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Nanomaterials for solid state hydrogen storage

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Abstract

A short review of the materials under investigation suitable for solid state hydrogen storage is presented, with emphasis on the experimental activity carried out at the laboratory of Hydrogen Group of Padova University.

1. The problem of hydrogen storage

In the last years, the international interest towards the development of hydrogen based technologies, particularly the area of fuel cell electric vehicles, is greatly increased. The more and more alarming news about climate changes caused by fossil fuels and, moreover, the technological advances of fuel cells,

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particularly the so called PEMFC (proton exchange membrane fuel cells), have contributed to this interest. In a fuel cell hydrogen reacts electrochemically with oxygen producing electricity (and heat). The efficiency of process can be 50-60%, more than twice that of a thermal cycle, and the exhaust produced is only pure water. Hydrogen can be employed as a fuel even in current internal combustion engines, where it burns quickly with atmospheric oxygen. However, the efficiency of the conversion from chemical to mechanical energy is limited by the typical efficiency of a thermal engine which doesn't exceed 25%. There are many problems to be solved before ~~to see~~ a large scale marketing of technologies related to hydrogen as an energy vector.

Besides the lack of infrastructures for hydrogen (production, distribution, refuelling, etc.), very important is the problem of hydrogen storage for vehicular applications. Hydrogen can be stored as compressed gas in high pressure cylinders, as liquid hydrogen in suitable cryogenic tanks, or in solid state as in metallic hydrides or in materials suitable to retain it in considerable quantities, as alanates, amides and imides. Even if the use of high pressure cylinders is simple and inexpensive, it presents serious problems of size, weight and safety. A tank of liquid hydrogen concentrates a larger quantity of hydrogen in the volume unit, but involves problems related to refrigeration costs, safety, manipulation and losses by evaporation.

The use of solid absorbers such as metallic hydrides allows volumetric densities comparable or higher than liquid hydrogen and doesn't imply particular risks. However, the weight of the retaining material is very high compared to the weight of stored hydrogen. Moreover, it is necessary to have materials which can be easily loaded with hydrogen and which release it in a controlled way under acceptable pressure and temperature conditions. These are ~~therefore~~ the problems to which nowadays much interest is addressed, with the consequent start of cooperations between research institutions, industries of oil, industries of production and distribution of energy and technical gases. ~~These researches are often carried out in collaboration in the frame of national and international research projects.~~

2. Metallic hydrides

~~It is known that~~ some metals and alloys are able to absorb chemically hydrogen and then to reversibly release it. The thermodynamic aspects of hydride formation from gaseous hydrogen are described by the PCI (pressure-composition isotherm) curves as shown in Fig. 1 (left). These curves are obtained in the following way. At a given temperature and with a low hydrogen pressure, the host metal begins to dissolve a small quantity of hydrogen in solid solution (α phase), after the dissociation of the H_2 molecule into atomic hydrogen at the surface of the material. When the pressure increases,

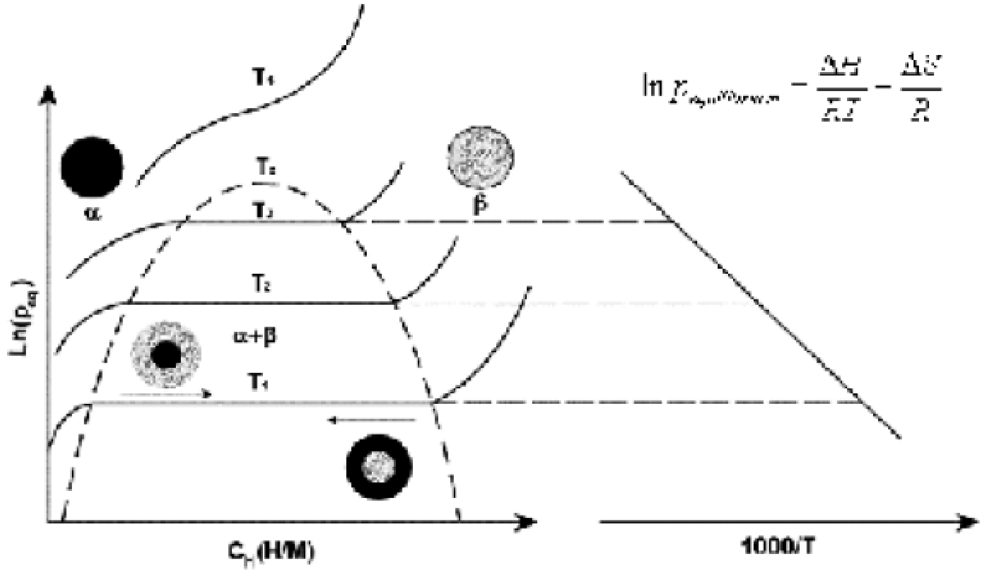

Figure 1. Schematic representation of pressure-composition-isotherms (left) of a typical hydrogen absorption or desorption process and corresponding van’t Hoff plot (right).

the hydrogen concentration in the metal undergoes small increments and then the local interactions between hydrogen atoms become more and more important up to the nucleation and growth of the hydride phase β. As long as the solid solution and the hydride coexist, the isotherm curves (hydrogen pressure at a given temperature as a function of hydrogen concentration in the material) present a plateau; the length of this plateau represents the hydrogen amount which can be reversibly stored at that temperature by small pressure changes. When the α→β transition is completed, the hydrogen pressure begins again to sharply increase with the concentration. ~~Higher~~ is the temperature shorter is the length of the pressure plateau. The region of the diagram in which the two phases coexist ends at a critical point T_C, over which the α→β transition is continuous. The equilibrium pressure (position of the plateau) strongly depends on temperature and is related to the enthalpy and entropy changes, ΔH and ΔS respectively, by the Van’t Hoff relation, reported analytically and graphically in Fig. 1 (right).

The enthalpy changes related to the hydride formation or dissociation, ~~then,~~ can ~~obtained experimentally~~ from the slope of Van’t Hoff's plots. While the enthalpy term depends on the metal-hydrogen bond stability, the entropy term corresponds essentially to the transition from molecular hydrogen to atomic hydrogen, necessary for the passage from gaseous to solid phase and is similar for all the known hydrides. The working temperature of a metal/hydride system is fixed by the thermodynamic equilibrium pressure and by the overall reaction kinetics. In order to make metal hydrides interesting for the use in hydrogen reservoirs, the working pressure and temperature should be in the ranges 1-10 bar and 20-100 °C, respectively, corresponding to an enthalpy change between 15 and 24 kJ/mol of hydrogen. A further problem, already mentioned, concerns the weight of the absorbing material, thus light metal hydrides containing an high amount of hydrogen are preferable. Table I presents some features of the main hydrides studied so far [1]. The reported values of hydrogen capacity by weight and the temperatures at which the plateau pressure is 1 bar are typical of the different AB5, AB, A2B hydrides ~~of which in the table are given examples, together with the Mg hydride.~~

Figure 2 shows as an example the characteristics measured (at Padova laboratory, unpublished) of a $MmNi_{4.7}Al_{0.3}H_6$ hydride (Mm=mischmetal, a La-based natural mineral) which is a particular AB_5 type system. The PCI curves evidence the typical low hydrogen capacity (1.3 wt %) of this kind of materials, according to the previous table. It is to be noted that by rising the temperature, the plateau pressure increases and the curve loses its flatness. A kind of hysteresis can be noticed between the absorption and desorption curves at the same temperature. The hysteresis is originated by strain and disorder of

Table I. Characteristics of some of the most studied hydrides.

Metals	Hydrides	Hydrogen capacity (wt %)	T for 1 bar (°C)
$LaNi_5$	$LaNi_5H_6$	1.37	12
FeTi	$FeTiH_2$	1.89	–8
Mg_2Ni	Mg_2NiH_4	3.59	255
Mg	MgH_2	7.60	279

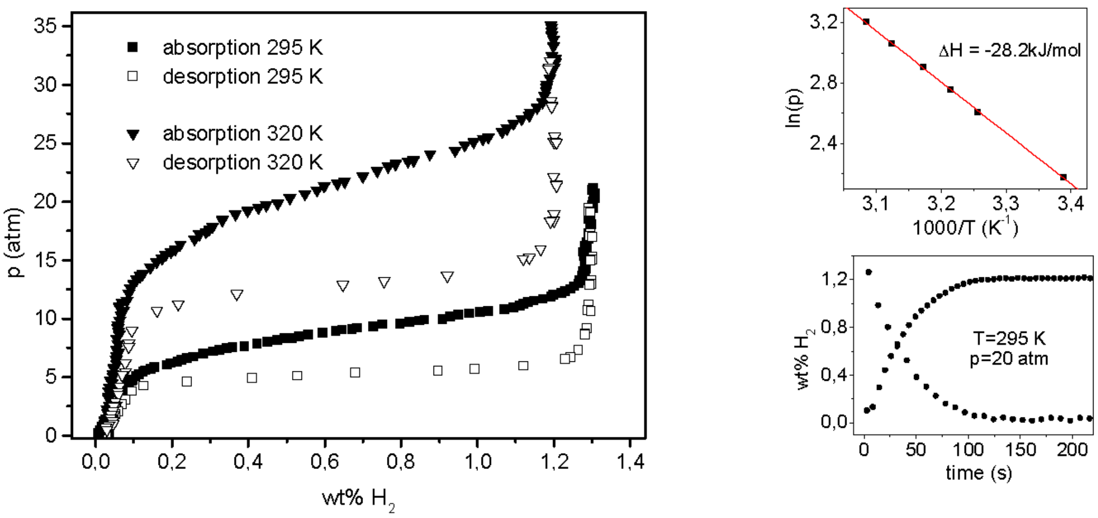

Figure 2. Characterisation of the $MmNi_{4.7}Al_{0.3}H_6$ hydride (Mm=mischmetal): pressure composition isotherms (left), Vant'Hoff plot for desorption process (right up) and absorption/desorption kinetics (right down).

the hydride phase lattice, due to expansion during absorption, higher if compared to relaxed strain and disorder during desorption: higher strain and disorder increase the plateau pressure, which is lowered by their relaxation. On the right side at top it is shown the van’t Hoff plot deduced from a number of PCI data, ~~by which it is possible to evaluate the ΔH of the reaction.~~ Besides the mentioned thermodynamic aspects, also the hydrogen absorption and desorption kinetics, i.e. the rate at which these processes occur, have a primary importance for practical applications. Figure 2 (right down) shows that for this AB_5 system the reaction kinetics is very favourable, because the absorption and desorption times are very short.

Recently, hydrides of AB_5 (e.g. $LaNi_5$), AB (e.g. FeTi), AB_2 (e.g. ZrV_2) and A_2B (e.g. Mg_2Ni) types alloys have been commercialized and are supplied in special vessels. AB_5 alloys absorb quickly and reversibly hydrogen at a pressure of few bars at room temperature or close to it. Moreover, they stand repeated cycles of absorption/desorption without loss of storage capacity [2]. Their weak point is the low weight percent of stored hydrogen (less than 1.5), which makes the reservoir too heavy. Among the goals that, according to the U.S. DOE (Department of Energy), should be achieved within the 2010 with the materials used for hydrogen storage, there are a hydrogen weight percent equal to 6 and an operating temperature lower than 80 °C. Therefore, the AB_5 alloys are not ideal for the use in an hydrogen reservoir, while they are more suitable as electrodes in a fuel cell [3]. The Fe-Ti alloy, studied since the 70’s and cheaper than the $LaNi_5$ alloy, forms the hydrides FeTiH and $FeTiH_2$ [4]. It allows absorption and desorption operations in thermodynamic favourable conditions, but it requires a too high activation temperature and the weight percent of stored hydrogen (less than 2) also in this case is too low. AB_2 alloys present, with respect AB_5 alloys, a better reaction kinetics and a lower cost, but are more sensitive to contaminants. Mg_2Ni alloy has a higher hydrogen capacity (up to 3.6 wt%), but the required working temperature for absorption and desorption reactions is higher than 200 °C. As a conclusion, none of the up to now studied hydrides presents at the same time all the required characteristics for the practical functionality of a hydride-based hydrogen reservoir. The worldwide research is addressed to an hydride with a low ΔH and having, at the same time, good reaction kinetics and high gravimetric hydrogen capacity.

3. New light metal hydrides

An high weight percent of stored hydrogen can be achieved only by using light elements like magnesium, which forms the hydride MgH_2 with a theoretical hydrogen capacity of 7.6 wt% [5]. The use of magnesium presents two main difficulties. First, due to the high stability of Mg-H bond, the plateau pressure of the system is too low in the temperature range of applicative interest (it is only 0.36 mbar at 100 °C). In order to get desorption pressures near atmospheric, it is necessary to raise the temperature to about 300 °C. Moreover, even at 300 °C the hydrogenation and dehydrogenation reactions are extremely sluggish. It has been shown that the use of nanostructured magnesium hydride produced by high energy milling is more convenient than the massive material [6]: the presence of sub-micrometric grains reduces the hydrogen diffusive path in solid phase and the high concentration of defects and grain boundaries offer preferential paths for gas escape and also nucleation sites for metallic Mg. Good absorption and desorption kinetics were achieved around 230 °C by milling metallic magnesium or its hydride with or without the addition of catalysts [7-10].

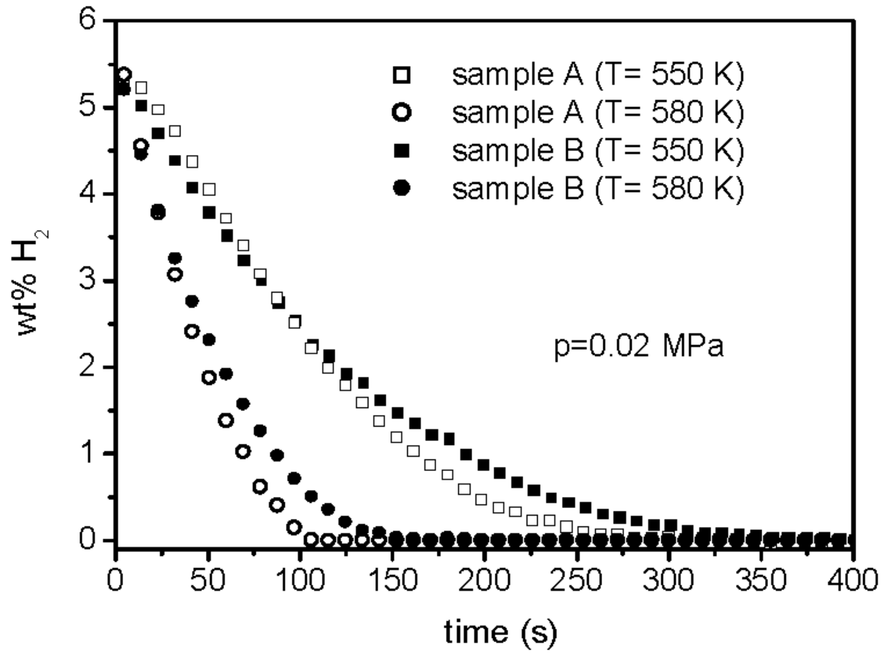

Figure 3. Hydrogen desorption kinetics at 550 and 580 K under a hydrogen pressure of 0.02 MPa for samples A and B (see text).

Several studies have been carried out also in our laboratory on nanostructured Mg hydride, both as thin films ion-beam implanted with V and Pd [11] and as ball milled powders with a variety of additives: graphite [12], Nb_2O_5 [13], La_2O_3 [14], Fe and Fe_2O_3 [15]. In all these studies the additives can improve the kinetics, but are unable to ~~diminish~~ the too high hydrogen dissociation temperature of the Mg hydride. In addition to the mentioned systems, magnesium-rich Mg-Ni-Fe intermetallic compounds have been prepared [16,17] by two different ~~routes~~: a) short time ball milling of ribbons obtained by melt spinning (sample A); b) long time ball milling of a mixture of

MgH_2, Ni and Fe powders (sample B). The first type of samples displays an hydrogen desorption kinetics better than the second one, as shown in Fig. 3. Pressure composition isotherm measurements of Fig. 4 exhibit for both type of samples two plateaux, the lower and wider corresponding to the MgH_2 phase and the upper and shorter corresponding to the Mg_2NiH_4 phase. The presence of the two types of hydrides is confirmed by X-ray diffraction analysis [16]. Mössbauer spectroscopy [17] shows that in melt spun and subsequently milled samples iron is mainly in a disordered structure and segregates after hydrogenation, while in directly milled powders remains mainly unalloyed. After multiple hydrogen absorption/desorption cycles the main part of iron is in metallic state in samples of both types, those of first type preserving better hydrogen desorption kinetics.

The absorption and desorption kinetics of MgH_2 doped with Nb_2O_5 [13] are about 2-3 times slower than for Mg-Ni-Fe type materials, but are acceptable for some practical applications at temperatures not higher than 573 K. Moreover, the maximum hydrogen content is higher: more than 6.0 wt% against 5.1÷5.4 wt%. A two stage metal hydride reservoir has been designed [18] consisting on a primer stage with 0.5 kg $LaNi_5$ and a main stage with 1.6 kg MgH_2 doped with Nb_2O_5 distributed in 6 vessels of 270 g each. Taking into account the need to heat the MgH_2 for hydrogen dissociation, the net hydrogen amount useful to feed the fuel cell is 3.8 wt%. This reservoir can feed a fuel cell to run an electric engine of 1kW for 1h suitable for a very light vehicle. A schematic view of such reservoir is reported in Fig. 5.

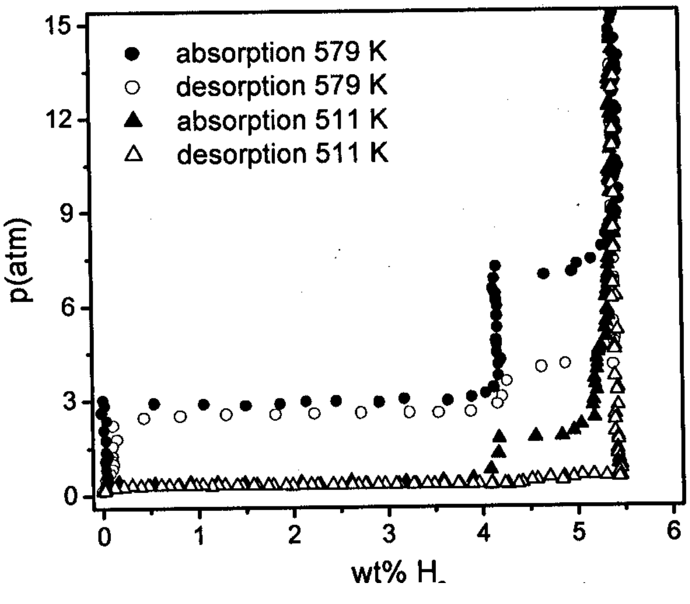

Figure 4. Pressure-composition isotherms (PCI) at 579 and 511 K, in absorption and desorption mode for sample A. The lower plateau corresponds to MgH_2 and the upper one to Mg_2NiH_4.

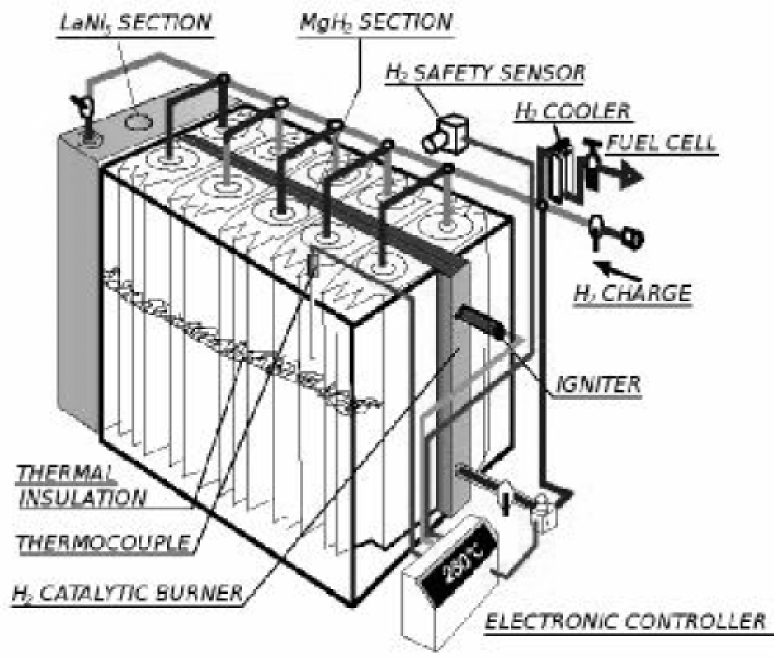

Figure 5. Functional two stage metal hydride reservoir (schematic). The main stage is made by a number of vessels filled with doped MgH_2, while the primer stage is filled by $LaNi_5$ hydride.

Alanates like $NaAlH_4$ have a relatively high hydrogen weight capacity, but present reversibility problems and not low enough decomposition temperatures (more than 150°C are required for hydrogen release). These materials are promising because the addition of some suitable catalysts makes reversible the hydrogen absorption/desorption reaction at lower temperatures [19]. Materials of this type are under investigation also at Padova laboratory.

New materials are also under investigation in some laboratories [20], as the so called complex hydrides, interesting because of their light weight and a ΔH value lower than that of MgH_2. Figure 6 shows preliminary results obtained in our laboratory on the nanostructured $1.1MgH_2 + 2LiNH_2$ complex hydride prepared by ball milling [21]. It is evidenced that a considerable high plateau pressure is reached at temperatures lower than for MgH_2: the obtained value of ΔH = -40 kJ/mol allows a plateau pressure of about 40 bar at 493 K and, by calculations, a plateau pressure of 1 bar at about room temperature, with a hydrogen capacity of about 4.5 wt %. These thermo-dynamic characteristics are very good in the present panorama, even though the absorption kinetics should be improved with suitable catalysts. Work is in progress with this purpose.

Besides the experimental work, a phenomenological study on the nature of hydrogen bond has been performed by our group on the $LaNiSnH_2$ and NdNiSnH hydrides [22]. A Mössbauer structural characterization of the same two systems is reported in [23].

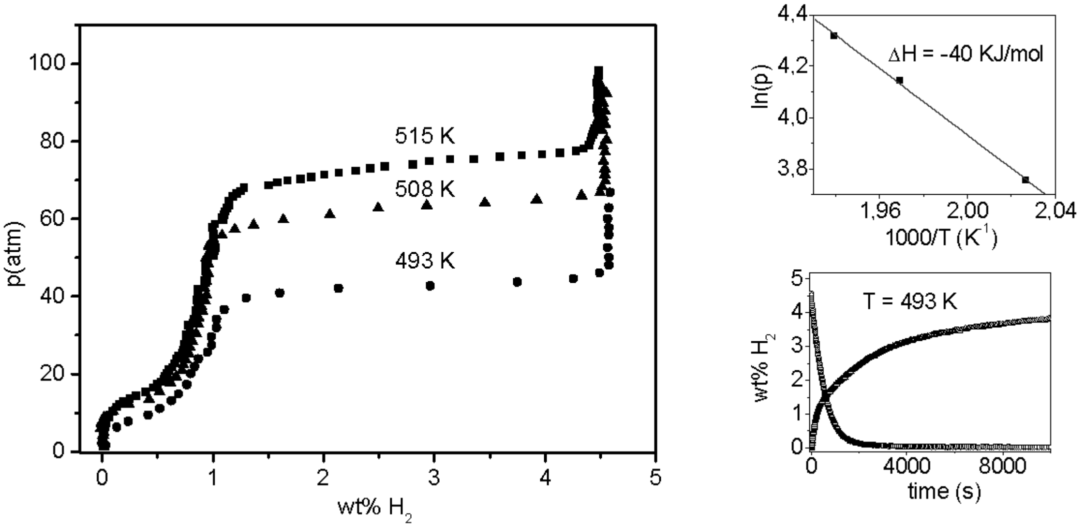

Figure 6. Characterisation of the $1.1MgH_2 + 2LiNH_2$ complex hydride: pressure composition isotherms in desorption mode (left), Vant'Hoff plot (right up) and absorption/desorption kinetics (right down).

Conclusions

The research on new materials for solid state hydrogen storage indicates that up to now none material presents at the same time all the required characteristics for practical applications on a large scale. Nevertheless, niche applications are already possible. Moreover, many innovative systems are promising enough to justify active research in the next years, in order to offer to the market efficient, safe and possibly cheap hydrogen reservoirs.

Acknowledgements

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