

Workshop Scientific Report

Title: Simulations and Experiments on Materials for Hydrogen Storage

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Scope of the workshop (1-2 paragraphs):

The main objective of the workshop is to discuss computational and experimental challenges in the field of solid state materials for hydrogen storage. Particular attention is paid to methodological aspects, such as the accurate calculation of the phase diagram of molecular solids, the simulation of thermally activated processes (that might occur through very complex mechanism in these materials), the inclusion of nuclear quantum effect on hydrogen atoms.

Main outcome of key presentations (one page):

This section is divided in two parts. In the first part we report about the result of (mainly) simulations and experiments as they emerged from the presentations. In the second part we summarize the most relevant conclusions about theoretical and methodological aspects.

Computational and experimental results on materials for hydrogen storage.

Materials of interest for hydrogen storage can be classified in four groups: metal hydrides and hydrides of complex alloys, Metal Organic Framework (MOF), carbon nanostructures and hierarchical materials. The main questions addressed by simulations and experiments are: the maximum content of hydrogen and how to improve it (i.e. material engineering), the thermal stability of the materials and how to improve it (must be such that the uptake and release can occur in the range of usability for 'on board' applications, i.e. $\sim 5-150$ °C), the mechanism of the reaction of uptake and release of hydrogen, including the diffusion of the H_2 gas and the other intermediate species in the sample.

Metal hydrides: A useful way to characterize a metal hydride is the temperature at which the material is in equilibrium with 1 bar of H_2 , i.e. the temperature at which the DG of the reaction $MH_n \leftrightarrow MH_{n-2} + H_2$ is zero. In the engineering of new materials this question is inverted and one asks what is the material which is at the equilibrium with 1 bar of H_2 at a temperature T in the range 50-150 °C. No hydrides of light metals satisfy this condition. On the contrary, in the field of alloy hydrides, $LiBH_4$ is a very promising material.

Carbon Nanostructures: The consensus is that the maximum hydrogen content at operational conditions for the carbon nanostructured materials investigated so far is too low. The importance of quantum effects on the maximum hydrogen content in graphene sheet and graphene bilayers was discussed with negative conclusion.

Metal Organic Framework : It was reported that a particular structure of $\text{Ti}_{12}\text{C}_{60}$ (i.e. Ti-doped C_{60} fullerene) has a theoretical gravimetric hydrogen content as high as 13%. Unfortunately, the most stable $\text{Ti}_{12}\text{C}_{60}$ structure is a different one in which the Ti atoms are clustered and, as a result, the maximum hydrogen content of a material based on $\text{Ti}_{12}\text{C}_{60}$ would be much smaller. Two possibilities have been proposed to overcome this problem: i) to replace Ti with Ca, which has a lower tendency to clusterize, and ii) to anchor Ti, the active component for the H_2 binding in $\text{Ti}_{12}\text{C}_{60}$, on another substrate on which the clustering does not occur, e.g. on silica.

Hierarchical materials: These materials are made of molecules containing (releasable) hydrogen that can form a crystal containing cavities that, in turn, host hydrogen molecules. Depending on the nature of the chemical species forming the crystal, the hierarchical materials can have a hydrogen content of up to $\sim 20\%$ in hydrogen. Moreover, thanks to the ready releasable hydrogen contained into the cavity, the overall kinetics of dehydrogenation is very convenient. One typical hierarchical material is NH_3BH_3 , that forms a clathrate structure containing hydrogen in the cavities. One major problem of this class of materials is that they are usually formed under extreme conditions (very high pressure). One solution presented in the workshop was to operate under tensile instead of hydrostatic conditions (i.e. at 'negative' pressure). Simulations have shown that these materials might become stable at moderate conditions under tensile stress.

Methodological challenges in the simulation of materials for hydrogen storage.

The main challenges in the modeling of materials for hydrogen storage and reactions/processes occurring in them are of three kinds: i) identification of the most stable structure of a sample at a given stoichiometry, ii) accurate calculation of the phase diagram of a given material, iii) determination of the dehydrogenation mechanism and kinetics. Of course most of these challenges are common to other application domains. However, some features of the materials and reactions of interest in this field make it possible to develop techniques targeted to hydrogen storage. For example, the PEGS method is designed to identify the most stable structure in alloy hydrates. Since these alloys are made of negative AHn^{m-} and B^{m+} units, where A and B are the two chemical elements forming the alloy, a reasonable approximation consists in approximating the material as composed of two particles with an effective charge m^- and m^+ (indeed, the method is not limited to binary alloys). A set of metastable structure is identified using this approximation and then refined via DFT. Finally, the most stable structure is identified by comparing the free energy of the structures identified following the method summarized above (here only the vibrational entropy is taken into account to compute the free energy of a structure).

A relevant problem in the calculation of phase diagram and simulation of chemical reaction is to perform simulations of solid state materials with a very high accuracy. In fact, while DFT, very often used in solid state calculations, is quite accurate for the determination of the atomic structure, usually it is not enough for the determination of the relative stability of different phases of a material or states of a reaction. More accurate hybrid functional and Meta-GGA functionals are becoming available in periodic DFT packages but they are still

computationally very expensive. Moreover, for some of the materials mentioned in the previous section, also Van der Waals interaction must be included in the force model which raises the question: can DFT-D provide a reliable solution to this problem? Typical methods of quantum chemistry, such as Coupled Cluster or other post-Hartree-Fock methods, are also used in this field. However, these methods are too expensive to be used in combination with methods for exploring the configurational space for the identification of new phases/metastable states or reaction paths. Therefore, quantum chemistry methods can be used only in those cases in which relevant structures are known from experimental data or less accurate methods.

One relevant question remained essentially unaddressed in the presentations, that of the simulation techniques for modeling hydrogenation/dehydrogenation processes. The problem in this case is twofold. First, identifying the relevant degrees of freedom to describe, in a coarse grain representation, these chemical reactions is very complex as, in solid state, the process might be collective, i.e. might involve many chemical units. Second, the complete process consists in the combination of the dehydrogenation reaction and the diffusion of H₂ and the other products of the reaction in the sample. The two steps are characterized by very different free energy surfaces. Chemical reactions are typically characterized by a single high free energy barrier, while diffusion processes are characterized by many not-too-high free energy barriers. Unfortunately, typically simulation methods address either one or the other problem.

To what extent were the objectives of the workshop achieved? (one paragraph at least)

Due to the absence of some of the originally invited speakers, not all the topics that we had planned to address were discussed in detail. In particular, there was little chance to discuss the state of the art and make progress on the issue of simulating hydrogenation/dehydrogenation processes. Another topic that was not discussed in detail was the development/use of classical or semi-empirical force models to perform large-scale simulations.

In spite of these omissions, however, most of the objectives of the workshop were achieved. First of all, it was a very good opportunity to put in contact the experimental and computational communities. They have presented to each other their results and discussed what each community expects from the other in order to progress. In particular, it came out that experiments need simulations to obtain an atomistic level interpretation of their data as they give only an indirect evidence of what is occurring at the microscopic level, and there are not simple models to interpret it. At the same time, theoreticians need hints from experimental data to set up simulations and to eliminate unreasonable possibilities in the reaction mechanism. In fact, neither brute force nor advanced sampling techniques available nowadays are adequate for modeling the most relevant processes in this field without an *a priori* knowledge of some minimal facts that can drive the computational investigations. Examples of these facts are, for example, the presence/absence of specific intermediate states. Finally, this

workshop was a good chance to confront different techniques used to address similar questions both in the computational and experimental domain.