Capacitive Deionization and Energy Storage

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27-28 June 2019  
San Giovanni in Monte Complex, Bologna, Italy
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International Workshop on Supercapacitor & Energy Storage

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NARRANDO, born as spin off of the University of Salerno, has developed a nano dosimeter for real time, *in vivo* measurement of radiation, based on graphene- or carbon nanotube modified electrode of a miniaturized ionization chamber. Main fields of application are radiotherapeutics and radiodiagnostics.

NARRANDO, has to date major know-how in the development of nanomaterials and nanomaterials-based devices for application in energy, environment, health, food, transportation, electronics, biotechnology.
FISCIANO, A SUSTAINABLE CAMPUS
CAPACITIVE DEIONIZATION AND ENERGY STORAGE

![Graph showing water resources and water per person]
With rapid population growth and ever-changing technology development, the increasing demand for water and energy is a major challenge worldwide.

The interdependence between water and energy (i.e., water–energy nexus) has been of great concern in recent years.

Conventional water desalination technologies (thermal-based processes and membrane-based processes, etc…) are energy intensive. Enormous efforts have been made to reduce the energy requirements for water desalination, especially for reverse osmosis (RO).
Electrochemical systems are mainly associated with energy storage, including batteries and supercapacitors.

Other electrochemical systems, such as capacitive deionization (CDI), have been identified as promising solutions for energy- and infrastructure-efficient brackish water desalination.

The capacitive water purification is based on capacitive deionization. CDI systems desalt feedwaters by applying electric fields.
Supercapacitors (SCs) address the need in energy storage devices with high capacitance, high power density, fast charge-discharge and long cyclic stability.

The research in SCs focuses on various aspects of supercapacitor principles, including advanced electrode materials, electrolytes, design and modeling.

A new wave of interest in the SCs technology is correlated to the application of SCs devices for capacitive water purification.
Desalinizzazione

**Processi a membrana**
- RO: Osmosi Inversa
- ED: Elettrodialisi

**Sistemi termici**
- MED: Distillazione multi effetto
- MSF: Distillazione flash multistadio
- MVC: Compressione meccanica mediante vapore
Scientific Publications (Scopus)
CDI & Energy Storage

1960 → CDI conceptual study

1970 → Ion absorption potential modulated and flow system concept

1995 → Application of carbon aerogel

2006 → Application of CNTs

2009 → MCDI theory

2009 → Application of graphene-based electrodes

2010 → Fe₃O₄-functionalized CNTs for As removal

2011 → Functionalized graphene for the removal of high concentrations of As

2012 → CDI and MCDI operating at constant current

2012 → Functionalized carbon nanotubes for the As and salts removal

2014 → Hybrid CDI

2015 → Inverted CDI

2016 → Water Desalination

2018 → Ion selectivity in CDI with functionalized electrode

2019 → Nitrate removal and recovery

2012 → Functionalized graphene for the removal of high concentrations of As

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Time gap
System detail.

- Ion migration to two electrodes with a high surface area under the action of a potential difference of 1-4 V.
- Energy is also accumulated.

Since the adsorption mechanism of CDI is the same as that of the electric double-layer capacitors for energy storage, except the electrolyte (brackish water, in the case of CDI) is flowing and cycling in the cell in most cases, the devices were initially called flow-through capacitors.

After the electrodes become saturated by salt ions, they can easily be regenerated either by reversing the potential between the electrodes or by shorting the circuit.
It has been demonstrated that CDI is a

• robust,

• energy efficient,

• and cost-effective technology for desalination of water with a low or moderate salt content.
CDI: MAIN ADVANTAGES

• It is not based on the concept of filtration to obtain water purification. It combines the benefits of ion exchange and reverse osmosis treatment (RO), eliminating the disadvantages, as well as removing the hardness, bad tastes and odors.

• It also removes the main pollutants present in water such as arsenic, phosphates, nitrates, mercury, chromium, cadmium, boron, hydrogen sulfide, chlorine and pesticides substances harmful to health.

• Heavy and expensive working conditions are not required, the technology works at low pressure and temperature.

• The CDI cells also accumulate energy, becoming a candidate for potential storage systems that, together with water purification, contribute to the development of the new generation of distributed electricity networks.
The equipment is eco-compatible, as it does not use chemicals.

It tends to reduce the bacterial load, avoiding the growth of colonies, the reduction can be estimated at 90%.

It does not require any special pre-treatment, as it is not affected by the presence of suspended solids - chlorine - organic substances.
Similarity CDI cell & EDLC supercapacitors

Both technologies:

• use nanoporous carbon electrode materials,

• operate within a limited voltage window bounded by the voltage for water splitting (ca. 1.2 V cell voltage)

• store ions in nanopore EDLs, and undergo charge/discharge cycling.

CDI cells store energy during desalinating and release energy during electrode regeneration (discharging).

CDI field has been supported by the parallel development of nanoporous carbons for supercapacitors.
Why nanocarbons as CDI electrodes?

- High specific surface areas.
- Exceptional mechanical, thermal and electrical properties.
- Cheap.
- Easy to prepare.
NARRANDO AND NANOMATES WERE CURIOUS OF CHECKING SOME ASPECTS

Literature comparison

- Nanocarbons, such as multi-walled carbon nanotubes and graphene, were studied for this application.

- Single or double-walled carbon nanotubes have never been studied.

- A systematic study of the effect of superficial functionalization is lacking.

- Low concentration studies are lacking.
Preparation of materials

**Catalysed chemical vapor deposition**
*Feed: CH$_4$/H$_2$*
- **Catalyst:** Co/MgO
- **T=1000°C, P=1 atm**
- **HCl to remove catalyst**

**Hummer’s method modified**
1. **Sulfuric acid:** partial exfoliation of graphite.
2. **Potassium permanganate:** functionalization.
3. **Water:** finish the functionalization reaction
4. **Hydrogen peroxide:** metal ions removal.

**Functionalization**
- **Part of functional groups removal by Thermal treatment 25-300°C P=1 atm**
- **CNTp**
- **CNTf**
- **CNTftt**
- **GO**
TEM Images

20 nm

2,5 nm

20 nm

XRD patterns

Raman Spectra

FT-IR Analysis

Cyclic Voltammetry curves of CNT in 1M H$_2$SO$_4$ aqueous electrolyte

\[ C = \frac{\int i \, dV}{u \, mV} \]

Cyclic Voltammetry

\[ \text{a} = \text{CNT}_{f}; \text{b} = \text{CNT}_{ft}; \text{c} = \text{GO} \]

NaCl aqueous solution, 1 mg/L

As aqueous solution, 1 mg/L
### Electrochemical results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific Area [m²/g]</th>
<th>Capacity [F/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>CNT_{f_{tt}}</td>
<td>540</td>
<td>356</td>
</tr>
<tr>
<td>CNT_{f}</td>
<td>595</td>
<td>298</td>
</tr>
<tr>
<td>GO</td>
<td>230</td>
<td>145</td>
</tr>
</tbody>
</table>

The measured capacitances are in the order: CNT_{f_{tt}}>CNT_{p}>CNT_{f}>GO in H₂SO₄

CNT_{f_{tt}}>CNT_{f}>CNT_{p}>GO in arsenite/arsenate and NaCl electrolytes.

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## Arsenic Removal

<table>
<thead>
<tr>
<th>MATERIA</th>
<th>INITIAL CONCENTRATION [mg/l]</th>
<th>AFTER CHARGING [mg/l]</th>
<th>EFFICIENCY [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO</td>
<td>2.15</td>
<td>1.4</td>
<td>34.8</td>
</tr>
<tr>
<td>CNTf</td>
<td>2</td>
<td>0.9</td>
<td>55</td>
</tr>
</tbody>
</table>
CDI evolution: systems and mechanism

The simplicity of CDI makes this approach very attractive as an alternative method to more classic approach for both static and mobile water desalination and purification applications.

To develop next-generation electrochemical systems for water desalination, it is convenient to take inspiration from the highly developed energy storage field.

As demonstrated by CDI cells, energy storage electrodes can be successfully applied as efficient water desalination electrodes (while maintaining their energy storage functionality).

A large and promising category for exploration are the materials that store ions via processes other than capacitively in charging EDLs, such as pseudocapacitive electrodes.
Input coming from sodium batteries studies

New materials to be investigated

Na2FeP2O7 as a Novel Material for Hybrid Capacitive Deionization

Seonghwan Kim, Jaehan Lee, Choonsoo Kim, Jeyong Yoon

*Electrochimica Acta, 203 (2016) 265*
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Thank you for your attention

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