of the Yukawa well to a radius of 30.6 femtometers, to represent the peak energy of a $1s^-$ electron orbital and the radius at which that orbital’s energy drops to one-half its peak value. However, differences

in the results of those calculations were found to be negligible; for brevity the results have not been included in this paper.

2.2 Systems Studied

Transmission of a deuteron through a single deuterium was studied first, followed by an examination of the additional resonances generated in transmission through two atoms. Finally, results of the two-atom case were compared with those of a system with three atoms.

3. Results

3.1 Single Atom Transmission

Single-atom transmission is perhaps the least interesting case studied, with several resonances below the hard-core energy of 100 MeV, but no unit resonance until well above the hard-core energy. A plot of the result can be seen in Fig. 2.

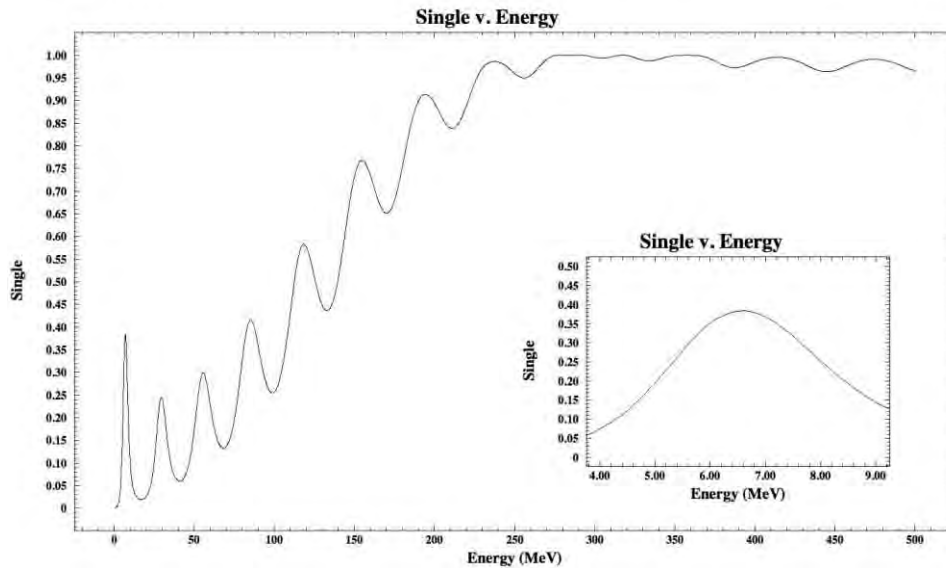


Fig. 2 – Transmission through a single basic atom; the inset shows magnification of the first peak.

3.2 Two- and Three-Atom Transmission

Fig. 3 and Fig. 4 show the transmission through two atoms and three atoms, respectively. Atoms in the system calculated were duplicates of the basic atom above, separated from one another by a distance of one angstrom.

Perturbation of the energy levels in any of the atoms in the multi-atom system had very little effect on the structure of the results, except for changing the particular energies at which resonance bands occur. For brevity, plots have not been included here.

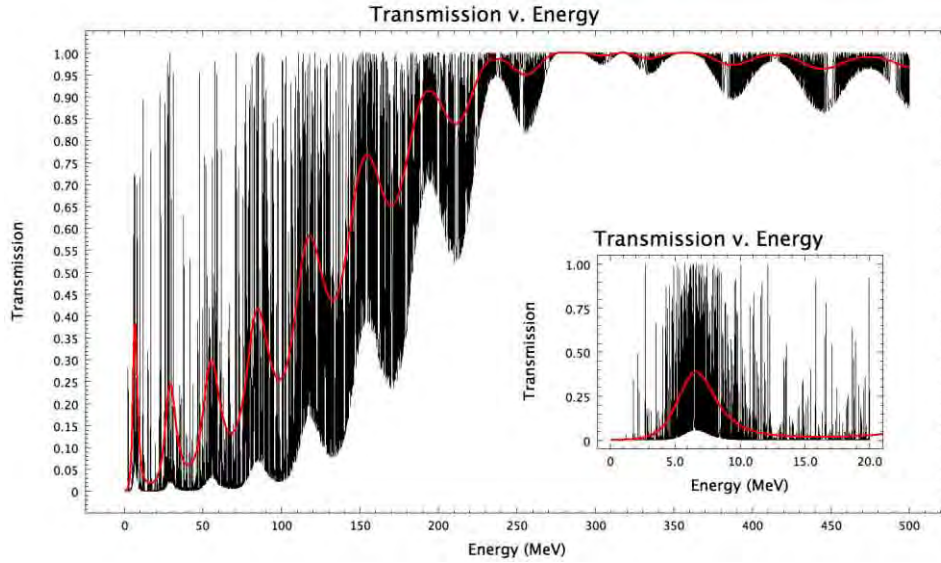


Fig. 3 – Transmission through two atoms separated by 1 angstrom (black curve); the single atom transmission curve from Fig. 2 is shown in red. The inset shows magnification of the first peak in the single-atom spectrum.

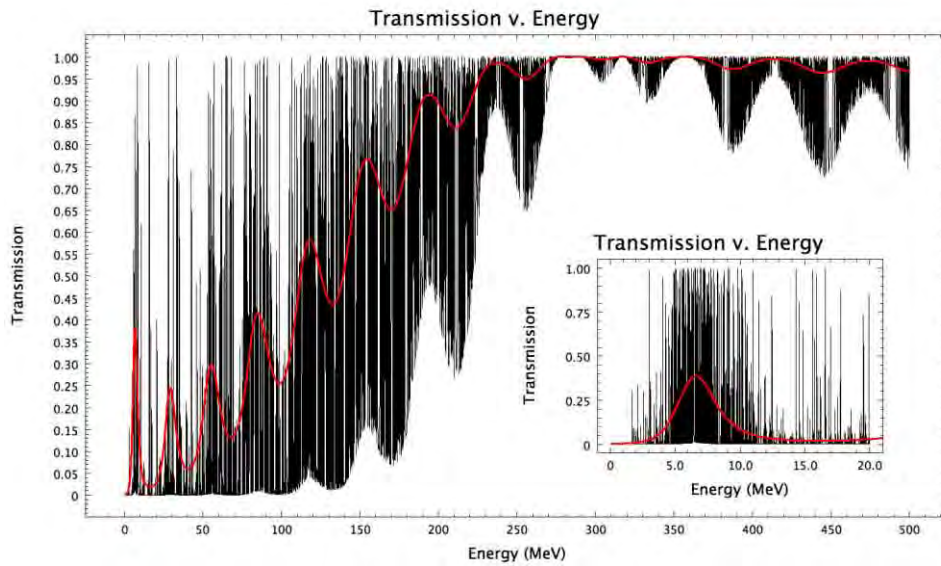


Fig. 4 – Transmission through three atoms separated by 1 angstrom (black curve); the single atom transmission curve from Fig. 2 is shown in red. The inset shows magnification of the first peak in the single-atom spectrum.

Zooming in on various energy regions to examine the resonance bands in greater detail revealed two interesting phenomena. First, the difference between the two-atom case and the three-atom case was noticed to resemble the peak splitting observed in optical spectroscopy or magnetic resonance imaging. A plot of this splitting is shown in Fig. 5.

Second, even at very low energies, the resonance bands that look like spike noise in the coarse plots of Fig. 3 and Fig. 4 were revealed to be *unit* transmission peaks. A plot at low energy with greatly increased resolution can be seen in Fig. 6. The plot illustrates the unit-transmission character of only one peak, but others were examined and found to also be peaks of unit transmission. This character was not obvious in the above figures because the resonance peaks have such narrow energies: a high degree of granularity was required in the transmission calculation to produce transmission values of one.

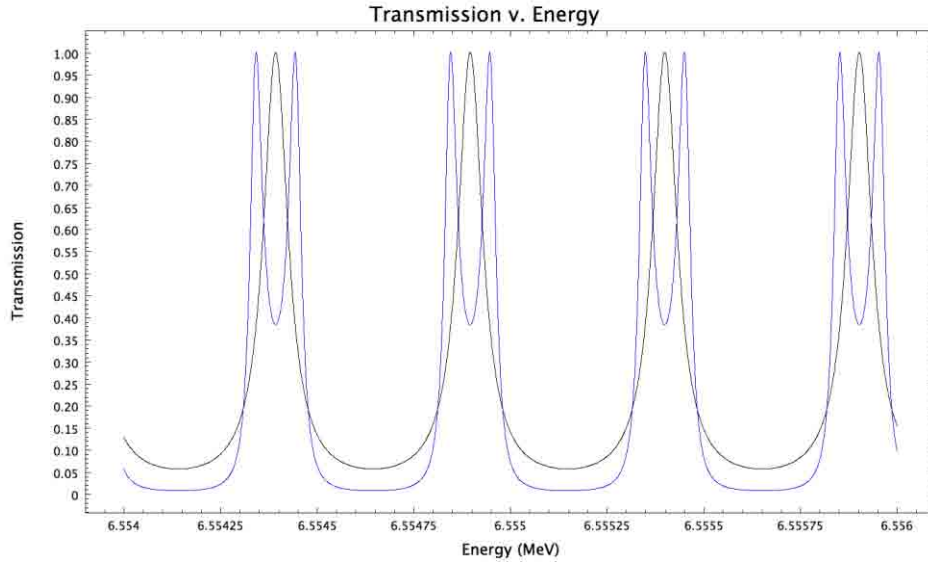


Fig. 5 – Peak splitting observed between two-atom transmission (black curve) and three-atom transmission (blue curve)

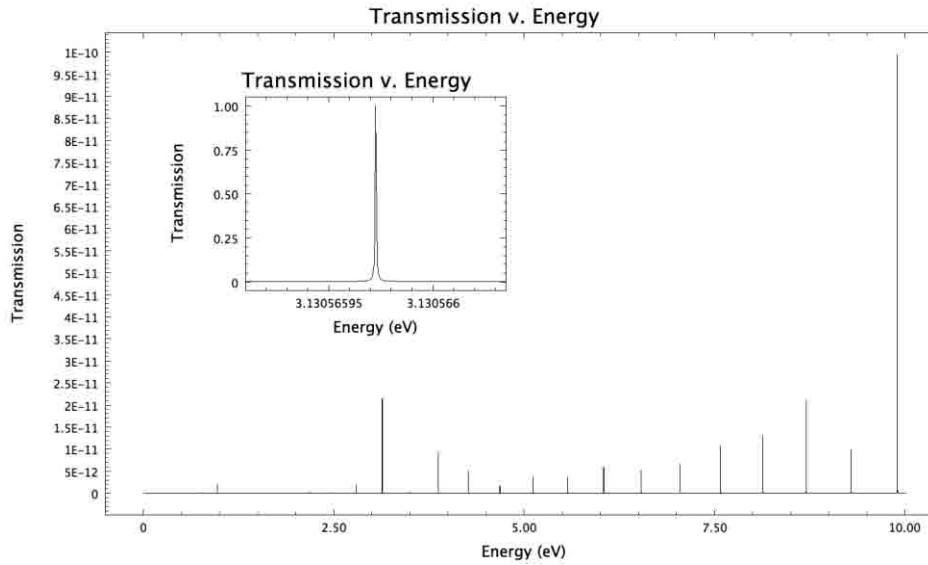


Fig. 6 – Resonance peaks from 0 to 10 eV (outer plot) and the particular peak near 3.1306 eV (inset plot); the ordinate scale on the outer plot is narrow only because the energies in the curve were too coarsely spaced to include larger transmission values – high granularity at each resonance was required in order to observe unit transmission.

4. Conclusions

Transmission has been estimated for a deuteron through one or more deuterium atoms. The estimate was approximate, but the resonance structure observed should represent that of real systems.

A complicated structure of unit-transmission resonance was found for multi-atom systems, even for transmission through a two-atom system.

Large (1%) perturbations in the deuterium-deuterium attractive or repulsive potential energies had very little effect on transmission resonances.

Resonance peaks observed in transmission through two- and three-atom systems are regularly spaced, and a comparison of the two systems illustrated peak splitting reminiscent of optical spectroscopy or magnetic resonance imaging in the chemistry lab.

Resonance peaks at low deuteron energies were extremely narrow.

5. Discussion and Future Work

The narrowness of resonance peaks would imply that transmission is highly improbable when deuteron waves encounter deuterium particles in free space; this is due to the broad, continuous energy distribution of particles in free space. However, deuterium atoms trapped in a lattice structure would behave as “particles in a box”, and hence have quantized energy levels. Therefore it is possible that overlaps between the quantized energy levels of trapped deuterium atoms in a palladium lattice, and the narrow resonance peaks for transmission, could lead to an increased probability of transmission, and therefore an increased probability of D-D fusion in the lattice-bound system.

First and foremost, the next segment of this research should relate transmission spectra – such as those included in this paper – with fusion interaction probabilities. For instance, the area under the curve for the 3.1306-eV resonant peak shown in Fig. 6 is only 8.9×10^{-10} eV. However, it is not immediately obvious how this relates to a reaction cross-section.

Future work in this field should include a study of the energy levels deuterium atoms may occupy within a palladium lattice, and some examination of whether those energy levels may overlap with resonance peaks for transmission through real bound-deuterium systems, thereby increasing the fusion probability.

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Exotic Nuclear Physics: From Cold Fusion To Antikaonic Nuclear Clusters

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Abstract. A short review of the status of the experimental searches and theoretical speculations on the possible existence of the AntiKaonic Nuclear Clusters is given. There are no scientific relationships with the possible Cold Fusion phenomena, but some similarities and differences in the perception and acceptance by other communities of physicists.

1. Introduction

I am very happy to attend again a Conference on Cold Fusion, ICCF15 and meet old colleagues and friends. As a matter of fact I had the opportunity to hear, nearly exactly twenty years ago (November 1989) the first seminar given in Europe, at CERN, on Cold Fusion by Martin Fleishmann.

I will never forget the enormous interest by the audience, and also the strong, a priori, skepticism. I have always worked in experimental Nuclear Physics, with quite huge detectors in big international Laboratories, but the strong interest in this potentially new class of phenomena convinced me to start with some of my younger collaborators an experimental activity, following a brief theoretical speculation [1]. From 1989 to 1998 I performed several experiments, mainly with the gas-loading technique paying a particular care to the detection of 2.5 MeV neutrons [2,3] and afterwards of ^4He [4,5]. The results were in line with those reported by other Groups, i.e. the possible detection of sporadic emissions of particles, with low statistical significance and not reproducible. During these years I attended all ICCF's from 1 to 7. As a matter of fact I organized also, with G. Preparata, ICCF2 at Villa Olmo, on the Como Lake.

My activity on Cold Fusion was stopped in 1999, not for overwhelming difficulties in the funding by public Agencies or private Companies but by the awareness of not having enough personal competence in Condensed Matter Physics, which is to my opinion the key point for understanding Cold Fusion.

However I never denied the reality of the scientific case of Cold Fusion, whereas I was (and I still am) very skeptical about possible applications.

A few years after my return at full time to Nuclear Physics, I faced a scientific problem that presents some similarities with Cold Fusion, but also differences in the acceptance by the other colleagues. This is the reason for which I accepted to give the present talk, scientifically very far from Cold Fusion and not easy to follow for many colleagues not experts of the sector. It is interesting to follow the conclusions.

2. The AntiKaonic Nuclear Clusters

I report here a brief account of a recent Invited Talk that I gave to the big Conference PANIC08 [6]. By AntiKaonic Nuclear Clusters (AKNC) we indicate nuclear states in which a $\bar{K}$ (K^-) is strongly bound to some nucleons.

The first speculation about the possible existence of AKNC's is due to Wycech [7], based on the observation that the driving $\bar{K}N$ interaction in the isospin $I=0$ channel is strongly attractive near threshold. A large Binding Energy B of about 100 MeV was found, but with a similarly large value of the width Γ .

The theme received a strong boost by the prediction from [8] of the possible existence of narrow discrete AKNC few-body nuclear systems. The $\bar{K}$ -nucleus potential was derived from a phenomenological ($\bar{K}N$) potential accounting for several observables, with particular emphasis to the rôle of the $\Lambda(1405)$, assumed to be a bound (K^-p) system.

The predicted B for $\bar{K}$ -few nucleons systems were quite large (from 50 to more than 100 MeV), but the distinctive feature was the narrowness (Γ of 20-30 MeV). It was due to the circumstance that, due to the high value of B , the main decay channel (K^-p) ($I=0$) $\rightarrow \Sigma\pi$ is energetically forbidden, and the decay to $\Lambda\pi$ is suppressed by the isospin selection rules.

A very important feature predicted for AKNC was a large density, up to 10 times the normal nuclear density. This possibility is very interesting for explaining the structure and the evolution of the neutron stars.

The K^-pp bound system was studied in Ref [9] by a coupled-channel Faddeev calculation obtaining a B of (55-70) MeV and a quite large Γ , of the order of 95-100 MeV.

Recently Ref [10] examined the possible existence of AKNC by using energy dependent ($\bar{K}N$) interactions derived with the s-wave coupled-channel amplitudes involving the $\Lambda(1405)$ and resulting from the chiral SU(3) dynamics, plus p-wave amplitudes dominated by the $\Sigma(1385)$. It was concluded that AKNC can possibly exist with B from 60 to 100 MeV, but with Γ of similar magnitude. This paper contains a quite complete list of the theoretical papers on the subject. In 2004 the Collaboration KEK-PS E471, working at the 12 GeV PS at Tsukuba (Japan) published a paper with the triumphant title: "Discovery of a strange tribaryon $S^0(3115)$ in ^4He (stopped K^-p) reaction" [11] based on a narrow peak observed in the semi-inclusive proton spectrum. There were some discrepancies between the features of the $A=3$ AKNC supposedly discovered and the original prediction but anyway this result played the major role at several Conferences and Workshops in the following two years. Unfortunately the same Group, from a further data taking with larger statistics withdrawn the result as due to an experimental artifact [12].

Thanks to the clever design of the FINUDA spectrometer, installed at one of the two interaction regions of the DAΦNE collider at Laboratori Nazionali di Frascati (Italy) and aiming at a series of studies of Hypernuclear Physics [13], the detector was able to identify in a clean way Λ -hyperons emitted following the interaction of stopped K^- with light nuclei (^6Li , ^7Li , ^{12}C). Fig 1a) shows the invariant mass (I.M.) of a proton and a π^- for the events in which these two particles are observed out from the nuclear targets [14]. The peak position agrees well with the known Λ mass and the width of the peak is as narrow as 6 MeV/ c^2 . Quite surprisingly the above events in coincidence with a further proton emitted in the interaction of the stopped K^- are strongly back-to-back (b.t.b.) correlated. Fig. 1b) shows the angular correlation, acceptance corrected, for the (Λ,p) events.

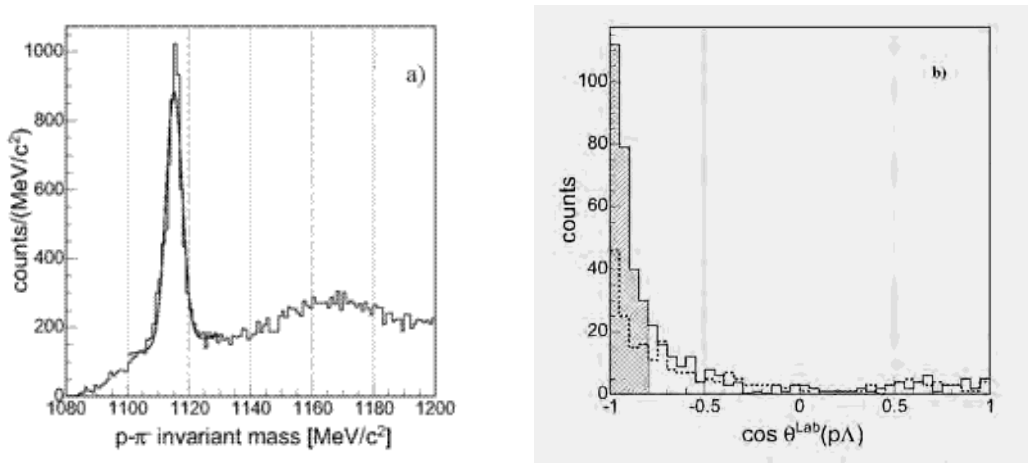


Fig. 1. - a) I. M. distribution of a (p,π^-) pair for all the events in which these two particles are observed [4]. b) Opening angle distribution between a Λ and a p : solid line, ^6Li , ^7Li and ^{12}C targets; dashed line, ^{27}Al and ^{51}V targets. The shaded area is selected as that of b. to b. events. From [14]

A logical consequence of the observation of the Λ - p b.t.b. correlated events was that of determining their I.M in order to verify whether they could be the result of the decay of an $A=2$ AKNC. Fig.2 shows the I.M. spectrum for the Λ - p events for the lighter targets. A relatively narrow bump is observed, with $B=115\pm 9\text{MeV}$, $\Gamma=67\pm 15\text{MeV}$. I notice that, whereas the value of Γ is rather compatible with the prediction of [8], the value of B not; the experimental value is about twice.

Alternative conventional explanations for the above observed bumps were put forward. In [15] the bump in the Λ - p I.M. spectrum was explained as an artifact of the angular cuts applied to the flat spectrum of I.M. of Λ - p events resulting from genuine b.t.b. pairs formed in simple $K^-(np)$ interactions in the target nuclei that suffered a Final State Interaction.

Even though such a mechanism cannot be completely excluded, other arguments are contradicting it as discussed in [6].

The consistent theoretical effort and the first results coming from experiments with K^- stimulated the search for AKNC also in reactions induced by other projectiles.

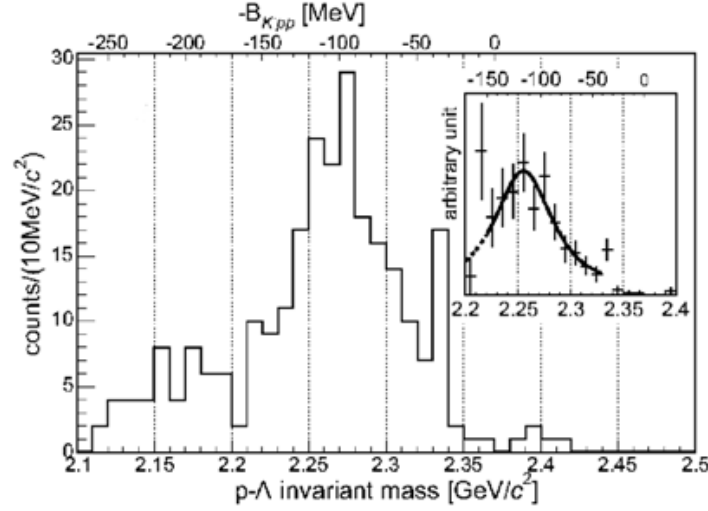


Fig. 2. - I. M. of a Λ and a p in a b. to b. correlation from light targets before the acceptance correction. The inset shows the result after the acceptance correction. From [14].

The best evidence for the possible existence of a narrow $A=2$ (K^-pp) AKNC was very recently provided by a reanalysis of the data on annihilations of p at rest on ^4He [16,17] collected with the OBELIX spectrometer which operated from 1991 to 1996 at the LEAR complex at CERN. Both the reactions of possible production of the $A=2$ AKNC and the steps in the data analysis are too complicated or technical to be outlined here. The final result of the I.M. of the Λ -p system, the same studied in FINUDA but produced with a different mechanism is shown by Fig.3). The signal has a statistical significance of 4.9σ with a B of 151.0 ± 4.4 MeV and a Γ less than 33.9 MeV.

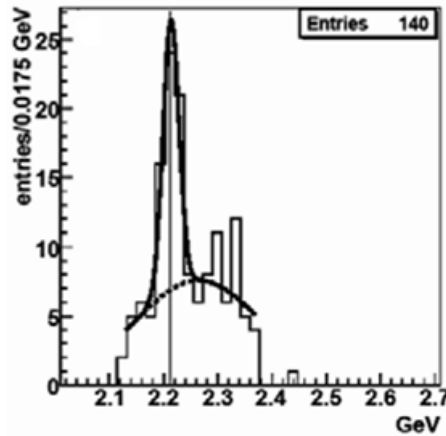


Fig. 3. - I.M. of a Λ and p observed in events produced by the annihilation of p at rest in ^4He . From [17].

Finally the data collected by the DISTO Collaboration at the Saturne accelerator in Saclay on the $pp \rightarrow pK^+\Lambda$ reaction at 2.85 GeV were reanalyzed with the aim of finding signatures compatible with the formation of the $A=2$ AKNC. A strong signal that may be interpreted as due to a state with $B = (105 \pm 2)$ MeV and a similar Γ was reported [18]. I notice that the B value agrees within the errors with that reported in [14], but Γ is twice.

Table1. Comparison between the Binding Energies B and Widths Γ of the (K^-pp) system reported by experiments and Theory.

		B(MeV)	Γ (MeV)	Ref.
$^2_{\bar{K}}\text{H}$	K^- at rest	115 ± 9	67 ± 15	[14]
$^2_{\bar{K}}\text{H}$	$\bar{p}$ at rest	-151.0 ± 4.4	≤ 33.9	[17]
$^2_{\bar{K}}\text{H}$	$pp \rightarrow pK^+\Lambda$	-105 ± 2	118	[18]
$^2_{\bar{K}}\text{H}$	Theory	-48	61	[8]

Table 1 summarizes the values of B and Γ reported by the three experiments which investigated with different reactions the possible production of the archetype A=2 AKNC, as well as the theoretical prediction. A remarkable disagreement between the different sets of results is apparent. A similar disagreement exists if one tries to compare by a simple hadronic model the capture rates reported by FINUDA [14] for stopped K^- with those reported by OBELIX [16,17] for stopped p. A detailed discussion on this subject as well as a possible explanation based on the hypothesis of a Quark Gluon Plasma formation in p annihilation can be found in [19].

3. Conclusions on the present status of the search for AKNC

From the short review given in Sec.2 the following conclusions can be drawn:

- a) the first experiment dedicated to the search of AKNC (KEK-PS E471), which claimed triumphally the discovery of such exotic systems [11] was afterwards obliged to withdraw the claim, recognizing that it was due to an experimental artifact;
- b) three other non-dedicated, general purpose experiments (facilities), namely FINUDA at LNF [14], OBELIX at CERN [16,17] and finally DISTO at Saclay [18] reported the observation of signals that could be interpreted as due to formation of the A=2 AKNC.

However:

- i) the statistical significance is in some cases not very good
 - ii) the reported results disagree each other and with the theoretical prediction [8];
- c) all theoretical approaches to the problem predict a quite large binding energy B (of the order of 100 or more MeV) of an Antikaon to few nucleons; however all approaches predict a width Γ for such a state of the same order of B. Only the phenomenological approach by (8) suggests a value of Γ of the order of about 30 MeV, then experimentally accessible. In spite of the above difficulties the problem of the existence of AKNC is one of the hot spots in Hadronic Physics and the debate is very vivid at all the Conferences and Workshops in this sector. It is expected that the final analysis of the data collected by FINUDA with a six times larger statistics as well as the new data that will come from the dedicated experiments E15 and E27 at J-PARC (Japan) and FOPI at GSI (Germany) will clarify the situation in the near future.

Comparison of the AKNC and Cold Fusion cases

In table 2 I report a personal classification of the merits of Cold Fusion (C.F.) and AKNC scientific cases. I will not comment in detail the above classification, but add only a few remarks. The first is the similarity of the two cases with regards to the experimental and theoretical situation. Points a), b) and c) of Sec.3 are reminiscent of similar situations occurring in the C.F. research, in particular at the beginning. The second is the reaction by the community of Nuclear Physicists. After a short transient time, lasting not more than a couple of years, the result was a stopping of the financing by public Agencies in nearly all Countries, a disappearance of papers on C.F. in nearly all the more important Journals in Physics, a disappearance of the C.F. scientific case in all general Conferences of Nuclear Physics. Exactly the opposite occurs for the AKNC's scientific case. In addition, instead of stopping the activity, new dedicated experiments were approved by the Scientific Committees of world leading Laboratories with top priority and adequately financed.

As an old Nuclear Physicist, my concluding wish is that, after recognizing the excellent work carried out in twenty years by a few clever and motivated Groups, Cold Fusion physicists will return again in the community of Nuclear Physics.

Table 2. Personal classification of the merits of C.F. and AKNC scientific cases (*=minimum,*****=maximum)

	CF	AKNC
Applications	*****	*
Impact on media	*****	*
Scientific interest	*****	***
Acceptance by theoreticians	*	****
Acceptance by experimentalists	**	*****
Papers on Physics journals	*	*****
Financement by Public Agencies	*	*****
Positions for young reaserchers	*	***
Interest by students	*****	***

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A Possible Mechanism For Cold Fusion

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Abstract. We describe a mechanism for cold fusion that is able to explain how two hydrogen ions may come close enough so as to fusion as well as many of the different and independent experimental observations made during years of experiments. We present the mechanism, its weak points, the way it explains the respective phenomena and suggest some experiments that may validate further the model described by us.

The initial work of Fleischman and Pons [1] was published more than twenty years ago but the acceptance of the facts by the wide scientific community is still to be obtained. While experiments are beginning to become reproducibile (see www.lenr-canr.org), it remains the problem that there is no clear explanation on how two positive ions may get so close, at room temperature, so as to fusion. We show how such a mechanism may exist and explain this “exotic” phenomenon. We start from two observations: a) from the literature [2] it results that in Pd hydrogen exists in Pd as a positive ion; b) the ions are moving in a periodic electrostatic potential given by the periodic location of the host lattice ions, being a superposition between the electrostatic screened potential made by the positively charged metal ions. This last aspect suggests an analogy with the case of electrons in solids [3]. Starting from this point and having in mind also the theory of the Kronig-Penney potential [4] that predicts formation of energy bands in case of periodic potentials, we may conclude that the hydrogen ions exists in such energy bands in the solid. Each type of isotopes has its own energy band structure. A model based on energy band structure for the hydrogen ions was proposed earlier by [5], but we follow another route as compared to it, route that allows us to explain the main aspects of the mechanism and why cold fusion may take place at room temperature. The energy bands may be separated by forbidden energy gaps or may superimpose, as in the case of metals. We refer from now on only to the energy band structure corresponding to hydrogen ions. Following the usual route in solid state physics, we describe the kinetics of the hydrogen ion by its energy E and its wavevector k . There is always a relation $E = E(k)$ between these two parameters, relation that is called the dispersion relation. We may deduce from it the ion effective mass m^* :

$$\frac{1}{m^*} = \left(\frac{\partial^2 E}{\partial^2 k} \right) \quad (1)$$

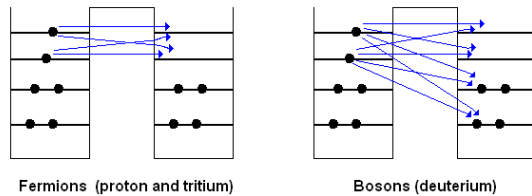
The effective mass (generally, it is a tensor) is applicable especially when considering the particle at one of the energy band edges, namely upper edge or lower edge. At the lower edge the effective mass is positive. At the upper edge the effective mass is negative [3]. An electrically charged particle with negative effective mass behaves in an electric field like a particle of positive effective mass but having an opposite charge [3], which means that a H ion that is excited at the top of an allowed energy band has a negative effective mass and it behaves, in an electric field, as a negative ion with a positive effective mass. This is a very important feature and is the key to our model. A particle may reach the upper part of an energy band only by excitation (thermal or of other nature) and it will stay only a certain interval of time in the respective state because of scattering on different quasi-particles (phonons, lattice ions, impurity ions, etc.). For the sake of simplicity, we consider throughout the work that hydrogen does not form any hydrides or, if it forms, the hydrogen concentration in the material is so high that all the hydride-type bonds are saturated with hydrogen and the remaining hydrogen ions are moving relatively free within the “lattice” formed by the potential wells.

The mechanism we propose is as follows: a hydrogen ion is excited to an upper energy state having negative effective mass. This excited ion will stay a time τ in the excited state. During this period, the excited ion may interact electrostatically with another hydrogen ion that has a positive effective mass. The system of two ions behaves similar to two particles of opposite charges attracting each other. They move in a central potential field, similar to electrons in atoms or two electron and hole in an exciton.

Thus, the combination of the Coulomb potential and the negative effective mass is the mechanism that allows the two H ions to approach each other. It is mandatory to mention the fact that the two ions must be in different allowed energy bands (different Brillouin zones [3]) so as they be able to form a closely orbiting system. If we take into account that heavier ions will get closer than lighter ones, the sequence of fusion probability will be given by $T > D > H$, where T stands for tritium, D for deuterium and H for proton. For example, deuterium is twice heavier than proton, so that we expect that the orbiting radius for the case of deuterium be approximately half of that corresponding to the proton. In other words, the heavier isotopes are the most probable to fusion by such a mechanism, since the orbiting distance between them will be smaller. Another possibility is that the ions directly collide / coalesce. For the orbiting case, a first temptation is to use the expression of Bohr radius but replacing the electron mass with that of the hydrogen ion. This approach indicates an orbiting radius of few tens of femtometers, small enough so that nuclear fusion takes place with a certain probability. This approach is only generic and useful for showing that, in principle, the two ions may get close enough so as to fusion. The (constant) effective mass formalism is applicable when the interaction potential is of the order of several eV to even few tens of eV. In reality, the overall potential (electrostatic repulsion + lattice) changes as the two ions get close each other. In such a situation, the energy band structure changes as well with the distance between ions and so does also the effective mass. An iterative computation is needed for obtaining a correct estimate of the orbiting distance. Moreover, the host lattice expands as hydrogen is incorporated into it. This means that the band structure (and the effective mass) varies with the content of hydrogen. Such a mathematical computation is complex and, especially, needs a high computational power so as to tackle the problem with sufficient precision. When the two ions get very close to each other, the applicability of the effective mass formalism is not valid anymore. Even if we may still speak about ion mass (positive or negative mass) since the ion is characterized by a certain dynamics inside the periodic crystal, the mathematical use of the respective formalism is questionable. A first approach may be that of considering an effective mass that is energy (and, thus, position) dependent. This approach is based on the observation that the energy band structure is a continuous function everywhere in the lattice, as well as are its first and second derivatives with respect to the coordinates and, respectively, to the wavevector of the ions. It is obvious that the band structure varies dramatically in the region where the two ions interact, but there can still be defined a band structure and a local (energy / position dependent) effective mass. Such an approach may lead to significant computational complexity. Another approach can be that of considering a tight binding model, since the electrostatic interaction at distances useful for fusion process is of the order of tens of keV. Such a starting point model could be that of [6]. However, the aim of this paper is to present the physical mechanism leading to fusion at room temperature and the consequences of it. The elaboration of the mathematical formalism to be used for describing the process is an open matter and does not represent the scope of the paper. However, even with this problem, the model can explain in a unitary manner many experimental results presented in the literature, as will be seen further. This lack of an appropriate mathematical formalism is the weak point of our model. When orbiting, the two ions form a bound system having a discrete energy spectrum, as in the case of excitons in solids [3] and electrons in atoms [4]. Because the interaction energy at such short distances is of the order of tens of keV, we expect that the specific energy spectrum of such a bound system be active in the X-rays region. Emission of X-rays with specific wavelengths was experimentally proven in [7-8]. In [8] the authors claim that the emitted X-ray wavelengths are not specific to any characteristic X-ray spectrum of the known elements. We consider that the X-rays are emitted by the bound system formed by the two orbiting ions, during system de-excitation to a lower energy state, analogue with the case of electrons in excited atoms. Because of the specific, discrete energy levels of the bound system, the emitted X-ray spectrum has wavelengths that are specific for the difference in energy between the levels involved in the de-excitation transition, wavelengths that are not encountered in any of the characteristic X-ray spectra of the known elements. An interesting consequence of our model is that illuminating a hydrogen loaded sample with X-rays having wavelengths identical to these experimentally determined ones (that have a specific emission spectrum during reaction) will reduce the reaction rate. This is so because resonant excitation of the bound system will increase the orbiting radius, similar to electrons in atoms (resonant illumination of an atom excites the electron on a state that is further from the nucleus than is the fundamental state). This is a theoretical prediction that, to our knowledge, was not yet reported experimentally. Its experimental verification will check the validity of our model. Let us now consider the ways in which an ion may be excited to the upper energy state of negative effective mass. One way is by excitation at thermal equilibrium, when collisions with different quasi-particles existing in the lattice may give the ion enough energy to reach the top of the energy band. The higher the temperature is the greater is the number of ions with negative effective mass. Another way is to use external factors such as illumination with photons or bombardment

with energetic particles (electrons, ions) [9]. Since we have an energy band structure, only photons with appropriate wavelengths may excite the ions to the energy states of negative effective mass. Such a resonant / selective excitation is observed in [10]. In this case, the energy of excitation may vary from several meV up to several eV. Such a situation is encountered in [10-11]. We mention that in [11] the energy difference between the two incident light beams is claimed to have effect in enhancing the fusion process. It seems that the two beams excite a phonon in the metal, in the THz frequency range, this quasi-particle being responsible for the enhancement. Such a phonon may interact with a hydrogen ion and excites it resonantly at the top of the energy band. We assert that the Born-Oppenheimer approximation [3] is applicable to the hydrogen ion also. We make this assertion because we expect that the mass of the hydrogen ion in the lattice do not differ significantly with respect to hydrogen mass in vacuum. This assumption is based on the analogy with electrons in crystals. Hydrogen has a relatively high mobility in heavy metals that have an atomic mass of at least tens of hydrogen atomic mass. For example, Pd has an atomic mass that is 106 times greater than hydrogen mass [www.webelements.com]. On the other hand, hydrogen diffusion in metals is a slow process, the hydrogen ions being all the time in thermal equilibrium with the lattice / metal ions. Because of these two reasons, hydrogen ions are approximately ten times faster than the lattice ions, so that Born-Oppenheimer approximation may be applied without introducing great errors, of only few percent. As numerical values, we mention that an error of less than 10 % for proton in Pd and of approximately 16 % for tritium in Pd is obtained. These are acceptable errors. The Born-Oppenheimer approximation indicates to us that we may look at the "lattice" formed by the potential wells (for the hydrogen ions) as being frozen, hydrogen ions moving within this lattice. Because such a potential well is formed by the contribution of several atoms that oscillate in an uncorrelated manner, the potential well is also squeezed at the same frequencies as those of atom oscillations. Since the displacements of atoms, at room temperature, are small compared to the interatomic distance within the metal lattice, we may consider that the deformation / squeezing of the potential wells is small compared to the well size.

A very important aspect is that two hydrogen isotopes are fermions (proton and tritium) while deuterium is a boson. This is a very important feature. Consider two adjacent potential wells, one having a higher



number of hydrogen ions than the other, as depicted in figure 1. In the left part, we have the case of fermions. In the right part, we have the case of bosons. We simplify and consider discrete energy levels, but the explanation may be extended in a straightforward manner to band structure also.

Figure 1 – Sketch of the way in which fermions, respectively bosons, diffuse.

Let consider fermions first. The fermions from the left quantum well may diffuse / tunnel only on the unoccupied states in the right quantum well because of the Pauli exclusion principle. This means a low number of available states for transfer, as seen from figure 1. In the case of bosons, there is no exclusion principle and they may diffuse / tunnel on any of the states existing in the right-side quantum well since several bosons may share the same energy state. This means a higher probability of transfer from one well to the other than in the case of fermions because of the greater number of available states able to receive an ion. The same arguments are applicable also to the boson ions lying on the lower energy states of the left quantum well from figure 1. Because of that all the bosons participate in the diffusion process and not only those from upper energy levels. Thus, the energy band model may explain why deuterium diffuses easier in metals than the other hydrogen isotopes. Because of the same reason, the boson character makes Pd able to load a very high concentration of deuterium as compared to the case of proton. The normal sequence for the diffusion coefficients would be $H > D > T$, since the heavier a particle is the lower is its diffusion coefficient. But taking into account the fermion / boson character of each ion and the above arguments, the correct sequence for the diffusion coefficients is $D > H > T$, as is observed experimentally. Taking into account that the orbiting distance is smaller for heavier isotopes, it results that the most favorable isotope for observing cold fusion is deuterium. This is due to its higher mass (that allow him a smaller orbiting radius than in the case of proton) and to its bosonic character that allow him to diffuse faster and be incorporated in a greater amount than the other isotopes. As regards the true potential in which the ions move, let's consider a direction in the crystal that is along the great diagonal of the lattice cube of Pd. This great diagonal passes through the center of the cube and also through two of the host lattice nuclei. Taking into account that hydrogen interacts electromagnetically with the screened

electrostatic potential of the lattice ions but has also the ability to present strong interaction, it results that the hydrogen ion sees a potential formed by two kinds of quantum wells: electromagnetic and nuclear, as depicted in figure 2. The nuclear quantum well corresponds to the lattice ion. From the quantum mechanics point of view, there is no formal difference between an electromagnetic potential well and a nuclear potential well. Thus, we may consider that for the hydrogen ions there is a coupling between lattice energy levels and host nuclei levels. This is so because solving the Schrödinger equation for this system of quantum wells will result in energy levels / bands that are common to both types of wells, electromagnetic and nuclear. This phenomenon is specific only to the host lattice in its solid state. This fact suggests the possibility that nuclear reactions in solid state occur in a slightly different manner than in the liquid or gaseous state of the host lattice, cold fusion being only a particular case of that. The situation depicted in figure 5 is idealized, in the sense that we have drawn rectangular walls for the potential wells.

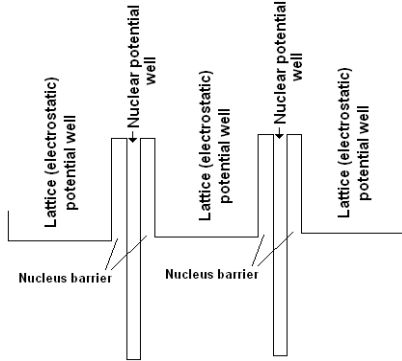


Figure 2 – The true quantum potential for the hydrogen ion in solids.

Let's now consider the behaviour of the system when cold fusion takes place. Suppose that in a certain place in the host metal a fusion process is initiated by using some means. The occurring of the nuclear fusion in that region of the metal produces heat, heat that locally increases the host temperature. Because of the increase in temperature, there will be an increased number of ions excited to higher energy states that are characterized by a

negative effective mass. Thus, the number of ions with negative effective mass is increased. This increase in their number has as a result the increase in fusion processes that, at their turn, increase further the local temperature. In this way, a positive feedback appears, in the sense that, once initiated, the fusion process may go further without the need of any external action and can even be self-sustained as described in [12]. Self-sustainability appears in the case when the system generates more energy than it dissipates. There is also a negative feedback, given by several mechanisms such as: a) the lifetime τ in the excited state decreases with increasing temperature because of the increased scattering on lattice specific quasi-particles, thus decreasing the available time for the two ions to approach each other enough for fusing; b) consumption of reactant particles (at that specific site in the lattice) as a consequence of the fusion process, process that is faster than the supply made by diffusion from outside; c) the deterioration, and even melting, of the host lattice as a result of the collisions of the energetic ions resulted from fusion, deterioration that mitigates the local energy band structure and thus mitigates the mechanism for hydrogen ions approaching; d) hydrogen out-diffusion from the regions where fusion takes place, this process being due to the fact that an increase in local temperature produces an increased diffusion of hydrogen ions from the warmer region to the colder ones, this out-diffusion being able to reduce or even reverse the flux of ions coming from regions with a higher ion concentration; e) heat dissipation rate to the exterior, dissipation that allows the crystal to not overheat excessively (as in the case when is mounted in vacuum) and thus to limit the positive feedback loop. This process of dissipation depends on the metal (through density, specific heat and thermal conductivity) and on the cooling boundary conditions. If non-equilibrium (illumination or particle bombardment) excitation of hydrogen ions is made, a good dissipation of the generated heat to the exterior can make the difference between a successful experiment and an experiment having a more violent, explosive character. These negative feedback mechanisms may dominate at higher reactions rates because of the reasons told above. Thus, we may expect a reaction rate that depends on temperature in a non-linear fashion, having a maximum value at a certain temperature, as described in [13]. This happens because below that temperature, the dominant role is taken by the positive feedback, which tends to increase the temperature. Above the temperature corresponding to the maximum of the reaction rate, the negative feedback becomes dominant, which tends to reduce the reaction rate. Thus, an oscillatory behaviour may be expected for the reaction rate. There is necessary a threshold value of the hydrogen concentration because under this value: a) the fusion processes are rare; b) thermal conduction of the metal carries out the heat sufficiently fast so as the positive feedback be insignificant and no experimental observation of the heating be made; c) let "d" be the mean free path of a negative mass ion during its stay in the excited state. If this mean free path is less than the average distance between ions (equal to $N_0^{-1/3}$ where N_0 is the total ion concentration), then the probability that the excited ion encounter another ion is reduced. As a consequence the reaction rate is reduced correspondingly.

Increasing concentration lowers the average distance between ions and the encounter probability becomes higher, the same happening for the reaction rate. Let denote by “ f ” the fraction of ions having a negative effective mass and N_0 be as above. “ f ” depends on temperature and is equal to 0.5 when temperature tends to infinity. It may be computed from the Fermi-Dirac or Bose-Einstein distribution function (depending on the type of isotope) and the density of states specific to the respective ions. The concentration of ions with negative effective mass is thus equal to $f \cdot N_0$ while the concentration of ions with positive effective mass is equal to $(1-f) \cdot N_0$. The fusion reaction rate is equal to the product of these two concentrations (there is also the reaction cross-section that multiplies these two concentrations), being equal to $f \cdot (1-f) \cdot N_0^2$. Thus, from our model, it results that the fusion reaction rate is proportional to the square of the hydrogen ions concentration, as is observed experimentally. There is enough experimental evidence that shows that heat emission takes place only after a certain concentration of hydrogen is obtained in the Pd lattice. This can be explained by two main aspects. First, the observation of rise in temperature produced by the nuclear reaction depends on the sensitivity and speed of the devices used for measuring temperature (thermometer, infrared camera) and by the thermal noise of the Pd+calorimeter system. A very sensitive apparatus and a Pd/calorimeter system with very low noise will show a lower threshold concentration. The generated heat flux must be at least comparable to the heat loss flux in order to produce an observable effect (else, the signal is small and extinguishes fast with time). A system with a lower heat dissipation rate will show a lower threshold concentration. Secondly, it must be taken into account the explanation given above when comparing the average distance between hydrogen ions with the mean free path of the negative mass ion. A higher concentration increases the probability of encounter and thus the reaction rate. As regards the generated heat, there is an infrared emission of the metal surface, the spot corresponding to the highest temperature having a position that varies randomly onto the surface [14]. As we have mentioned earlier, a necessary condition for reaction is the thermal excitation of the hydrogen ions on energy states with a negative effective mass. This is a random process. A greater thermal fluctuation at a point may produce a greater reaction rate, with heat emission. The temperature increases at that point and positive feedback is triggered (above a threshold determined by the heat loss rate). This positive feedback consumes some part of the hydrogen at that point, so the spot extinguishes in time. Then, another fluctuation appears at other place, in a random manner (the temperature and concentration fluctuations are random processes) and the process is repeated. A consequence of this explanation is that the bright spot never appears twice at the same place (or at least appears after a long enough time so as the ions concentration be recovered at that place), since the hydrogen ions in that place are consumed during the first spot. We don’t have yet data or experimental results to prove this last assertion, it results from the model proposed by us. The excitation of hydrogen ions to upper energy states with a negative effective mass is taking place all the time. Thus, even if the loading process is finished since a certain time interval, these excitations take place and may generate heat by the mechanism proposed by us. This fact explains why is observed the so-called “heat after death” [12], since the excitation processes are independent on the loading means and are occurring all the time during loading and after that. This has as one of the consequences the fact that emission of X-rays with specific wavelengths should be observed even after the external excitation of the Pd loaded sample is switched off, since the start of orbiting of the two hydrogen ions is not necessary to be made directly on the fundamental state of the ions bound system. This may offer an explanation for the experimental data obtained in [15]. These are some of the experimental results that can be explained by our model. Our model does not contradict that one based on the screening effect made by the free electrons of the metal, since screening proves a support for the ions to get closer. As regards the plasma wave model proposed by [16], the plasma wave may be considered as exciting the ions to upper energy states where they acquire a negative effective mass. However, the [16] model cannot explain why X-ray radiation with specific wavelengths is emitted during reaction and why the effect observed by Letts and Cravens is taking place. A similar effect as in [9-10] must be observed by using THz / mm / sub-mm radiation, with a frequency similar to or close to that mentioned in [10]. This is so because of the resonant excitation (direct or phonon mediated) of ions to energy states with a negative effective mass. However, the use of THz / mm / sub-mm radiation should be more favorable to observe enhancement effects than the use of visible or near-infrared lasers, because the skin penetration depth of the THz / mm / sub-mm radiation is larger than the skin depth corresponding to visible or near-infrared light. This feature makes that a greater number of hydrogen ions be excited with THz / mm / sub-mm radiation than with optical light, fact that will increase the amount of generated heat. This assertion is also a theoretical prediction and should be checked experimentally. Another experiment that should be done is that of cyclotronic resonance in deuterium loaded Pd (both at low and at high hydrogen concentration), so as to measure the effective mass of hydrogen in the metal lattice. This measurement should give an experimental indication when

trying to compute the concrete band structure for the hydrogen ions. In conclusion, some experiments that are based on our prediction may be done so as to check our model: a) illuminating a hydrogen loaded sample with X-rays having wavelengths identical to the specific ones emitted during reaction to see if the reaction rate will be reduced; b) illuminating with THz / mm / sub-mm radiation to see if an enhancement effect greater than that reported by Letts and Cravens is obtained; c) X-ray reflection spectra of hydrogen loaded samples, to check if “unusual” absorption lines appear. Caution should be made when exciting the Pd+deuterium system by non-equilibrium means (photons, particle bombardment), since this may end with very energetic, explosive processes, as could be the case reported in [17].

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The FCC Substructure of the Nucleus and the Magnetic Interaction among Nucleons

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Abstract. The FCC lattice model of nuclear structure unifies the liquid-phase, gaseous-phase and cluster models within a self-consistent theoretical framework. By discarding the completely fictitious long-range “effective” nuclear force employed by the shell model and yet maintaining the nucleon build-up procedure in the independent-particle model, the FCC model retains the principal strengths of both the liquid-drop and the shell models. In place of the effective nuclear force, we employ the short-range magnetic attraction between suitably aligned nucleons to obtain nuclear binding.

1. Introduction

The strongest objection to “cold fusion” research since 1989 has been the assertion by nuclear theorists that low-energy nuclear reactions (LENR) “violate everything known about nuclear physics.” We argue to the contrary that LENR are consistent with quantum mechanics (QM), and “violate” *only* various questionable assumptions of the 30+ models used in nuclear structure theory [1]. In fact, the various nuclear models are known to be mutually-contradictory (a liquid nuclear interior in the liquid-drop model [LDM], a gaseous-phase in the shell model; local cluster formations in the alpha-particle model, no local interactions in the Fermi-gas model; a short-range nuclear force in the LDM, a long-range “effective” force in the shell model; etc.) and clearly indicate that nuclear structure theory itself is unfinished business [2].

2. The FCC Lattice Model

We have previously shown that one model of nuclear structure (the face-centered-cubic [FCC] lattice model) is consistent with both QM (and the shell model description of nucleon states) and the many empirical indications of an extremely high-density LDM-like nuclear interior [2-4] (Fig. 1). Here, we demonstrate that the nuclear force that binds nucleons together into this lattice configuration *cannot* be a fictitious potential-well acting over more than 10 fm (as in the shell model), but, rather, must be a spin- and isospin-dependent, short-range force acting over distances of less than 3.0 fm, as already well-known from nucleon-nucleon experiments. The only known force of sufficient strength to overcome the Coulomb repulsion between two protons is an in-phase magnetic force [5]. That is, at a center-to-center distance of 2.0 fm (which gives the known nuclear core density of 0.17 nucleons/fm³), the surface-to-surface distance of singlet-paired, same-isospin nucleons (each with an RMS radius of 0.86 fm) is only 0.28 fm, corresponding to an attractive magnetic force of ~3 MeV. Triplet-paired nucleons of opposite-isospin show similar attraction (details of the magnetic interaction in Section 3).

In our previous work [2-4], we simply assumed that a strong, short-range force – similar to that in the LDM – allows for condensation of nuclear matter. A comparison of various lattice configurations of nuclear matter ($Z=N$) showed the relative stability of an antiferromagnetic FCC lattice with alternating isospin layers (Fig. 1). It is also noteworthy that this same FCC lattice of nucleons has been shown from QM calculations [6] to be the lowest-energy condensate of nuclear matter, possibly present in the crust of neutron stars (although absent in the neutron star “core” consisting of only neutrons or hyperons).

But the most surprising fact about the FCC lattice is that, by placing a tetrahedral alpha particle at the center of the system, it reproduces the entire shell/subshell nucleon build-up procedure that is known from the independent-particle model (IPM) model and empirically well-established. In other words, the *n*-shells and *j*-

subshells that are the essence of the shell model are uniquely reproduced as spherical shells (n) and cylindrical subshells (j) in the antiferromagnetic FCC lattice with alternating isospin layers. Moreover, using a realistic, short-range nuclear force, the lattice gives binding energies and nuclear radii that are essentially identical to those of the LDM [2-4]. While difficult questions concerning the nature of the nuclear force have remained unanswered in the lattice model – and indeed in all nuclear models! – we have taken the remarkable reproduction of both shell and liquid-drop characteristics within the FCC lattice as *prima facie* evidence that normal nuclei at normal nuclear densities are configured as a lattice. This idea was first voiced by Wigner in 1937 [7], and later developed independently by several others [8, 9].

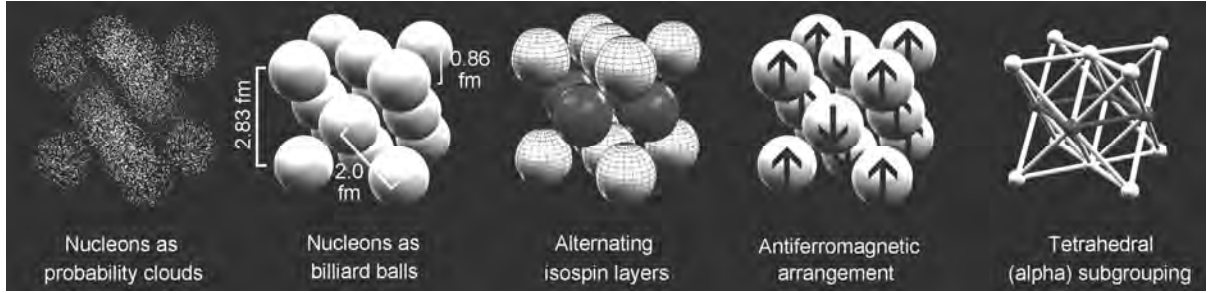


Fig. 1 - The FCC unit structure with dimensions that give the known nuclear density.

3. The Magnetic Interaction among Nucleons in the FCC Lattice

We have previously reported theoretical work on the magnetic interaction among fermions in a lattice [5]. In the traditional Biot-Savart formula, the mutual force between two coils is obtained as the contribution of infinitesimal length elements of currents and ignores any phase relationship between them. In contrast, we have found that the currents of two neighboring coils in a lattice are correlated since there is periodicity. Contrary to the Biot-Savart result in which the potential energy of the two coils is dependent on their separation as $1/y^3$, there is a strongly enhanced contribution which behaves as $1/y$. This energy turns out to depend on the radius R of the coils and increases when this radius decreases.

We have examined the cases in which the coils are on the same plane, as well as on parallel planes along the same axis. If current coils describing the nucleons have radius=0.5 fm, the energy gives the correct order of magnitude for nuclear binding. P-P, N-N and N-P energies for first neighbor bonds give an average value of 2.8 MeV (and this value reproduces the nuclear binding energy curve for all nuclei $Z>7$).

Figure 2 shows the case of two coils side-by-side. The current elements $d\vec{l}$ have an angle between them in general with no definite relation, varying between $-\pi$ and $+\pi$ and leading to a cancellation of their projections one on the other. In the case in which they are part of coils on a lattice, however, there will be a constant angle between the two, since the current will be periodic along the coils. Therefore the circulation of current in one coil will be repeated periodically in all the coils.

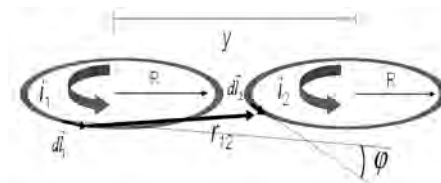


Fig. 2 - The magnetic force between two coils. Unlike the Biot-Savart calculation, the phase relationship between the current elements is taken into consideration.

The magnetic field of the first coil is given by

$$\vec{B}_1 = \frac{\mu_o i_1}{4\pi} \int_{C1} \frac{d\vec{l}_1 \wedge \vec{r}}{r^3} \quad (1)$$

The force on the second coil is

$$\vec{F}_{12} = i_2 \int_{C2} d\vec{l}_2 \wedge \vec{B}_1 \quad (2)$$

Therefore, we obtain

$$\vec{F}_{12} = \frac{\mu_o i_1 i_2}{4\pi} \int_{C2} d\vec{l}_2 \wedge \int_{C1} \frac{d\vec{l}_1 \wedge \vec{r}_{12}}{r_{12}^3} \quad (3)$$

This can be expressed as:

$$\vec{F}_{12} = -\frac{\mu_o i_1 i_2}{4\pi} \int_{C2} \int_{C1} \frac{d\vec{l}_2 \cdot d\vec{l}_1}{r_{12}^3} \vec{r}_{12} \quad (4)$$

As an example, consider two coils with the same axis, separated by a distance y . By using cylindrical coordinates, this equation becomes:

$$\vec{F}_{12} = \vec{j} \frac{\mu_o i_1 i_2 R^2}{2} y \int_0^{2\pi} \frac{\cos \varphi}{(y^2 + 2R^2(1 - \cos \varphi))^{\frac{3}{2}}} d\varphi \quad (5)$$

where $\varphi = \varphi_1 - \varphi_2$ expressing any phase relation between the two currents and $\vec{j}$ is the unit vector along the y direction. .

A more general expression can be derived for two coils of different radii R_1 and R_2 as follows:

$$\vec{F}_{12} = \vec{j} \frac{\mu_o i_1 i_2 R^2}{2} y \int_0^{2\pi} \frac{\cos \varphi}{(y^2 + R_1^2 + R_2^2 - 2R_1 R_2 \cos \varphi)^{\frac{3}{2}}} d\varphi \quad (6)$$

From the force we can calculate the potential energy, V_{12} .

When no phase relationship exists between the currents, we find that

$$F_{12} = \left(\frac{\mu_o i_1 i_2 y k}{2\sqrt{R_1 R_2 (1 - k^2)}} \right) [(1 - k^2)K(k) - (1 - k^2/2)E(k)] \quad (7)$$

where

$$k = \sqrt{\frac{4R_1 R_2}{(R_1 + R_2)^2 + y^2}} \quad 0 < k < 1$$

and

$$K(k) = \int_0^{\frac{\pi}{2}} \frac{d\theta}{(1-k^2 \sin^2 \theta)^{1/2}}; \quad E(k) = \int_0^{\frac{\pi}{2}} (1-k^2 \sin^2 \theta)^{1/2} d\theta$$

are elliptic integrals.

V_{12} in this case is composed of terms depending on distance whose leading term is $1/y^n$, where $n=3$.

$$V_{12} = \frac{\mu_o m_1 m_2}{\pi} \frac{1}{y^3} \quad (8)$$

This is the usual Biot-Savart dipole magnetic interaction leading to weak potential energy. However, if a relationship exists between the currents in a lattice we find that

$$V_{12} = \frac{\mu_o m_1 m_2}{\pi} \frac{\langle \cos \varphi \rangle}{R^2 y^3} \quad (9)$$

where for convenience we have introduced the magnetic moment $m = i\pi R^2$. Contrary to the Biot-Savart result in which the potential energy of the two coils is dependent on their separation as y^{-3} , there is a contribution which behaves as $1/y$, strongly enhanced with respect to the Biot-Savart value. This is a much stronger interaction than the usual dipole interaction. Here $\langle \dots \rangle$ indicates the average value of the quantity. This energy turns out to depend from the radius R of the coils and increases when this radius decreases.

A definite phase relation is expected to exist for coils in a lattice with $\langle \cos \varphi \rangle \approx 1$, eventually vanishing at large distances (in the absence of long-range order). We find that the ratio between the in-phase and the out-of-phase of the two expressions is $(y/R)^2$ thus becoming very large for small R .

Similar results can be established for coils on a plane. It follows that the in-phase This energy turns out to depend from the radius R of the coils and increases when this radius decreases.

We have examined the cases in which the coils are on a same plane as well as on parallel planes with the same axis. It follows that V_{12} has quadrupole dependence. When the two coils are side-by-side (with the magnetic moments perpendicular to the vector $\vec{r}$ connecting their centers), the potential energy differs from the case of two coils with the magnetic moments parallel to $\vec{r}$. Also, the phase factor may decrease exponentially with distance, which mimics a “Yukawa” shape of V_{12} .

The force from currents in phase can be reinterpreted as arising from circular motion of charged particles, the current being determined by the motion of the particles. We can use in such a case the Biot-Savart formula for the magnetic field of one coil and the Lorentz force expression to calculate the force on the particle of the second coil. For two circulating particles on parallel planes at distance y on orbits with centers on the y axis we find (for $\varphi = 0$):

$$F_{12} = \frac{\mu_o}{4\pi} q_1 q_2 \frac{v^2}{r^2} \quad (10)$$

where v is the common velocity and q their charge. This can be rewritten in terms of the magnetic moments on the orbits $m = qvR/2$ so that the resultant V_{12} will be coincident with equation (9).

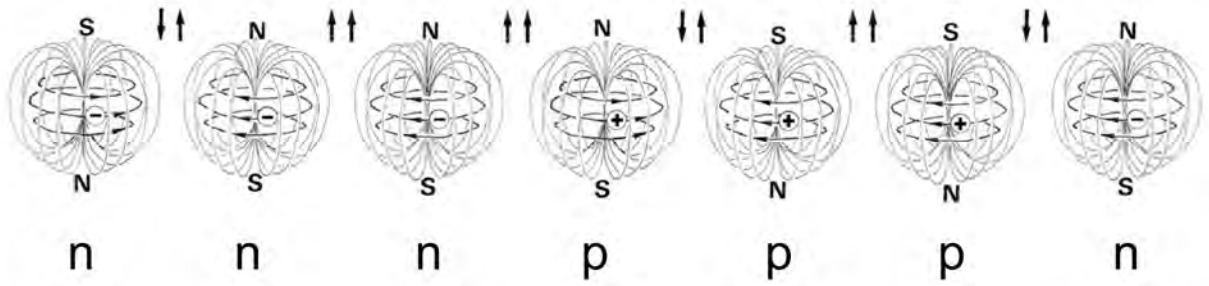


Fig. 3 - The six types of attractive and repulsive magnetic interaction among nearest-neighbor spin up/down protons/neutrons.

Table 1: Numerical estimates of the attractive nucleon interactions at an internucleon distance of 2.0 fm, in comparison with traditional Biot-Savart results ($y=2.0$ fm; $R=0.5$ fm; $\cos \varphi=1$). The average value is 2.82 MeV.

Nucleon pair	V(MeV)	V (MeV) _{Biot-Savart}
P-P (singlet)	3.93	$4.2688 \cdot 10^{-3}$
N-N (singlet)	1.84	$4.2688 \cdot 10^{-3}$
N-P (triplet)	2.69	$4.2688 \cdot 10^{-3}$

4. Discussion

The following properties are found for the in-phase interaction of two particles: The interaction is consistent with a Yukawa form, leading to short-range effects as a result of a dephasing factor with distance and is quadrupole-like, changing according to the angle made by the vector connecting any two coils and the magnetic moments. An interesting feature is the change from attraction/repulsion for first/second neighbors according to the antiferromagnetic arrangement of nucleons in the lattice. The interaction exhibits the right order of magnitude (~ 1 -10 MeV) for nucleons. Higher order terms with increasing distance are much smaller, and are found to produce effects at the normal level of a magnetic force (< 100 keV). At large distances the interaction becomes consistent with a generalized OPEP interaction

$$V_{12} = -CS_1S_2m_1m_2 \left\{ 1 + 2 \left[1 + \frac{3}{m_\pi y} + \frac{3}{(m_\pi y)^2} \right] \right\} \frac{e^{-m_\pi y}}{m_\pi y}$$

where S are the spins, m_π the pion mass, y the distance, C a constant. At leading order in $1/y$ this becomes

$$V_{12} = -3CS_1S_2m_1m_2 \frac{e^{-m_\pi y}}{m_\pi y}$$

In the picture of revolving charges as constituents of the coils, a new feature arises as the time-varying attraction between adjacent coils, when particles are located in the orbit so as to have parallel velocities along the same line. This leads as a consequence to a situation of cancellation of the magnetic attraction and maximization of the Coulomb repulsion between pieces of the nucleus determined by cutting it along suitable planes.

External interactions, like the one produced by particles with a magnetic moment, can also weaken the magnetic interaction through a dephasing of the force, leading to an overall instability of the nucleus. Along particular planes this could again favor the Coulomb repulsion to split the nucleus into (non-symmetrical) parts.

5. Conclusions

We conclude that the so-called “strong” nuclear force that is responsible for the binding of nucleons into stable nuclei may have a classical electromagnetic basis (Figure 4). The effect is essentially the Biot-Savart magnetic force, but what is new in our calculation is the phase-relationship between the currents in neighboring “coils” within the nucleons themselves.

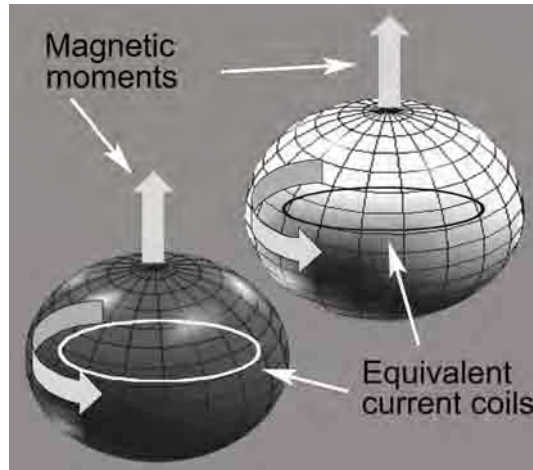


Fig. 4 - The magnetic moments of nucleons viewed as equivalent current coils.

With regard to “cold fusion,” the most important implication of our calculations on the magnetic interaction of nucleons in a nuclear lattice is that the magnetic environment may play a role in facilitating or inhibiting low-energy nuclear reactions. Such effects have been reported by Letts in experiments where excess heat production could be turned on or off with 90 degree shifts in magnetic field orientation [10]. Both our theoretical calculations and Letts’s experimental results indicate the need for more careful study of classical electromagnetic effects before indulging in quantum mechanical speculations.

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Simulation of Palladium Transmutation Products

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Abstract. The build-up procedure for the Palladium isotopes is known from the independent-particle model and implies specific 3D structures for these isotopes in the nuclear lattice model [1]. Using those lattice structures, the favorable modes of fission have been simulated and the fission fragments compared with the transmutation products, as reported by Mizuno [2]. It is shown that (i) the changes in relative abundance of the Pd isotopes, and (ii) the main transmutation products in Mizuno-style LENR studies are consistent with the idea that the bulk of the energy released in such experiments is due to the fission of Palladium isotopes.

1. Introduction

The low-energy transmutation of nuclear species was discovered in 1938 and soon put to military and peaceful uses. Despite remarkable experimental and technological advances, nuclear theory has been *unable* to explain the asymmetrical (3:2) masses of the fragments produced by the fission of the actinides. After 7 decades of theorizing, most specialists on fission frankly agree with Moreau & Heyde [3] that “the theoretical description of the fission process is the *oldest problem* in nuclear physics, [but] it appears that a consistent description is still very far away.”

A second form of relatively low-energy transmutation of nuclei has been reported in the “cold fusion” literature – specifically, the transmutation of Palladium isotopes ($A=102\sim110$) into a variety of small nuclei ($A=30\sim80$) subsequent to electrolysis in deuterated solutions. Theoretical controversy continues with regard to the inducing mechanism that leads to the generation of excess heat, but the measured changes in the ratio of Palladium isotopes and the deposition of many small nuclei on the surface of pure Palladium electrodes are strong indication of the fission of the Palladium nuclei. It therefore appears that there are at least two distinct stages in the “cold fusion” reaction: (i) the tunneling of deuterons into the Palladium nucleus, and (ii) the break-up of the Palladium nuclei themselves. The mechanisms of stage (i) remain controversial, but the nuclear transmutation data of stage (ii) have been replicated several times, and have remained essentially unexplained. In computer simulations, we have studied questions concerning the isotopic changes of the Pd electrode themselves [4] and found the Mizuno data [2], in particular, to be self-consistent and indicative of nuclear transmutation. In the present study, we have again made a comparison of simulation results with the experimental data on the Palladium fission products.

2. Simulation of the Fission of Uranium

We have previously reported that a lattice model of nuclear structure [1, 5, 6] – essentially, a “frozen” liquid-drop that is mathematically identical to the standard “independent-particle model” (IPM) – predicts the *asymmetrical* fission fragments produced by the thermal fission of the actinides [5, 7] *without* using any “adjustable parameters” to produce the asymmetry (Figure 1). The basic effect is a consequence of the fact that scission along oblique lattice planes of the somewhat oblate FCC structures for the actinide nuclei requires breaking fewer nearest-neighbor nucleon-nucleon “bonds” than vertical or horizontal slices through the same structures. Because of the large excess of neutrons that give the actinides an oblate shape, the oblique slices through the lattice structures show a 3:2 mass ratio. That result can be verified using the *Nuclear Visualization Software*, available at: <http://www.res.kutc.kansai-u.ac.jp/~cook>. Similarly, the fission of Palladium (Section 3) can be easily simulated using the same software, and shows that the *symmetrical* fission of the approximately spherical Palladium isotopes is energetically favored.

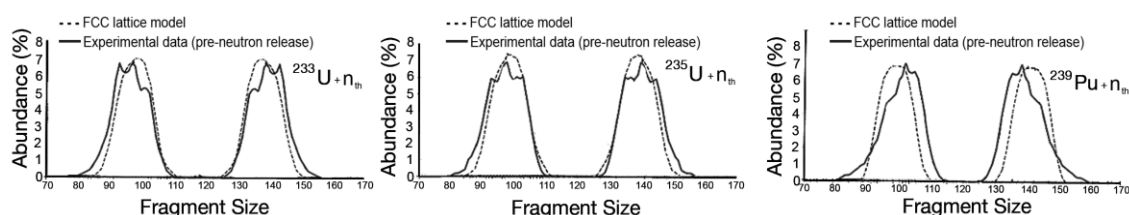


Fig. 1 - The prediction of asymmetrical fragments in the thermal fission of the actinides [5, 7] using a model that employs no parameters to produce the fission phenomena.

3. Simulation of the Fission of Palladium

Here, we apply the *same* lattice technique to the fission of the six stable Palladium isotopes. In a preliminary study, we calculated the total binding energy across each scission plane minus the Coulomb repulsion between the fragments. The lowest energy fission events in each of 6,000 randomizations were then collected (Figure 2). Most fragments were stable or led to rapid β^- -decay, with a predominance of ^{24}Cr final products and little ^{23}V , qualitatively similar to the spectrum of deposits on Pd, as reported by Mizuno [2] (Figure 2b, c).

The qualitative agreement between the experimental data and the simulation using the lattice model were encouraging (Figure 2c), but far from definitive. In a recent simulation, we have used a quantitative calculation of the magnetic force between nucleons that is both spin- and isospin-dependent, in order to obtain more precise predictions about the transmutation products. Details of the force are provided in a separate contribution to this Volume [8]. The simulation procedure was similar to that described in [5] and [7], but was done using the magnetic force between nucleons. Specifically, the previous nuclear force was a phenomenological estimate of the mean nearest-neighbor binding among nucleons in the lattice model (i.e., 2.78 MeV). That level of nucleon-nucleon binding among nearest-neighbors has been shown to reproduce the approximate nuclear binding-energy curve of all but the smallest nuclei, but had no dynamical basis. In the present study, we used the spin-, isospin- and distance-dependent magnetic nuclear force described in [8] to calculate the likelihood of scission along various lattice planes. For the purposes of the simulation, it was sufficient to use fixed values for various spin- and isospin-combinations for nearest-neighbors.

The simulation procedure was as follows:

Each of the six stable isotopes of Palladium was individually constructed in the NVS software following the known (IPM) nucleon build-up sequence. By default, this leads to relatively compact lattice structures, but there are necessarily a large number of alternative surface positions for both protons and neutrons that give similar numbers of total nucleon-nucleon bonds and similar total Coulomb effects for the same Z and N . For simulation of fission fragments, each isotope underwent surface randomization 1000 times and a

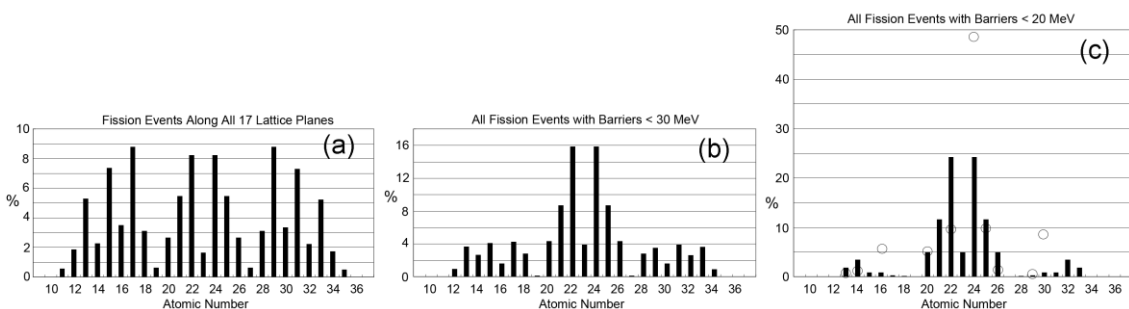


Fig. 2 - Parameter-less lattice model predictions of transmutation products following Pd fission. Circles in (c) indicate the data, as reported by Mizuno [2]. Note that most of the fragments found on the Palladium electrodes are roughly 1/2 the atomic number of Palladium itself (90% between $Z=16\sim30$) – strongly

indicating that they are indeed fission fragments and **not** transmutations built from the repeated addition of neutrons, etc.

small number (arbitrarily set to 9) showing the greatest nuclear binding were retained. These relatively stable structures were then scissioned along 17 lattice planes passing through or near to the center of the lattice. For each isotope undergoing such scission, the lowest energy scission plane was chosen, and the proton and neutron numbers of the fragments were saved for statistical analysis. A total of 46.2% of the Palladium fission products were stable nuclei, 53.8% were unstable. For all unstable fission fragments, the stable end-products were then calculated (without exception a stable isotope was obtained by one or two β -decay conversions of neutrons into protons). Half-lives ranged from 33 seconds to 5.8 minutes, with a small number leading to exotic decays. Finally, the percentages of such fragments were adjusted in light of the different natural abundance of the six Palladium isotopes (Pd^{102} 1.02%, Pd^{104} 11.14%, Pd^{105} 22.33%, Pd^{106} 27.33%, Pd^{108} 26.46% and Pd^{110} 11.72%).

The results of the simulation in comparison with the Mizuno data [2] are shown in Figure 3(a). The large excess of Chromium isotopes found experimentally was well-reproduced, but other aspects of the results indicate that a wider spectrum of simulated Palladium structures should have been sampled (arbitrarily set to the 9 most stable nuclei – i.e., specifically restricted to the most stable, most compact Palladium structures) to avoid the production of the fission products from highly unstable Palladium isotopes). Specifically, fragments with relatively large and small atomic numbers (12, 14, 16, 20, 29 and 30) were not found in the simulation, but would have been obtained if less-compact lattice structures were retained for the simulation of fission (as in Figure 2). By restricting the simulation to the nine most stable lattice structures, the primary fission fragments from each of the Palladium isotopes was Chromium. Relatively strong contributions of Vanadium ($Z=23$) and Manganese ($Z=25$) were found in the simulation but not found in the Mizuno data.

Mizuno also reported the abundances of Chromium isotopes before and after the deuterated electrolysis experiments [2, Plate 15]. Specifically, he found that, although the natural abundances of the four principal isotopes (Cr^{50} , Cr^{52} , Cr^{53} and Cr^{54}) are known to be 4.3%, 83.8%, 9.5% and 2.4%, respectively, they were found at abundances of 14.3%, 50.9%, 23.8% and 10.9% in the experimental “ash” following the presumed fission of Palladium. These numbers are of interest primarily because an explanation due to “contamination” with Chromium is extremely unlikely: even if Chromium from the experimental apparatus had somehow appeared on the Palladium electrodes, they should appear at the natural abundances, whereas quite “unnatural” abundances were obtained. In our simulation, the abundances of these isotopes were 0.0%, 7.9%, 76.8% and 15.3%. Clearly, the simulation exaggerated the isotope shifts, but in the right directions for three of the four Chromium isotopes: a significant decrease in Cr^{52} and significant increases in Cr^{53} and Cr^{54} (Figure 3(b)).

The results of computer simulations of all kinds are highly-dependent on the underlying theoretical model and the choice of parameters used. The present simulations are no exception, so that the theoretical results must be considered in full light of the theoretical input. In this regard, it is relevant to note that the FCC

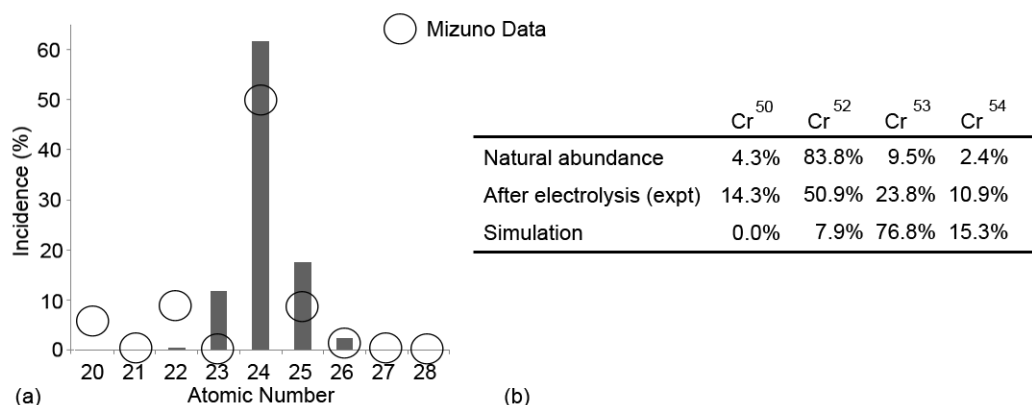


Fig. 3 - (a) A comparison of simulation results (bar graph) and the data from Mizuno [2], indicated by the open circles. (b) A comparison of the changes in the natural abundances of the four main Chromium isotopes following electrolysis with the simulation results.

lattice model that has been used so simulate the fission of both the actinides ($A > 230$) and Palladium ($A \sim 106$) was devised, first and foremost, to explain how the long-standing, mutually-contradictory nuclear models in nuclear structure theory can be viewed in a self-consistent manner [1, 4-6]. For that purpose, the lattice model requires both isospin and orthogonal spin layering of nucleons; those are assumptions that must be made to “make the model work” – specifically, to reproduce the known IPM nucleon texture in the lattice. Only much later after the development of the basic model was it realized [7] that scission of the lattice along lattice planes allows for an explanation of the “anomalous” asymmetry of the fission fragments of Uranium. No changes in the model itself and no *post hoc* addition of “asymmetry” parameters were needed to obtain specifically the 3:2 mass asymmetry of the fragments (Figure 1). On the contrary, it is inherent to the lattice build-up procedure that oblique slices through the lattice for oblate structures such as Uranium will produce asymmetrical fragments. In contrast, similar slices through the more spherical ($x=y=z$) structures of medium-sized nuclei, such as Palladium, lead to nearly symmetrical fragments. In other words, the predictions of both symmetrical and asymmetrical fission for Palladium and Uranium, respectively, are a consequence of the lattice geometry itself – and not a consequence of manipulation of the basic model.

4. Conclusions

Low-energy nuclear reactions continue to pose fundamental questions that conventional nuclear theory cannot answer. With regard to the fission of Uranium and all of the other technologically important actinides, the *asymmetry* of the fission products is regarded as “the perennial puzzle” of nuclear physics [9]. As noted by Vandenbosch and Huizenga [10], “no theoretical model ... has been sufficiently free of parameter fitting to be generally accepted.” Without a profusion of adjustable parameters, the LDM predicts *symmetrical* fission products and the shell model predicts fragments with “magic” numbers of protons and neutrons. Neither prediction is correct (despite what the textbooks assert), and has led to the development of hybrid models containing parameters that can be adjusted to fit the data. The most comprehensive modern study of asymmetrical fission is that of Möller and colleagues. In a computational *tour de force*, they concluded that “all of the observed fission phenomena [including the asymmetrical fragments] can be understood in terms of nuclear potential-energy surfaces calculated with five appropriately chosen nuclear shape degrees of freedom” in a 2.6-million parameter space. The inconclusive nature of such modeling, however, is apparent from the fact that the “appropriate” *post hoc* selection of parameters must be made in light of the experimental results [11]. Asymmetrical fission is *not predicted*, but rather *reproduced* by cherry-picking model parameters that give the desired results.

In contrast, we have shown that the FCC lattice model does not require any additional parameters to explain the *asymmetry* of Uranium fission fragments. The asymmetry is inherent to the scission of large, oblate nuclei along fission planes with the fewest “bonds” connecting the fragments. Similarly, we find that the *symmetrical* pattern of experimentally-known nuclear “ash” in Mizuno-style cold fusion studies is obtained from the same lattice-scission technique. We therefore conclude that the substructure provided by the nucleon lattice is a necessary addition to conventional nuclear structure theory and allows for an explanation of the masses of the fragments produced by both the thermal fission of Uranium and the nuclear transmutations detected in “cold fusion” experiments.

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Nuclear and Electronic Structure of Atoms

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Abstract. The plot of Extra Neutron number against the Z number of natural elements reveals a trend that shows the same periodicity observed in the chemical properties of elements. Nuclei appears to direct the electronic structure of atoms.

Different models of the nuclear structure have been proposed. When the electronic structure of atoms was elaborated, the nucleus only provided, with protons, a central positive charge to attract negative electrons [1].

The presence of a precise number of neutrons confers nuclear stability to selected isotopes of natural elements. The aim of the present work is to investigate whether a relationship exists between the number of Extra Neutrons ($EN=A-2Z$) in the nuclei of stable elements and the electronic structure of atoms.

Fig. 1 shows the number of EN in the nuclei of natural elements, plotted against the Z number. The weighted mean of EN for each element, calculated from [2], is reported. The electronic structure of atoms, the principal and azimuthal (letters) quantum numbers, and the atomic volumes [3] are also shown.

The addition of EN to nuclei with the increase of atomic Z number takes place with upsurges and pauses.

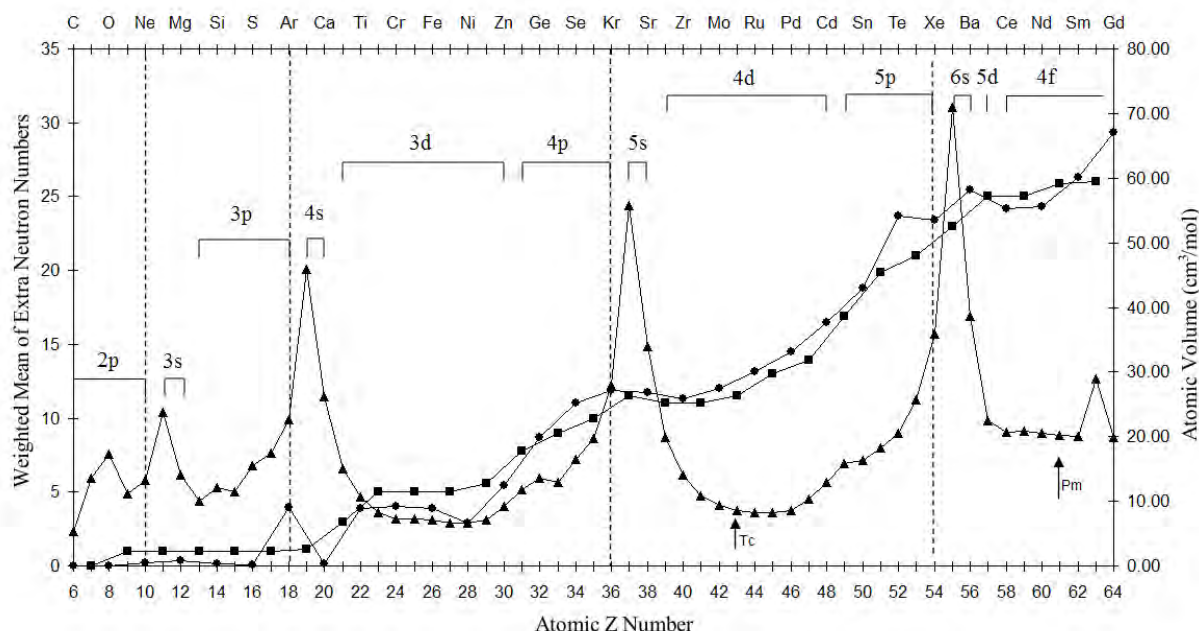


Fig. 1 - The figure shows, as a function of atomic Z number: 1) the weighted means of Extra Neutron ($A-2Z$) number for the isotopes of natural elements with even $\bullet$ and odd $\blacksquare$ values of Z; 2) The electronic structure of atoms, principal and azimuthal (letters) quantum numbers; 3) the atomic volume of atoms $\blacktriangle$.

Going from ${}_5\text{B}$ to approximately ${}_{64}\text{Gd}$, a sizable central share of the periodic table of elements, it is possible to single out four repetitive events (see also Fig.2) corresponding to the four sequences of electron additions: $2p \rightarrow 3s$; $3p \rightarrow 4s$; $3d \rightarrow 4p \rightarrow 5s$; $4d \rightarrow 5p \rightarrow 6s$. The sharp upsurges of EN addition to nuclei culminate at the completion of the six p electrons addition, leading to the electronic structure of the noble gases Ne, Ar, Kr and Xe. Following the noble gases, pauses of EN addition to nuclei, or even reductions in the number of EN, characterize alkaline metals and alkaline earths structures. Pauses extend somehow to 3d and 4d blocks. Hence, the trend of EN addition to nuclei of natural elements parallels the periodicity of the chemical and physical properties of elements, exemplified in Fig.1 by the values of the atomic volume. That is, EN addition to nuclei, a determinant of the stability of nuclear architecture, appears also as a determinant of the electronic structure of atoms.

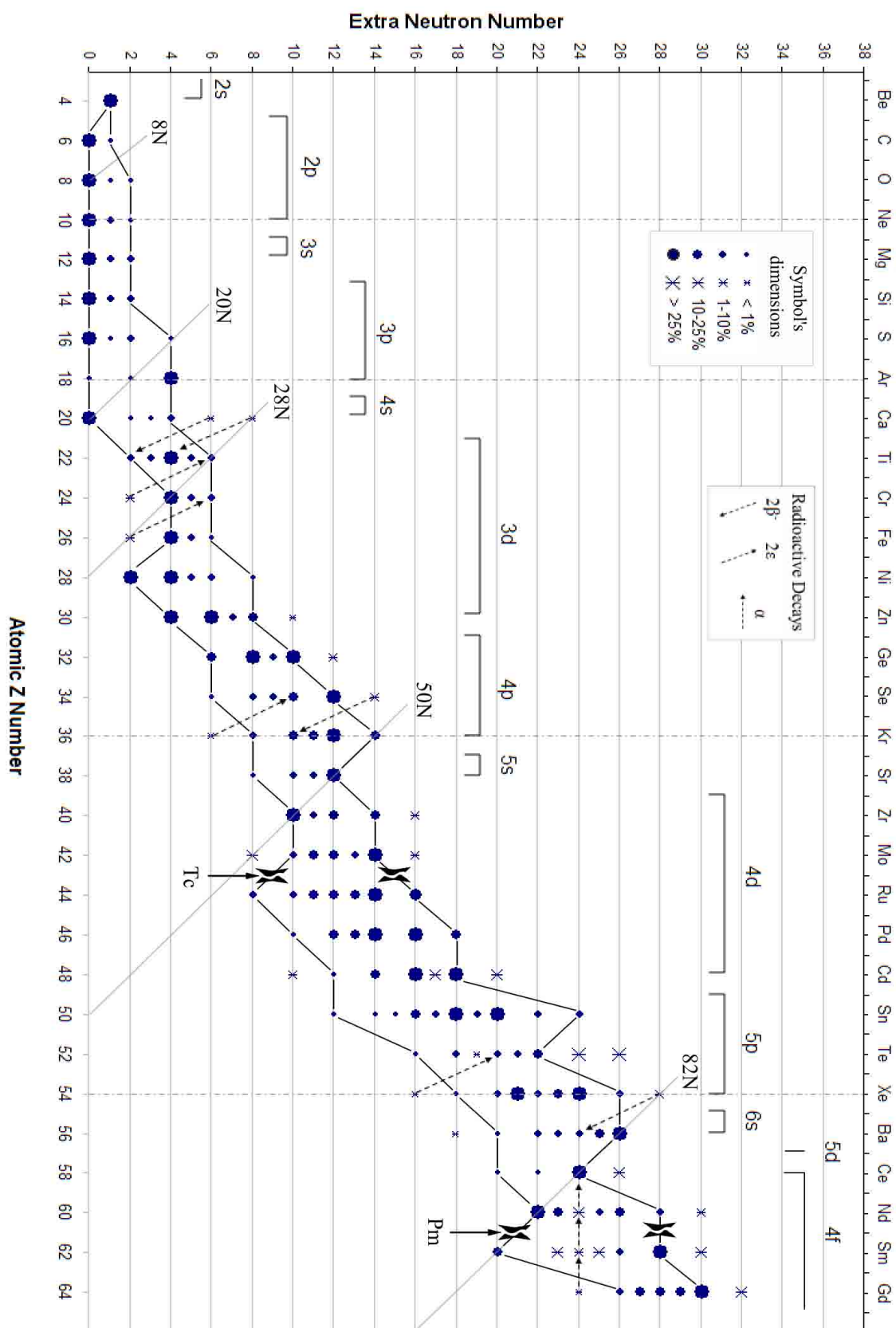
Moreover, the unstable elements Tc and Pm are both located seven places after the noble gases Kr and Xe. This can be read as a further link between the nuclear architecture and the electronic structure of atoms.

Fig. 2 shows the number of EN for the natural isotopes of each element [2] against Z number. Only the Z even elements are considered, a restriction not invalidating the substance of the present work. Lower and upper boundaries of the zone of stability of the isotopes of single elements are shown. Radioactive isotopes, even if extremely long lived, are distinguished from the stable isotopes and, for a few of them, the pathway of decay is shown. All decays lead to elements with stable isotopes inside the area of stability delimited by the two boundaries (Fig. 2). This may suggest that the existing natural radioactive isotopes have been frozen in such a state at the time and in the conditions of their nucleosynthesis, blocking an otherwise faster transformation to stable elements.

The trend of the lower and, in particular, that of the upper boundary of stability in Fig. 2, agrees with the trend of EN addition to nuclei presented in Fig. 1 and with the electronic structure of atoms. However, differences exist between the two boundaries suggesting that the lowest and the highest EN numbers, required for nuclear stability of the isotopes of single elements, may have different physical meanings. Inside the zone of stability all even mass atoms are stable, but several odd mass atoms are unstable (Fig. 2).

Table 1

Extra Neutron Number of Solar System Isotopes of different elements (Fig.2)	Total Trapped Nucleons in Solar System Isotopes of different elements (Fig.2)
0	9.780.897.635
1	5.253.208
2	13.943.984
3	12.118
4	48.644.906
5	1.115.578
6	290.119
7	3.367
8	52.588
9	1.069
10	6.308
11	849
12	7.953
13	91
14	1.665
15	24
16	240
17	55
18	193
19	44



The shell model of nuclear structure stems from the existence of magic numbers of nucleons (Fig. 2) that confer enhanced stability to particular nuclei. Moreover atoms with magic numbers of protons and or neutrons show enhanced natural abundance (n.a.). This is not always true. For example 28, a magic number of neutrons, shows its effect on ^{52}Cr (83.8 % n.a.) but fails to show a clear effect on ^{50}Ti (5.3% n.a.) and on ^{54}Fe (5.8% n.a.). Instead the isotopes of the above elements with the highest abundance are ^{48}Ti (73.72 n.a.) and ^{56}Fe (91.75 % n.a.) in spite of no magic neutron number in their nuclei. The mass of an isotope in Fig. 2 is obtained by the addition of its EN number to twice the value of its atomic number.

Inspection of Fig. 2 reveals that high natural abundance isotopes of different elements populate, in particular, the arrays with 0 and 4 EN.

This observation prompted the investigation of the Total Trapped Nucleons (TTN) in the nuclear species present in the arrays corresponding to single values of the EN number of Fig.2. Table 1 shows that 4 EN, and multiples of 4 EN in the nucleus, lead to enhanced Solar System Abundance (SSA) of the corresponding element's isotopes. Hence multiples of 4 EN appear to be a kind of magic numbers, at least up to 19 EN. This finding is particularly interesting in the case of ^{56}Fe , whose outstanding SSA does not find an explanation in the frame of classical magic numbers. TTN in a singular species was calculated as follows: TTN = SSA of an element, times the isotopic abundance of that species, times its atomic mass. SSA of elements, normalized to 10^6 atoms of Si, was obtained from [4].

One further consideration. Among the different periodic tables of elements [5], the one suggested in 1929 by the French biologist Janet [6], with an eight-period instead of the classical seven-period format, is in best accordance with the periodicity of EN addition to nuclei (Fig. 1 and Fig. 2).

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