Benchmark of the CPMD code on the CRESCO clusters in ENEA-GRID enviroment.

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Abstract. Hydrogen desorption from a hydride matrix is still an open field of research. For this purpose, we want to set up a numerical model to perform first principle calculations based on the density functional theory, using CPMD code. To evaluate the suitable computational demand, we performed benchmarks of the CPMD code on the HPC ENEA CRESCO computing facilities taking in to account also the energy cost issue.

1 Introduction

Recent research in terms of replacement of fossil fuels with alternative energy sources goes in favour of widespread use of hydrogen as an energy source. However, there are technological problems of hydrogen storage primarily for mobile applications, i.e. in the automotive industry. Storing hydrogen in gas cylinders and cryogenic tanks have safety problem due to high pressure and low temperature, respectively [1]. In the case of storage in a solid state, hydrogen is stored in the form of chemical compounds (metal/intermetallic and complex hydrides), or adsorbed on materials with large specific surface area, such as carbon nanostructures and nano-porous materials [2, 3, 4]. Solid state storage is the safest and the most effective way of hydrogen handling. However, this method for hydrogen storage has also disadvantages such as slow sorption process and high temperature of desorption in case of hydrides, and small volumetric density in solids with large specific surface area. Magnesium hydride (MgH_2) is attractive material for hydrogen storage since it has suitable properties like high gravimetric (7.6 wt%) and volumetric densities (130 kg H_2/m^3), abundance, low price and non-toxicity. However, this hydride has not found wide industrial application because of its stability (enthalpy of formation is -75 kJ/mol H_2) and high desorption temperature T_d=720 K, which give rise to slow hydrogenation/dehydrogenation kinetics. Various physical and chemical processes can be used to enhance MgH_2 formation by promoting destabilization of MgH_2 lattice or surface modification and/or structural deformation. Mechanical milling without or with additives, and using ion irradiation are some of the methods for destabilization of MgH_2 structure [5, 6, 7, 8]. The most commonly used additives are transition metals and transition metal oxides [9, 10, 11, 12]. A number of experimental studies confirm that the addition of TiO_2 has beneficial effect on destabilization of MgH_2 matrix and can cause improvement of kinetic properties of this material [13, 14]. Several numerical studies on hydrogen motion on and through titanium oxide sur-

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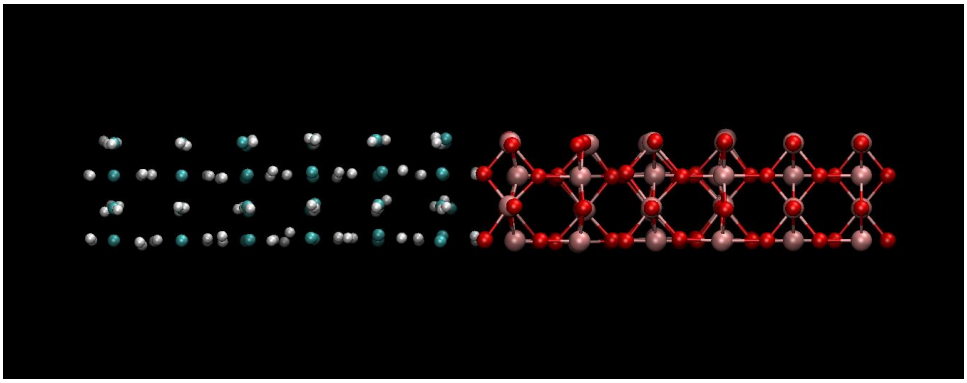

Figure 1: 1x1(110) slab supercell of MgH_2-TiO_2 interface after geometry relaxation. Mg atoms are in light blue, H atoms are in white, Ti atoms are in pink and O atoms are in red .

face has been done to understand the mechanism of the reaction [15, 16]. Namely, hydrogen interaction with TiO_2 surface is peculiar because the maximum H monolayer coverage on TiO_2 (110) surface is only 70% at room temperature, regardless of applied partial pressure of hydrogen, and during the heating of the hydrogenated sample, there no hydrogen desorption with temperature rise. The most probable cause is H diffusion into subsurface area. However, mechanism of the effect of TiO_2 on improving the kinetics properties of MgH_2 is still unknown. This is the reason why we performed numerical studies on MgH_2-TiO_2 interface. *Ab–initio* calculation based on density functional theory (DFT) implemented in Car-Parrinello Molecular Dynamics (CPMD) code was used [17, 18].

2 Computational details

CPMD code is an ab-initio electronic structure and molecular Dynamics (MD) program which uses a plane wave/pseudopotential implementation of DFT [19, 20]. In ab-initio MD simulation, the forces acting on atoms are calculated from an electronic structure calculation repeated every time step (on the fly). Thanks to electronic structure calculation which uses density functional methods, simulations of large systems with hundreds of atoms are now standard.

We use the CPMD compiled with Intel Fortran Compiler, MKL (Math Kernel Library), ACML (AMD Core Math Library) and MPI (Message Passing Interface) parallelization on the high performance ENEA CRESCO computing facilities [21]. We tested the CPMD code by using the system representing a MgH_2-TiO_2 interface constituted by 48 atoms of Ti and Mg, and 96 atoms of O and H. The whole system was consisted of 288 atoms. For all the calculations we employed the CPMD code with Martins-Troullier norm-conserving pseudopotentials for all atoms, together with The Perdew-Burke-Ernzerhof exchange-correlation functional [22, 23]. The electronic wave functions are expanded in a plane-wave basis set with a kinetic energy cut-off equal to 80 Ry.

3 Results and discussion

Slab supercell of TiO_2 and MgH_2 surface was constructed by 45 degree rotation of rutile TiO_2 (or rutile MgH_2) unit cell around x-axis in order to expose its (110) plane. This cell was extended in x-direction, containing 12 atomic layers A void region was on each side of the surface preventing the interaction between the external free surfaces. The final supercells parameters were $L_x = 50.4$ Å, $L_y = 12.6$ Å, and $L_z = 6.0$ Å. Two outer layers in TiO_2 slab, and two outer layers in MgH_2 slab were fixed playing the role

Table 1: Some of the hardware and software characteristics for the CRESCO clusters.

cores	CRESCO4	CRESCO3	CRESCO2a	CRESCO2b
Processor	Intel E5-2670	AMD 6234TM	Intel E5530	Intel E5345
Clock (GHz)	2.6	2.4	2.4	2.33
TDP (W)	115	115	80	80
Cores for node	2×8	2×12	2×4	2×4
RAM for node (GB)	64	64	16	16
Compiler	Ifort 14.0	Ifort 12.1	Ifort 11.0	Ifort 11.0
MPI Flavour	OpenMPI 1.4.3	OpenMPI 1.5.4	OpenMPI 1.2.8	OpenMPI 1.2.8
Math. Lib.	MKL 11.0	ACML 5.3.0	MKL 11.0	MKL 11.0

of bulk. TiO_2-MgH_2 interface was constructed using fully relaxed TiO_2 and MgH_2 surfaces (see Fig.1). Distance between internal surfaces was varied until the reaching the minimum of total energy of whole system. TiO_2 and MgH_2 have the same crystal structure with similar cell parameters and tailoring of interface should be with minimal strain. Total energy of the surfaces and interface was used to calculate work of adhesion W_a for TiO_2-MgH_2 interface and calculated value is $W_a = 991.66$ J/m^2.

Molecular dynamics calculation was performed from 300 K to 1000 K in step of 100 K. Hydrogen desorption from MgH_2 started at 1000 K, which is in agreement with experimental results.

To evaluate the computational cost of our simulations, some tests have been performed using the physical system previously described on the CRESCO clusters in the ENEA-GRID enviroment. Some of the hardware and software characteristics for the CRESCO clusters are reported in Tab. 1. Further details on ENEA-GRID computational infrastructure are in Ref.[21]. We checked the average time spent to perform a single step of MD simulations using different CRESCO clusters (see Tab. 2 and Fig. 2) and varying the number of cores utilized. From the data it is evident that CRESCO4 has the best performance independently from the number of cores. Moreover, in Fig 3a) we compared the data relative to the case in which 96 cores are used. It is highlighted how the times raise considerably changing the CRESCO cluster. Making a comparison respect to the CRESCO4 time, there is an increase of about 160% for the CRESCO3, and an increase of about 195% for CRESCO2a. Even more evident (340%) is the deterioration of the performance for the case of CRESCO2b.

Another important point to take in consideration is the energy consumption issue. For this reason we evaluated the power cost for a single MD step. In panel b) of Fig 3 we showed the energy cost for a MD step taking into account that 96 cores correspond to 12 cpus for CRESCO4, 8 cpus for CRESCO3, and 24 cpus for CRESCO2a and CRESCO2b. The different number of cpus utilized changes the evaluation on the CRESCO clusters. CRESCO4 is still the energetically most advantageous choice, however CRESCO3 is a viable alternative, the energy consumption raise is only 75%. On the contrary the CRESCO2 clusters are less energetically favorable choices, in fact they are more slow, and in addition, having each processor four cores, the number of cpus used is 24. This produce an increase of the energetic cost of about 300% and 500% compared to CRESCO4 case.

In conclusion, we performed benchmarks of the CPMD code to evaluate the performance on the HPC CRESCO computing facilities. The benchmarks reveal that CRESCO4 has the best outcome on both time and energy cost,

Table 2: Average time (s) for one MD step for different number of cores and for different CRESCO clusters.

cores	CRESCO4	CRESCO3	CRESCO2a	CRESCO2b
24	-	98.5	-	-
32	19.61	-	-	-
48	13.66	40.8	28.7	-
96	7.22	19.0	21.2	31.8
120	-	16.7	-	-
128	6.74	-	23.6	29.3
240	4.92	10.1	35.5	36.7
480	3.58	7.8	-	12.1
960	2.66	6.3	-	-

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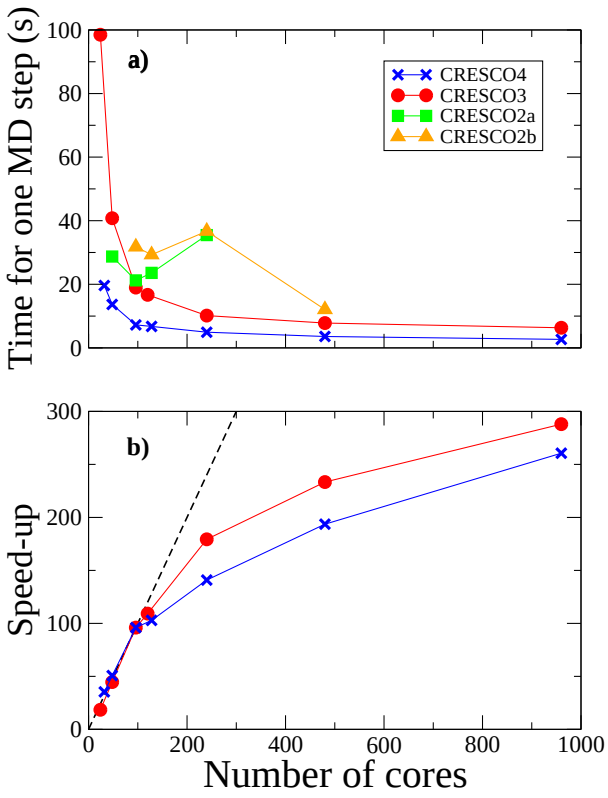

Figure 2: a) Average time for one MD step for different CRESCO clusters. b) Speed-up for CRESCO4 and CRESCO3 clusters.

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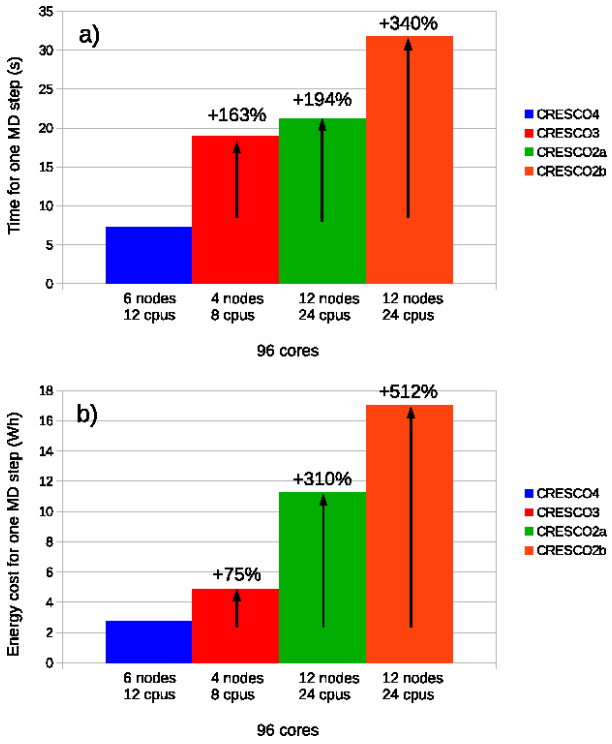

Figure 3: Average time (panel a) for one MD step for different CRESCO clusters using 96 cores and the corresponding energy cost (panel b).

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