Nanomaterials for hydrogen storage: renewable and clean energy

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Abstract

In recent years, the search of renewable and clean energy attracted great attentions from politicians as well as scientists, due to several factors including global warming, health problems and oil prices. Hydrogen is very promising as clean and renewable energy resource; therefore its use will improve significantly air quality, health as well as prevents global warming, caused by fossil fuels. Hydrogen have been stored as pressurized gas (high pressures vessels and risk of explosion) and as liquid using cryogenic vessels (energy of liquefaction, leaks), or an atomic "solid", e.g. in the form of a hydride (high density, reversible, safe).

Hydrogen Storage Materials (HSM) synthesized at the nanoscale regime attracted great attention in recent years due to their high hydrogen capacity and improved thermodynamic properties. In this paper, several types of materials will be presented and discussed in terms of synthesis, characterization and their corresponding thermodynamic properties (hydrogen capacity, desorption temperature, kinetics, etc), including conventional intermetallic hydrides ($LaNi_5$, FeTi), Mg-based materials, carbon nanostructures and finally light complex hydrides.

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1. Introduction

In recent years, the search of renewable and clean energy attracted great attentions from politicians as well as scientists, due to several factors including global warming, health problems and oil prices. Hydrogen is very promising as it is clean and renewable energy resource; therefore its use will improve significantly air quality, health as well as prevents global warming, caused by fossil fuels. Hydrogen have been stored as pressurized gas (high pressures vessels and risk of explosion) and as liquid using cryogenic vessels (energy of liquefaction, leaks), or an atomic "solid", e.g. in the form of a hydride (high density, reversible, safe) [1]. Depending on the type of the technological application (stationary, mobile, etc), the thermodynamic properties must be optimized to the optimum operating values: H_2 storage capacity (storage density), dissociation temperature and plateau pressure (related with Van't Hoff equation: $ln(p) = \frac{\Delta H}{R} \cdot \frac{1}{T} + \frac{\Delta S}{R}$, where P represents the equilibrium pressure, T equilibrium temperature, R gas constant, ΔH and ΔS are the change in enthalpy and entropy of formation of the hydride), kinetics in solid-gas or/and alkaline solution, cycling (life time), etc [2]. It is important to note that hydrides stability depends mostly on the enthalpy term ΔH as ΔS term is negligible ($\Delta S = -130$ $J.K^{-1}$ mol. H_2, which corresponds to the change from molecule-H_2 to atomic-H) The new research and development challenges of hydrogen storage materials (HSM) are high-capacity cost-effective metal hydrides (> 6.5wt.% [3]) with faster kinetics and low decomposition temperatures, as the industry recommends (4-6 wt.% at 5 bars at temperatures 80-100°C). Recent D.O.E reports reveal that 6 wt. % is economically viable.
The synthesis route (melting, melt-spinning, mechanical milling, etc) of multi-component materials for H_2-storage plays an important role on the formation of phases with respected stoichiometry, precipitation of additional phases, contamination with impurities (i.e. formations of oxides), etc which affect the thermodynamic properties and kinetics.
It is found that the preparation of materials at the nanoscale induces a great impact on the H_2 storage and thermodynamic properties, including an increase in the kinetics of hydrogenation/dehydrogenation and lowering the hydrogen release temperature. In this review paper, many systems will be presented.

2. Results and discussion

Solid H_2 storage can be either (i) interstitial into tetrahedral/octahedral sites where at least one constituent element should be attractive to H_2 (form binary hydride such TiH_2, ZrH_2, VH_2, etc); (ii) adsorbed on surface and (iii) intercalated between layers (carbon nanostructures). The mechanisms involved during hydrogenation of metal hydrides are mainly 3 steps: (i) dissociation of H_2 molecules at the surfaces of particles that's why the presence of catalytic element is very important; (ii) H_2 toms are adsorbed at the surfaces of particles; and (iii) H_2 atoms diffuse from surface into interstitial sites, therefore the size of the interstitial site needs to be accessible by H_2 atoms.

2.1 Intermetallic hydrides

REM_5-based system where RE is a rare earth (RE=La, Ce, Mischmetal, etc) and M is a metal (M=Ni, Cu, Al, Si, Ge, etc) have been investigated for many years and been used as rechargeable nickel metal hydride batteries (NiMH) as well as tested as fuel cells for electric cars. The system crystallizes within a hexagonal crystal structure and the maximum hydrogen capacity is Hydrogen / Metal = 1.0. Multi-component systems have been studied extensively in both solid gas and electrochemical reactions. Its drawbacks are: (i) formation of oxides layers on the surface of particles therefore requires prior activation treatments before it reach its maximum reversible H_2-capacity; (ii) H_2-capacity depends on the nature and amount of both rare earth and M elements, however, the storage density is very limited. The effect of mechanical grinding combined with the addition of doping elements such Pd in solid gas reaction [4] show great improvements of the hydrogenation/dehydrogenation kinetics compared to the alloys prepared by conventional methods (melting). The mechanical grinding helps to clean the surface of particles from the oxides layers therefore the creation of very fresh and active surfaces, which are the origin of faster kinetics.

TiFe is another intermetallic compound which crystallizes within CsCl-type cubic structure and forms a stable hydride, $TiFeH_{1.9}$. Similarly to most of intermetallic hydrides and most critical problem for its use in practical applications, is its severe activation process

(heating up to 400-500°C under vacuum and subsequent exposure to high H_2 pressure up to 6.6 MPa). During the synthesis of TiFe by conventional methods (melting), the impurity Ti_2FeO_4 phase and other oxides are formed [5], which inhibits the H_2 absorption therefore the need of prior activation treatment. The Reaching its maximum H_2-capacity and enhancement of the kinetics have been achieved by various methods: (i) partial substitution on both metallic sites (Ti by Zr and Fe by Ni, Mn, etc) it was found that replacing 10% of Fe by Mn of very active ternary compound without altering the crystal structure of the parent compound TiFe [6]; (ii) milling TiFe powder under active atmosphere (H_2)[7]but the samples become very reactive once exposed to air therefore becoming inactive again; (iii) milling under inert gas (Ar) with the addition of doping element such as Pd [8], Ni [9], etc which serves as well as catalyst for H_2 molecules. The addition of Ni during milling did not alter the crystal structure of TiFe and no significant peak shift has been noticed [9]. Moreover, no peaks related to Ni metal have been noticed suggesting: (i) that probably some amount of Ni has been substituted into Fe within TiFe lattice (r_{Ni} = 1.24 Å ~ r_{Fe} = 1.26 Å) or (ii) formation of nanocrystals of Ni on the surface of TiFe particles. The milling results in particle size reduction from 200 μm (unmilled TiFe) up to 50 nm after 37 hours and finally 20 nm after 65 hours of milling (estimated using Sherrer's equation). Hydrogenation curves measured at 25°C under 2 MPa of H_2 pressure clearly show that TiFe alloy reacts with H_2 without any preliminary activation treatment and reach about 0.6 Hydrogen/Metal (H/M) after 6 hours (Figure 1), whereas unmilled TiFe do not show any significant H_2 uptake. It is noted also that maximum H_2 uptake and kinetics drastically depends on milling time, which can be associated with particle size reduction: longer milling results in obtaining very fine powders.
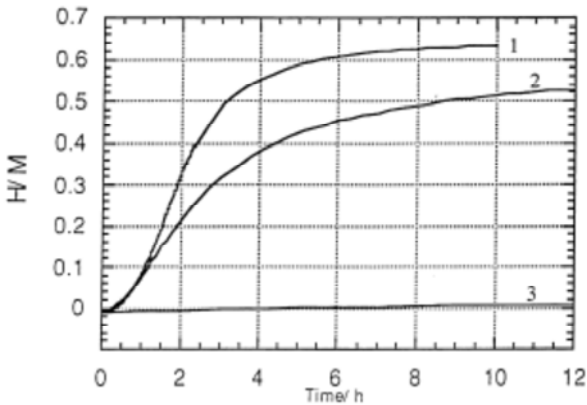
Fig.1: Hydrogenation of TiFe+Ni samples milled at various periods of time (1) 65 h, (2) 37 h and (3) 22 h [9].

2.2 Mg-based system

Mg$_2$Ni, Mg$_2$Co, Mg$_2$Fe and Mg absorb large amount of H$_2$, 3.7, 4.4, 5.3 and 7.6 wt, respectively (Mg$_2$NiH$_4$, Mg$_2$CoH$_5$, Mg$_2$FeH$_6$ and MgH$_2$). Unfortunately, the above hydrides have not been proposed for technological applications due to the high decomposition temperatures (higher than 300°C for Mg$_2$Ni and Mg) whereas Mg$_2$FeH$_6$ is difficult to synthesize.

Mg$_2$Ni compound reacts with H$_2$ to form 2-types of hydrides with different crystal structures: a low-temperature monoclinic phase (LT) and high-temperature cubic phase (HT) with CaF$_2$ type-structure [10] Mg$_2$Ni prepared by conventional methods also need preliminary activation treatment (several cycles of absorption/desorption using high H$_2$ pressures and temperatures) prior to carry out measurements. Nanocrystalline Mg$_2$Ni prepared by mechanical alloying and furthermore doped with Pd (less than 1 wt) [4], reveals H$_2$-uptake at room temperature without any activation process with an enhancement of the kinetics. Mg$_2$Ni milled under reactive H$_2$ atmosphere (limited pressure) [11] results in a limited hydrogenation of the starting alloy. Moreover, Tessier et al. [12] performed a milling of Mg$_2$Ni for 10 hours under moderate and high H$_2$ pressure, 0.5 and 1.0 MPa, respectively. The final sample contains mainly the LT-hydride, a small amount of HT-hydride and an amorphous phase. The

formation during milling of nanosized crystallites of Mg_2Ni with fresh surfaces in the presence of H_2 under pressure, allow a full hydrogenation of the Mg_2Ni alloy.

Shang et al. [13] reported a direct synthesis of Mg_2FeH_6 using a mixture of pure elements (MgH_2 and Fe with various ratios) using mechanical alloying under controlled atmosphere. The highest yield was obtained using MgH_2:Fe ratio close to 3:1. Similarly, a substituted ternary hydride, $Mg_2(Fe_{1-x}Cu_x)H_6$ compounds have been investigated, but the results show an important reduction of Mg_2FeH_6 yield to 40%, due to the formation of Mg_2Cu phase (which do not absorb hydrogen or decomposes into MgH_2 and pure Cu when reacted with H_2). Both samples show a great improvement of kinetics due to the formation of nanoscale crystallites and fresh surfaces during milling. It is important to note the formation of Mg oxide (MgO) probably due the residual pure Mg (5%) existing in the initial MgH_2 powder (as purchased) or may be to some leaks ($MgH_2 + \frac{1}{2} O_2 \rightarrow$ $NgO + H_2$).
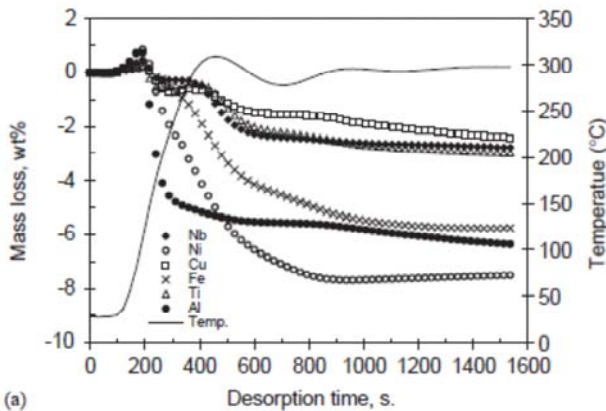

Figure 2. Dehydrogenation of MgH_2-M system [16].

Mg_2Co hydride exists within 2 types of structure: tetragonal β-Mg_2CoH_5 (which transforms into disordered cubic at 215°C) and orthorhombic γ-$Mg_6Co_2H_{11}$ [14]. Due to its high H_2-capacity compared to conventional hydrides, Mg-Co hydrides have been synthesised using several routes, such as milling of 2Mg-Co mixture under Ar atmosphere followed by reactive milling under H_2

atmosphere. Its important to note that the yield of Mg_2CoH_5 phase is only 50 wt.% after long milling periods of time (90 hours) with a starting decomposition temperature of 205°C [14], due to the formation of refinement of microstructure (first stage of milling) and nanocrystals of free Co which act as catalyst for H_2 molecules (during second stage of milling).

MgH_2 has a very high H_2-capacity than both Mg compounds, but its hydrogenation kinetic is very slow and the decomposition temperature is very high. The use of MgH_2 instead of pure Mg during milling has various advantages, including hydrides are more brittle therefore its easier to obtain nanoparticles in a shorter time with minimum contamination (milling for longer periods of time result in contamination of powder with materials forming the milling vial and balls such as Fe, Cr, and carbides as well formation of oxides due to leaks); (ii) the H_2 atoms present in MgH_2 material serve as H_2 source for hydrogenation; and (iii) reduces the formation of MgO if the milling is carried out carefully under controlled atmosphere. It is found that mixing Mg/MgH_2 with some transition metals[15],[16] and some oxides[17],[18],[19] leads to the formation of nanocomposite materials with improved kinetics and H_2 can be released at lower temperatures compared to unmilled MgH_2 and other conventional Mg-based related hydrides. It is very important to note that both the maximum released H_2 amount and the desorption temperature depend strongly on the nature of the element/oxide, its amount and milling time (see Figure 2).

2.3 Carbon Nanostructures

Carbon nanostructures include 2 varieties: carbon nanotubes (CNT) which exist as single-walled (SWNT) and multi-walled (MWNT) and carbon nanofibers (CNF) [20]. A recent review paper on theoretical calculations of H_2-storage in carbon-based materials have shown that H_2 can be stored by (i) physisorption (adsorbed at the surface with the assumption that no chemical process takes place between carbon and H_2 molecules) or either (ii) chemisorption ((reaction between H_2 and carbon occurs and leads to the formation of C-H bonds).

Depending on the interlayer distance for CNF, the H_2-capacity varies from 0.8 up to 12.5 wt, whereas for CNT depending on the nantotube diameter, the H_2 capacity varies from 0.4 up to 37 wt.% [21]. For CNF H_2 atoms can be adsorbed at surface then intercalated between carbon sheets (CNF interlayer distance is about $3.35 – 3.42$ Å which is close to the kinetic H_2 diameter of 2.89 Å [22]). Experimental results of H_2-uptake by various types of carbon nanostructures are widely dispersed, controversial and lack of reproducibility, from 0.2 up to 10 wt.% and even higher. Nevertheless, a recent study [23] revealed that the hydrogenation of CNF at 35°C under a H_2 pressure of 10 MPa for up to 20 hours, do not show any significant H_2-uptake. Several post treatments were applied, such as nitric acid reflux treatment which result in increasing the surface area of the CNF, but again no significant H_2-uptake have been noticed [23]. It is important to note that the most problematic in carrying out H_2-uptake measurement with carbon nanostructures, once should take into consideration various important factors that can cause dramatic errors: (i) even small leaks at high H_2 pressures; (ii) amount of carbon; (iii) use of high purity H_2 (more than 5 N if possible); (iv) remove of humidity and moisture existing in H_2 by using for example liquid nitrogen trap; (v) a better control of the room temperature; (vi) appropriate and accurate pressure transducer for measuring H_2 pressure at high pressures and measuring the small drop of pressure due to H_2 uptake by carbon material; (vii) precise calculations of H_2 amount by volumetric method using Virial coefficients, etc.
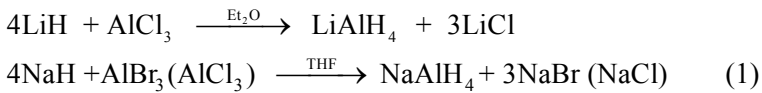
2.4 Light Complex Hydrides (LCH)

LCH combine an alkali metal (A= Li, Na) and a metal or non-metal (M=Al, B) to form a ternary hydrides with a formula AMH_4. Among the reported hydrides, LCH belongs to ionic family, with metallo- / non-metallo- hydride anions (such as AlH_4^-, BH_4^-) and alkali-metal cations (such Li^+, Na^+, K^+, etc). The nature of cations M defines the number of anions to form the ternary hydride.

Recently, LCH have attracted great attention as potential hydrogen storage materials due to their very high H_2-capacity compared to conventional metal hydrides, varying from 5.7 wt.% for $KAlH_4$ to 18.4 wt.% for $LiBH_4$ [24] (see Figure 3).
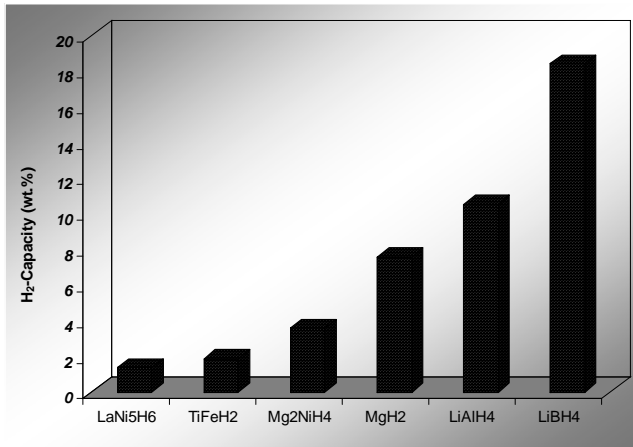
Fig. 3: H_2-capacity of selected LCH

In the past, these types of hydrides were prepared via chemical routes under high H_2-pressures, high temperatures require long periods of time and the use of solvents, such as, Et_2O [25] and THF [26]:

$$4LiH + AlCl_3 \xrightarrow{Et_2O} LiAlH_4 + 3LiCl$$
$$4NaH + AlBr_3 (AlCl_3) \xrightarrow{THF} NaAlH_4 + 3NaBr (NaCl) \qquad (1)$$

The most problematic of LCH are mainly the synthesis route, the reversibility of hydrogenation/dehydrogenation and their high sensitivity and instability to air and moisture. The most studied LCH are sodium alanates ($LiAlH_4$ and $NaAlH_4$).
It is important to note that Bogdanovic et al. [27] showed for the first time, that Ti and Zr compounds act as catalysts for the dehydrogenation of LCH and lowering the desorption temperature. Since that, extensive work has been reported, where several promising routes have been proposed including: (i) reaction of ternary hydrides with chlorides in appropriate solvent (Metathesis) to prepare $ZnBH_4$ [28] and $Mg(AlH_4)_2$ [29]; (ii) ball milling of ternary hydrides and chlorides (Mechanochemical without solvent) to prepare $Mg(AlH_4)_2$ using a mixture of ($MgCl_2$ + $NaAlH_4$) [30], $ZnBH_4$ by mixing $ZnCl_2$ + $NaBH_4$ [31], KBH_4 using MgH_2 (CaH_2 and NaH) with KBO_2 [32], $NaBH_4$ using mixture of MgH_2 + $Na_2B_4O_7$ [33], as

well as some quaternary compositions such as a modified Li aluminohydride [34]. The final products contain some salts (NaCl, oxides (MgO), etc and (iii) mechanochemical preparation (ball milling of ternary hydrides and chlorides) with subsequent wet chemical separation method for the preparation of $Mg(AlH_4)_2$, $Ca(AlH_4)_2$ and $LiMg(AlH_4)_3$ [35]:

$$Na(Li)AlH_4 + Mg(Ca)Cl_2 \longrightarrow Mg(Ca)(AlH_4)_2 + 2Na(Li)Cl \qquad (2)$$
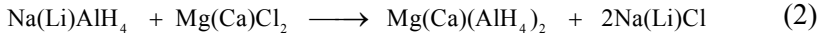
Moreover, several doping techniques have been investigated as well, including (i) a modification of the ball milling process where a metathesis reaction is facilitated via the bond breaking and transfer of energy to the mill charge (Mechanometathesis) has been applied to various compounds [26] and to prepare Ti-based catalyst doping of sodium alanate [26]. (ii) ball milling under H_2 atmosphere such as for $NaAlH_4$ and Ti metal [36] produce kinetically enhanced and reversible dehydrogenation behavior, inferiorly in comparison to ball milling under inert gas using Ti(III) and Ti(IV) dopant precursors, as well as the various doping methods [37],[38],[39],[40], and finally Ti(0) precursor [41]; (iii) co-doping of Ti-$NaAlH_4$ (2 mol% by wet procedure) with graphite (10 wt.%) by ball milling showed an enhancement of kinetics and lowering the dehydrogenation temperature by 15°C [42]. Moreover, doping $NaAlH_4$ with 8 mol% of CNT (optimum value) [43], revealed a better hydrogenation/dehydrogenation characteristics; and (iv) sonochemistry prior to ball milling: $TiCl_3$ was added to $NaAlH_4$ suspended in a mixture of decahydranapthalene and THF (Et_2O). The sonochemically/milled doped samples showed striking enhancement of dehydrognenation/hydrogenation kinetics and better cycling compared to wet doping prior to ball milling [44].

Even after the great improvements so far obtained in terms of synthesis routes, kinetics, better understanding of hydrogenation/dehydrogenation mechanisms, LCH still presents some drawbacks, such as the reversible amount, the desorption temperature, stability in air and moisture, and cycling remain. Therefore, many efforts are underway in order to resolve the above critical problems and to synthesise new compounds as well as complex compositions before that this type of hydrides can be proposed for technological applications.

3. Conclusion

The new challenges for H_2-storage materials for technological applications are a relatively high H_2-storage density with appropriate absorption/desorption temperature at moderate pressures. Most of developed countries have future plans for alternatives to replace some of their available energy resources by renewable and clean energy for several reasons: (i) to reduce pollution due to the high CO_2-emission and further global warming; (ii) the high demand for energy for developed countries (in particular China and India) and the expected high oil prices in the near future; (iii) the development of fuel cells for electric cars as well as the need of electronic equipments for long life rechargeable batteries, etc. Even potential efforts have been done on the search of new and cost-effective hydrides materials with high performances (H_2-capacity, kinetic, moderate pressure and temperature), much work in terms of the discovery, development and optimization of the thermodynamic properties of HSM with regard to special applications (stationary or portable), better understanding of the mechanisms involved during both hydrogenation/dehydrogenation processes, and large scale production, is necessary.

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