



## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Hydrogen

Hydrogen is the most abundant element in the universe (Becker, 2001). It is an ideal energy carrier, which has been considered as a clean and renewable fuel. It can be produced around the world from plentiful resources such as water (<http://www.cen-online.org>). Neither pollutants nor greenhouse gases are emitted, only water is generated, when it reacts with oxygen. It has a very high energy content by weight (about three times more than gasoline). On the other hand, it has a very low energy content by volume (about four times less than gasoline) (<http://www.cen-online.org>). Moreover, it has very light weight. These characteristics lead to challenges in storing hydrogen in a media. To reach the hydrogen economy, hydrogen storage must to be achieved.

#### 2.2 Hydrogen Storage

Hydrogen can be stored in many ways. Hydrogen storage describes the methodologies for storing hydrogen for subsequent uses. It is a material-science challenge according to requirement of either strong interaction between materials and hydrogen or without any reaction. An optimum hydrogen-storage material is required to have the following properties: high hydrogen capacity per unit mass and unit volume, which determines the amount of available energy, low dissociation temperature, moderate dissociation pressure, low heat of formation in order to minimize the energy necessary for hydrogen release, low heat dissipation during the exothermic hydride formation, reversibility, limited energy loss during charge and discharge of hydrogen, fast kinetics, high stability against O<sub>2</sub> and moisture for long cycle life, cyclibility, low cost of recycling and charging infrastructures, and safety (Sakintuna *et al.*, 2007). Most research in hydrogen storage is focused on storing hydrogen in a lightweight and compact package with cost effective and safe for mobile applications.

### 2.2.1 Compressed Hydrogen Gas

Storage of gaseous hydrogen in tanks is the most mature storage method at present. The compressed gas storage tanks are available at 5,000–10,000 psi. New light weight tank materials such as carbon-fiber-reinforced composites are used for these high-pressure tanks. The major drawback of gaseous storage for transportation applications are the small amount of hydrogen that can be stored in a reasonable volume and the energy content is significantly less than that for the same volume of gasoline (<http://www.sc.doe.gov/bes/hydrogen>).

### 2.2.2 Liquid Hydrogen Storage

Liquid hydrogen is stored in cryogenic tanks, which require insulation to prevent hydrogen loss, at  $-253^{\circ}\text{C}$  (21.2 K) and ambient pressure. Liquefied hydrogen is denser and has higher energy content than gaseous hydrogen in a given volume, thus liquid hydrogen tanks can store more hydrogen than compressed gas tanks. Nevertheless, the disadvantages of liquid hydrogen tanks are hydrogen boil off, the high energy required for hydrogen liquefaction, volume, weight, tank cost, and reduced system gravimetric and volumetric capacity by insulation (<http://www.eere.energy.gov/hydrogennandfuelcells/storage>).

### 2.2.3 Solid-state Storage

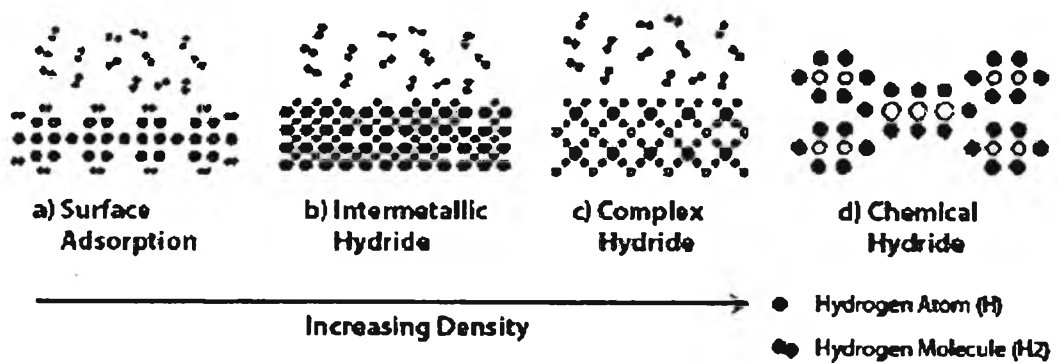
The solid-state hydrogen storage refers to the storage of hydrogen in metal hydrides, in chemical storage materials, and nanostructured materials (<http://www.sc.doe.gov/bes/hydrogen>). There are presently three generic mechanisms known for storing hydrogen in materials: absorption, adsorption, and chemical reaction ([http://www.eoearth.org/article/Hydrogen\\_storage](http://www.eoearth.org/article/Hydrogen_storage)).

*Absorption.* In absorptive hydrogen storage, hydrogen is absorbed directly into the bulk of the material. In simple crystalline metal hydrides, this absorption occurs by the incorporation of atomic hydrogen into interstitial sites in the crystallographic lattice structure ([http://www.eoearth.org/article/Hydrogen\\_storage](http://www.eoearth.org/article/Hydrogen_storage)).

*Adsorption.* Adsorption may be subdivided into physisorption and chemisorption, based on the energetic of the adsorption mechanism. Physisorbed

hydrogen is more weakly energetically bound to the material than is chemisorbed hydrogen. Adsorption processes typically require highly porous materials to maximize the surface area available for hydrogen sorption to occur, and to allow for easy uptake and release of hydrogen from the material ([http://www.eoearth.org/article/Hydrogen\\_storage](http://www.eoearth.org/article/Hydrogen_storage)).

*Chemical reaction.* The chemical reaction route for hydrogen storage involves displaced chemical reactions for both hydrogen generation and hydrogen storage. Hydrogen can be generated by reacting metals and chemical compounds with water. In many cases, the hydrogen generation reaction is not reversible under modest temperature/pressure changes. Although hydrogen can be generated on-board the vehicle, getting hydrogen back into the starting material must be done off-board ([http://www.eoearth.org/article/Hydrogen\\_storage](http://www.eoearth.org/article/Hydrogen_storage)).



**Figure 2.1** Hydrogen sorption on the surface of the solid (<http://www1.eere.energy.gov/hydrogenandfuelcells/storage/basics.html>).

Hydrogen can be stored on the surfaces of the solids by absorption. Figure 2.1, in adsorption (a), hydrogen attaches to the surface of a material either as hydrogen molecules (H<sub>2</sub>) or hydrogen atoms (H). In absorption (b), hydrogen molecules dissociate into hydrogen atoms that are incorporated into the solid lattice framework. This method may make it possible to store larger quantities of hydrogen in smaller volumes at low pressure and temperatures close to room temperature. Finally, hydrogen can be strongly bound within molecular structures, as chemical

compounds containing hydrogen atoms (c) (<http://www1.eere.energy.gov/hydrogenandfuelcells/storage/basics.html>).

In solid-state materials, hydrogen can be stored both reversibly and irreversibly. Reversible storage means that hydrogen is released by raising the temperature. Ideally, storage and release of hydrogen should take place at temperatures between 0 and 100°C and pressures of 1–10 bar and on time scales suitable for transportation applications (<http://www.sc.doe.gov/bes/hydrogen>).

#### 2.2.3.1 Metal Hydrides and Complex Hydrides

Hydrogen forms metal hydrides with some metals and alloys leading to solid state-storage under moderate temperature and pressure that gives them the important safety advantage over the gas and liquid storage. In addition, metal hydrides have higher hydrogen-storage density than hydrogen gas or liquid hydrogen. Thus, metal hydride storage is a safe and volume-efficient storage method for reversible on-board hydrogen (Sakintuna *et al.*, 2007).

Complex metal hydrides, which have low weight, such as alanates ( $\text{AlH}_4$ ), amides ( $\text{NH}_2$ ), imides, and borohydrides ( $\text{BH}_4$ ), have the potential for higher gravimetric hydrogen. Issues with complex metal hydrides include low hydrogen capacity, slow uptake and release kinetics, and cost (<http://www.eere.energy.gov/hydrogenandfuelcells/storage>).

#### 2.2.3.2 Chemical Hydrogen Storage

Chemical hydrogen storage is the storage technologies, in which hydrogen is generated via a chemical reaction. Regular reactions involve chemical hydrides with water or alcohols. Typically, these reactions are not easily reversible for on-board a vehicle. Hence, the "spent fuel" and/or byproducts must be removed from the vehicle and regenerated off-board (<http://www.eere.energy.gov/hydrogenandfuelcells/storage>).

#### 2.2.3.3 Nanostructured Materials

These types of materials include both carbon-based materials such as nanotubes and nanofibers and non-carbon-based materials made of other atoms including nanoscale version of the hydrides materials. The hydrogen-storage capacity for carbon materials was reported between 0.2 and 10 wt% (Sakintuna *et al.*,

2007). The small size of nanostructured materials strongly influences the thermodynamics and kinetics of hydrogen adsorption and dissociation by increasing the diffusion rate, as well as by decreasing the required diffusion length (<http://www.sc.doe.gov/bes/hydrogen>).

#### 2.2.3.4 High Surface Area Sorbents

One new area that may be promising is high-surface hydrogen sorbents based on microporous metal-organic frameworks (MOFs). Such materials are synthetic, crystalline, and microporous. They are also composed of metal/oxide groups linked together by organic struts. Hydrogen storage capacity at 78 K ( $-195^{\circ}\text{C}$ ) has been reported as high as 4 wt% via an adsorptive mechanism, with a room temperature capacity of approximately 1 wt%. However, due to their high porous nature of these materials, volumetric capacity may still be a significant issue ([http://www.eoearth.org/article/Hydrogen\\_storage](http://www.eoearth.org/article/Hydrogen_storage)).

## 2.4 Metal Hydrides and Complex Hydrides Materials

Hydrogen reacts at elevated temperatures with many transition metals and their alloys to form hydrides. Hydrogen atoms fit into octahedral or tetrahedral holes in the metal lattice. Atomic hydrogen stored in these interstitial sites recombines at particle surfaces to form molecular hydrogen upon release.

There are two possible ways of hydriding a metal, direct dissociative chemisorptions and electrochemical splitting of water.

These reaction are:



where M represents the metal elements, and x represents the number of desorbed and absorbed hydrogen. Whether hydrogen is released or absorbed depends on the value of the Gibbs energy at the reaction conditions.

$$\Delta G = \Delta H - T\Delta S \quad (2.3)$$

where,

$\Delta G$  = Gibbs Free Energy, kJ

$\Delta H$  = enthalpy change, kJ

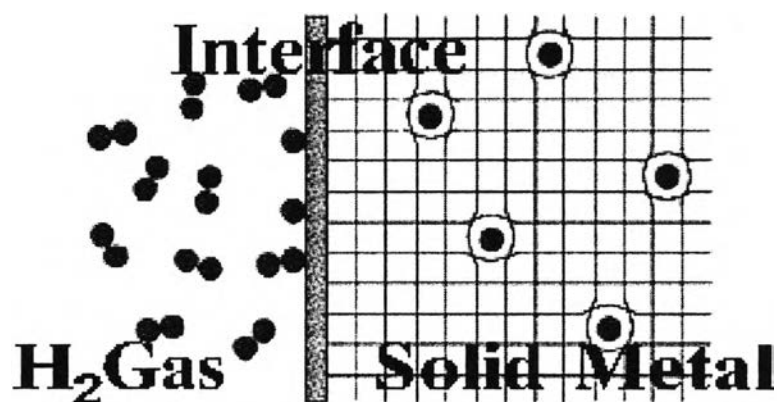
T = temperature, K

$\Delta S$  = entropy change, kJ K<sup>-1</sup>

Hydrogen is absorbed if  $\Delta G$  is less than zero and desorbed if  $\Delta G$  is greater than zero. Absorption and desorption are two steps involved to store hydrogen in metal hydrides. Energy is needed for the operation. The total energy required to operate a metal hydride storage system is about 12.5% of the low heating value of hydrogen and it is the lowest operating energy (Heung, 2003).

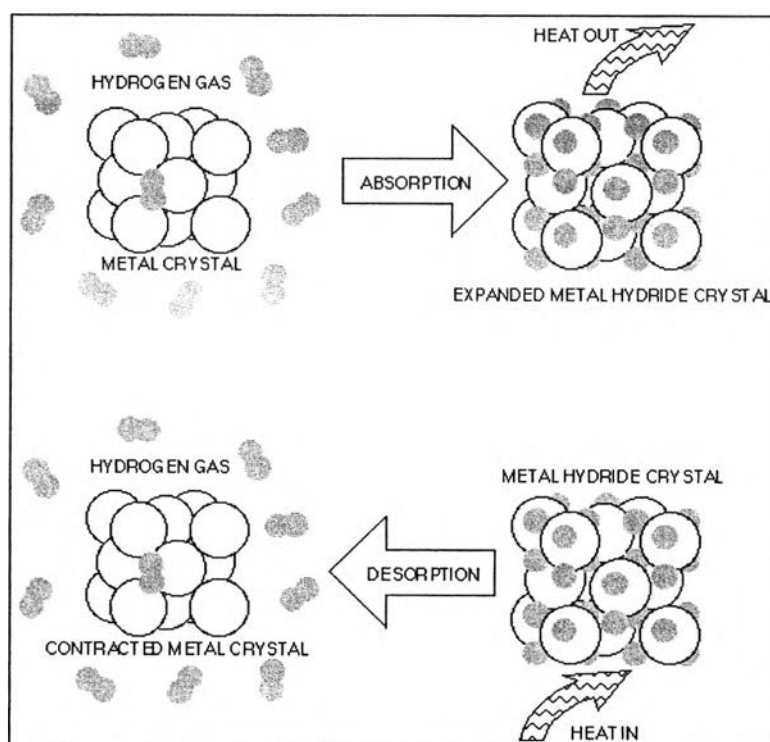
Metal hydrogen system consists of H<sub>2</sub> gas, interface region and solid metal as shown in Figure 2.2. At the interface, the molecule is dissociated and dissolves into the metal phase. The metal phase is known as  $\alpha$  phase, at which some hydrogen is absorbed. The fully formed hydride is known as  $\beta$  phase. Figure 2.3 shows the absorption/desorption system of metal hydrides. Metal absorbs hydrogen to form hydrides and releases heat. On the other hand, as the temperature increases, the metal hydride desorbs hydrogen.

The reaction of hydrogen gas with a metal is called the absorption process and can be described in terms of a simplified one-dimensional potential energy curve (Figure 2.4). The hydrogen molecule approaches to the metal atom by Van der Waals forces and forms a physisorbed state. Before diffusion into the metal, the hydrogen molecule has to overcome the activation barrier and dissociates to form a chemisorbed state (Züttel, 2003b).



**Figure 2.2** Model of the metal hydrides interaction

(<http://www.ovonic-hydrogen.com/solutions/technology1.htm>).

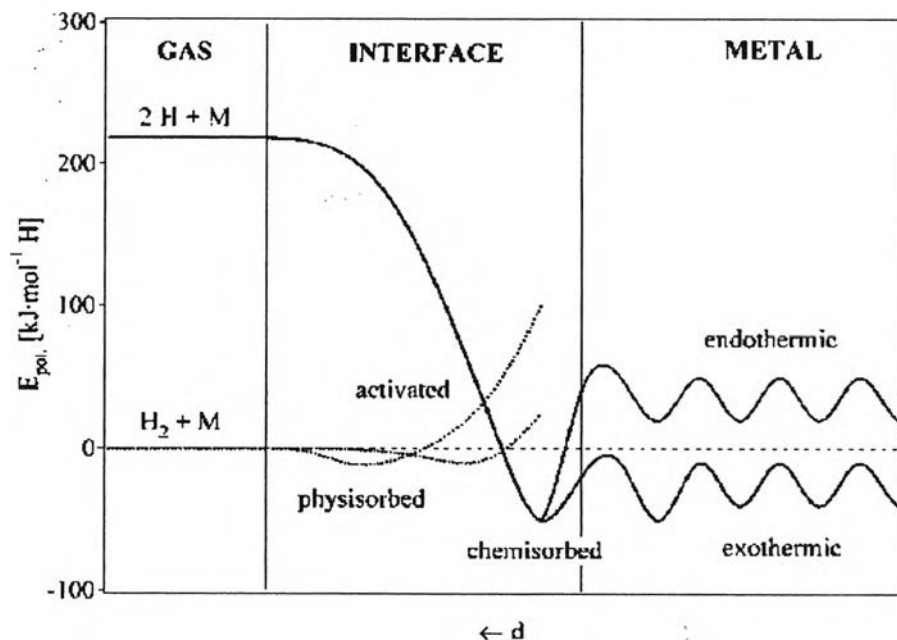


**Figure 2.3** Absorption and desorption of metal hydrides

(<http://www.hydrogencomponents.com/hydride.html>).

The hydrogen atoms contribute their electron to the band structure of the metal. At a small hydrogen to metal ratio ( $H/M < 0.1$ ), the hydrogen is

exothermically dissolved in the metal (solid-solution,  $\alpha$ -phase). Far from the metal surface, the potential of a hydrogen molecule and of two hydrogen atoms are separated by the dissociation energy. The first attractive interaction of the hydrogen molecule approaching the metal surface is the Van der Waals force leading to the physisorbed state approximately one hydrogen molecule from the metal surface. Closer to the surface, the hydrogen has to overcome an activation barrier for dissociation and formation of the hydrogen metal bond. The height of the activation barrier depends on the surface elements involved. Hydrogen atoms share their electron with the metal atoms at the surface and are then in the chemisorbed state. The chemisorbed hydrogen atoms may have a high surface mobility, interact with each other, and form surface phases at sufficiently high coverage. In the next step, the chemisorbed hydrogen atom can jump in the subsurface layer and finally diffuse on the interstitial sites through the host metal lattice (Züttel, 2003b).

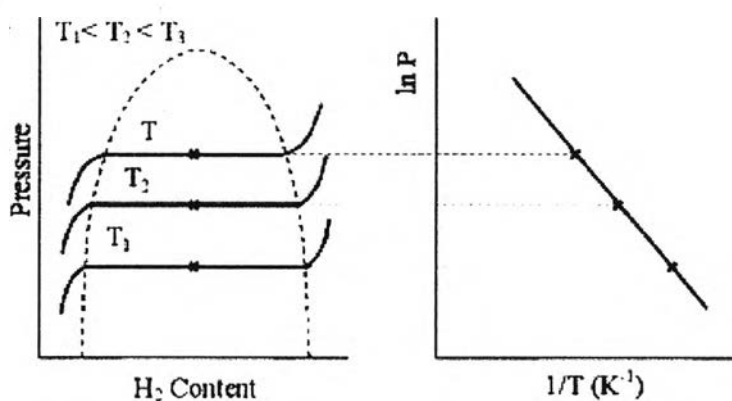


**Figure 2.4** Potential energy of a hydrogen molecule and of two hydrogen atoms (Züttel, 2003b).



At greater hydrogen concentrations in the host metal ( $H/M > 0.1$ ), a strong hydrogen-hydrogen interaction becomes important because of the lattice expansion, and the hydride phase ( $\beta$ -phase) nucleates and grows. The hydrogen concentration in the hydride phase is often found to be  $H/M=1$ . The volume expansion between the coexisting  $\alpha$ - and  $\beta$ -phases corresponds, in many cases, to 10–20% of the metal lattice. At the phase boundary, therefore, a large stress builds up and often leads to a decrepitating of brittle host metals such as intermetallic compounds. The final hydride is a powder with a typical particle size of 10–100  $\mu\text{m}$  (Züttel, 2003b).

Some hydrogen is dissolved in the host metal as a solid solution. The hydrogen pressure increases proportional to the hydrogen concentration and the hydride phase occurs. In both of the solid solution and hydride phase region ( $\alpha + \beta$  phase), the pressure change is small and size of the region depends on the hydrogen absorbed. Increasing hydrogen concentration until the phase completely changes to the pure hydride phase, the hydrogen pressure increases rapidly again (Schlapbach and Züttel, 2001). The hydrogen absorption on metal is represented by a PCT diagram as shown in Figure 2.5.



**Figure 2.5** Pressure-concentration-temperature curve (PCT diagram) and Van't Hoff plot (Logarithm of the equilibrium against the reciprocal temperature) (<http://www.ovonic-hydrogen.com/solutions/technology1.htm>).

The hydrogen pressure that is in equilibrium depends on temperature and it is defined by the Van't Hoff equation:

$$\ln P = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (2.4)$$

where  $\Delta H$  and  $\Delta S$  are the enthalpy and the entropy of the reaction, respectively,  $R$  is the gas constant and  $T$  is the absolute temperature. The logarithm of pressure and one over temperature ( $\ln P$  vs  $1/T$ ) are plotted, called Van't Hoff plot, Figure 2.5. The slope of the plot is related to the enthalpy of formation and the intercept is related to the entropy of formation. The enthalpy term gives the information about the stability of the metal hydrogen bond and the entropy term gives the information about hydrogen gas molecule to dissolved solid hydrogen (Schlapbach and Züttel, 2001).

Metal hydrides can be divided into two types, alkali and inter-metallic.

a) Alkali Metal Hydrides

The light metals such as Li, Be, Na, Mg, B and Al, form a large variety of metal-hydrogen compounds. They are especially interesting due to their light weight and the number of hydrogen atoms per metal atom, which is in many cases at the order of  $H/M = 2$  (Sakintuna *et al.*, 2007); such as alanates (aluminumhydrides), borohydrides, and imides, in which the metal atom is surrounded by four to six hydrogen atoms forming a complex negatively charged anion, mimic the structure of methane. Thus, these complex hydrides may have the greatest potential to provide both a high wt% hydrogen and desirable release/absorption kinetics (<http://www.sc.doe.gov/bes/hydrogen.pdf>). As shown in Table 2.1, their theoretical total hydrogen capacities are high (from ~7 to 18 wt%).

b) Inter-Metallic Metal Hydrides

Inter-metallic metal hydrides can perform many functions: (1) to enhance the hydriding-dehydriding kinetic characteristic by acting like a catalyst, (2) altering the equilibrium pressure of the hydrogen absorption-desorption process to a desired level, and (3) increasing the stability of the alloy and preventing dissolution or formation of a compact oxide layer. They consist of two or more metals, which are alloyed together to form new chemical compounds. The compounds are a combination of element A, with a high ability to absorb hydrogen, and element B, with a low ability to absorb hydrogen. The different families of intermetallic compounds are classified on the basis of their crystal structures, such as AB<sub>2</sub> type

(Laves phase), AB5 type phases and Ti-based body centered cubic, BCC. Alloys are well known as hydrogen-storage materials.

Intermetallic compounds are often obtained by combining an element forming a stable hydride with an element forming a nonstable hydride. As for the metallic hydrides, the dissociative chemisorption of hydrogen is followed by hydrogen diffusion into the interstitial sites (Sakintuna *et al.*, 2007). Some families of inter-metallic compounds are listed in Table 2.2.

Their low energy density per unit weight is an important critical disadvantage. Among the AB5 type alloys, due to their low working temperature and pressure, metal alloys containing high amounts of LaNi5 have been studied as hydrogen-storage materials by various research groups around the world. Some of the studies were carried with pure compounds, while others studied blending of the material with various metals through melting or mechanical alloying techniques (Sakintuna *et al.*, 2007).

**Table 2.1** Theoretical hydrogen capacities of metal hydrides and complex hydrides

Hydrides	Hydrogen, wt%	Reversibility
MgH <sub>2</sub> <sup>1</sup>	7.7	Yes (good)
LiH <sup>2</sup>	12.7	N/A
NaAlH <sub>4</sub> <sup>1</sup>	5.6	Yes (good)
LiAlH <sub>4</sub> <sup>3</sup>	10.5	No
Mg(AlH <sub>4</sub> ) <sub>2</sub> <sup>4</sup>	9.3	No
NaBH <sub>4</sub> <sup>4</sup>	10.7	No
LiBH <sub>4</sub> <sup>5</sup>	18.5	Yes
Mg(BH <sub>4</sub> ) <sub>2</sub> <sup>4</sup>	14.9	No
LiNH <sub>2</sub> <sup>6</sup>	6.5	N/A
Li <sub>3</sub> N <sup>6</sup>	10.4	Yes

<sup>1</sup>Sakintuna *et al.*, 2007; <sup>2</sup>Ichikawa *et al.*, 2005; <sup>3</sup>Blanchard *et al.*, 2004;

<sup>4</sup>Sandrock, 1999; <sup>5</sup>Jin *et al.*, 2008; <sup>6</sup>Isobe *et al.*, 2005.

**Table 2.2** Examples of inter-metallic compounds

Maximum Hydrogen Capacity				
Type	Intermetallic	H/M <sup>a</sup>	wt%	Temperature (°C) for 1 atm P <sub>desorption</sub>
A <sub>2</sub> B	Mg <sub>2</sub> Ni	1.33	3.6	255
AB	TiFe	0.975	1.86	-10
AB	ZrNi	1.4	1.85	292
AB <sub>2</sub>	ZrMn <sub>2</sub>	1.2	1.77	167
AB <sub>5</sub>	LaNi <sub>5</sub>	1.08	1.49	12
AB <sub>2</sub>	TiV <sub>0.62</sub> Mn <sub>1.5</sub>	1.14	2.15	-6

<sup>a</sup>H/M is the hydrogen-to-metal atomic ratio in the compound (Sandrock, 1999).

## 2.5 Dopants

The enhancement of kinetics at low temperatures and the requirement for high hydrogen storage capacity (>6.0 wt%) of hydrogen storage materials could be made possible by catalytic doping (Niemann *et al.*, 2008). For example, the addition of Ti-based compounds (such as TiCl<sub>3</sub> or Ti[OBU]<sub>4</sub> to NaAlH<sub>4</sub>) was found to lower the first decomposition temperature of the hydride, so that 3.7 wt% is released at 80°C, but at the expense of lowering the hydrogen content from 5.5 wt% in the hydride without a catalyst (<http://www.sc.doe.gov/bes/hydrogen.pdf>).

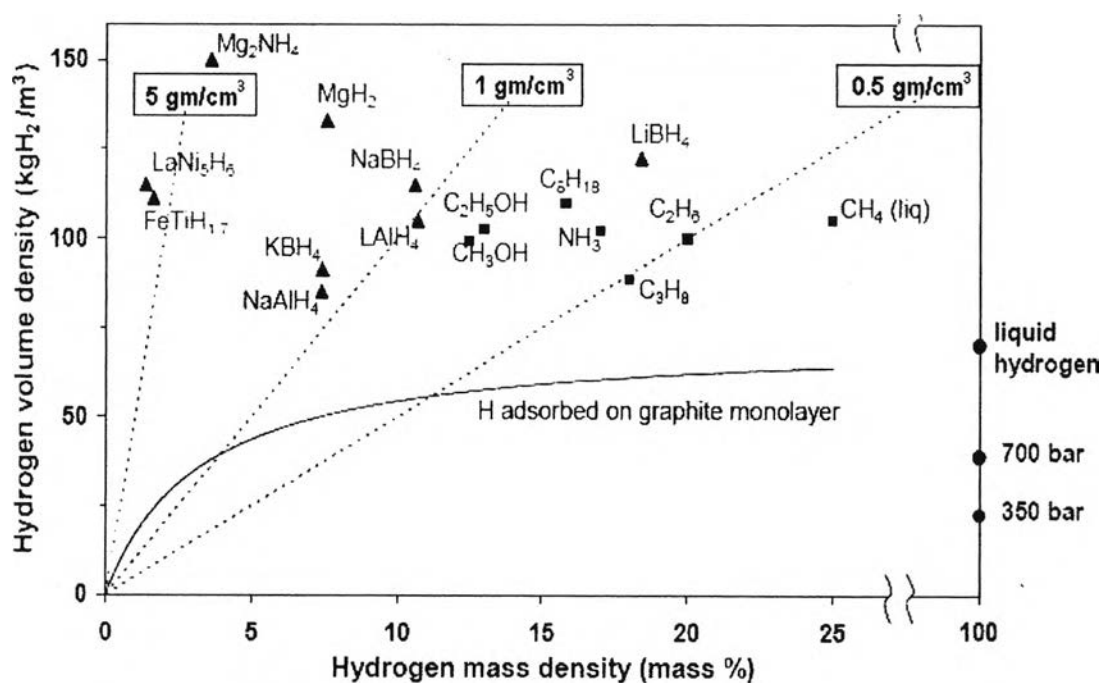
If nanostructured materials with high surface area are used as the catalytic dopants, they may offer several advantages for the physicochemical reactions, such as surface interactions, adsorption in addition to bulk absorption, rapid kinetics, low-temperature sorption, hydrogen atom dissociation, and molecular diffusion via the surface catalyst. The intrinsically large surface areas and unique adsorbing properties of nanophase catalysts can assist the dissociation of gaseous hydrogen and the small volume of individual nanoparticles can produce short diffusion paths to the materials' interiors. The use of nanosized dopants enables a higher dispersion of the

catalytically active species and thus facilitates higher mass transfer reactions (Niemann *et al.*, 2008).

Niemann *et al.* (2008) reported that introducing nano-Ni (particle size of 3–10 nm) with concentrations of 1, 2, 3, and 4 mol% in the new complex borohydride,  $\text{LiBH}_4 + 1/2 \text{ZnCl}_2$ , helped to lower the temperature of decomposition from  $120^\circ\text{C}$  down to  $100^\circ\text{C}$ . And a concentration of 3 mol% nano-Ni was found to be optimum for the gravimetric weight loss due to thermal decomposition at low temperature.

It was also confirmed from gravimetric analysis that nanocatalyst doping enhances the hydrogen storage characteristics such as reaction kinetics at low-decomposition temperature (Niemann *et al.*, 2008).

## 2.6 Comparison of Material's Hydrogen Storage Densities



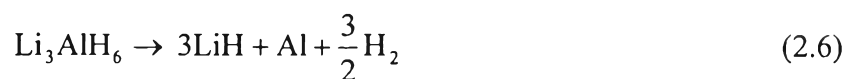
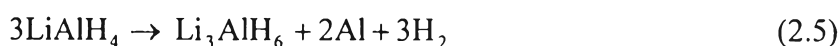
**Figure 2.6** Comparison of metal hydrides, carbon nanotubes, and other hydrocarbons (Storing in hydrogen per mass and per volume) (Schlapbach and Zuttel, 2001).

Candidate materials for hydrogen storage will need to have high hydrogen packing density, as well as low weight. This sidebar compares these two properties,

the mass density and volume density of hydrogen—for a number of different hydrogen-containing materials. The hydrogen density in the materials is simply proportional to the material density through the mass fraction. Three straightline plots are shown in Figure 2.6 for 5, 1, and 0.5 g cm<sup>-3</sup>. The best materials for hydrogen storage applications should be in the upper-right quadrant of the figure. Inter-metallic hydrides, such as LaNi<sub>5</sub>H<sub>6</sub>, have high volumetric densities, but generally are heavy—with specific gravities in the range of 5–10 g cm<sup>-3</sup>. They tend to populate the left-hand portion of Figure 2.6. Lighter compounds, with specific gravities of ~1 g cm<sup>-3</sup>, need to have high hydrogen-to-metal ratios to achieve high volumetric density. Some examples with high hydrogen contents are shown in the chart. Note that the hydrogen densities in solids tend to be comparable to the densities of hydrogen in hydrocarbon fuels, alcohols, and ammonia (<http://www.sc.doe.gov/bes/hydrogen.pdf>).

## 2.7 Li–Al–H System

Lithium alanate or lithium aluminum hydride (LiAlH<sub>4</sub>) has high hydrogen capacity for complete decomposition (10.5 wt%). It has multiple steps for decomposition:



The first step, reaction (2.5), takes place at 150–175°C and releases 5.3 wt% hydrogen. The second step, reaction (2.6), releases 2.6 wt% hydrogen and occurs at about 180–220°C. The last decomposition step occurs at high temperature, about 400°C (Blanchard *et al.*, 2004).

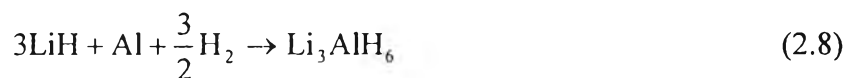
Blanchard *et al.* (2004) studied desorption of LiAlH<sub>4</sub> with Ti- and V-based additives. They found that ball-milling of LiAlD<sub>4</sub> in presence of VCl<sub>3</sub> or

$\text{TiCl}_3 \cdot 1/3(\text{AlCl}_3)$  could reduce its thermal decomposition temperatures by  $60^\circ\text{C}$  and  $50^\circ\text{C}$ , respectively.

Easton *et al.* (2005) studied factors which affect hydrogen released from  $\text{LiAlH}_4$ . They concluded that the mechanical milling of  $\text{LiAlH}_4$  with  $\text{TiCl}_3$  reduced the temperature for the thermal decomposition of  $\text{LiAlH}_4$  and  $\text{Li}_3\text{AlH}_6$ .

Suttisawat *et al.* (2007) investigated the effects of two transition metals, Zr and Hf, on the desorption/absorption of  $\text{LiAlH}_4$  with various amounts of doping from 0 to 9 mol% using thermovolumetric apparatus. It was reported that both  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  enhanced the desorption kinetics and decreased the desorption temperature.  $\text{ZrCl}_4$  was more effective in improvement kinetics, while  $\text{HfCl}_4$  was more effective in decreasing the desorption temperature. However, no hydrogen absorption was observed for the undoped or doped  $\text{LiAlH}_4$  at  $125^\circ\text{C}$  under 11 MPa of hydrogen pressure for 12 h. Moreover, XRD pattern indicated that both the as-milled sample and desorbed sample composed of Al, LiCl, and LiH. They concluded that  $\text{LiAlH}_4$  was unstable and decomposed during the milling process.

Zheng and Liu (2009) studied the hydrogen-storage properties of  $\text{LiAlH}_4$  both undoped and doped with 5 mol% catalysts such as, Ti, Ni,  $\text{Ce}(\text{SO}_4)$ , and  $\text{LaCl}_3$  by pressure–composition–temperature (PCT) experiment. They found that doping significantly decreased the amount of hydrogen release in the first and second steps, especially in the first step, except doping with  $\text{Ce}(\text{SO}_4)$  that had no significantly difference on the amount of hydrogen released.  $\text{LiAlH}_4$  began to decompose at  $148^\circ\text{C}$  and continued up to  $176^\circ\text{C}$ . Hydrogen was released from  $\text{LiAlH}_4$  about 4.0 and 2.0 wt% in the first and second steps, respectively. Effect on decomposition temperature of adding additives exhibited significantly difference—doping with Ti and  $\text{Ce}(\text{SO}_4)$  obviously decreased the first-step desorption temperature, by  $13^\circ\text{C}$  and  $38^\circ\text{C}$ , respectively. Rehydrogenation was performed at  $180^\circ\text{C}$  and under  $\sim 8$  MPa for 2 h—Ti-doped sample gave the most amount of absorbed hydrogen as 0.83 wt%, followed by  $\text{LaCl}_3$  and  $\text{Ce}(\text{SO}_4)$  which were observed as 0.62 and 0.12 wt% of absorbed hydrogen, respectively. The X-ray diffraction measurement exhibited two major phases of decomposed sample of 5 mol% Ti-doped  $\text{LiAlH}_4$  as Al and LiH. It was proved that  $\text{Li}_3\text{AlH}_6$  was reversible according to the following reaction:



Liu *et al.* (2009) investigated the effect of  $\text{TiF}_3$  on the hydrogen storage properties of  $\text{LiAlH}_4$  with various milling times from 0.5 h to 18 h using thermogravimetric analysis (TGA). They reported that the crystallite size of  $\text{LiAlH}_4$  got smaller (from 69 nm to 43 nm) and the desorption temperature became lower (from  $80^\circ\text{C}$  to  $60^\circ\text{C}$ ) with the increase in the milling time. After 18 h ball milling, 4 mol%  $\text{TiF}_3$  doped- $\text{LiAlH}_4$  released hydrogen about 5.0 wt% in the temperature range of  $60\text{--}145^\circ\text{C}$ . No hydrogen absorption was revealed under 9.5 MPa of hydrogen pressure. In addition, XRD pattern exhibited that  $\text{LiAlH}_4$  decomposed during the ball milling and  $\text{TiF}_3$  probably reacted with  $\text{LiAlH}_4$  to form  $\text{TiAl}_3$ , which acted as an catalyst.

## 2.8 Li–B–H System

$\text{LiBH}_4$  has a very high theoretical hydrogen capacity, 18.5 wt%, and even its reversible storage capacity is 13.9 wt%.



Unfortunately,  $\text{LiBH}_4$  is quite stable thermodynamically and its decomposition temperature under 1 bar of hydrogen is calculated to be above  $407^\circ\text{C}$ , which is above its melting point. Even worse is that it does not seem to become hydrogenated below  $600^\circ\text{C}$  under a hydrogen pressure of under 350 bar, which is not practical for automobile applications (Orimo *et al.*, 2005).

Züttel *et al.* (2003a) studied the structure and the thermal hydrogen desorption process of  $\text{LiBH}_4$ . The desorption experiments were carried out in a stainless steel cylinder and the desorbed gas was measured by means of a gas flow controller. For pure  $\text{LiBH}_4$ , the thermal desorption spectra showed a small amount of released hydrogen between  $100\text{--}200^\circ\text{C}$  of 0.3–1.5 mass%. The fusion was observed

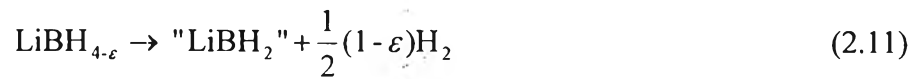


around 270°C. The first step desorption started at 320°C and released hydrogen 1 mass% while the second step started at 400°C and amount of desorbed hydrogen reached up to 9 mass% at 600°C. A total of 4.5 mass% of the hydrogen remained as LiH in the decomposition product. The thermal desorption spectra of mixed LiBH<sub>4</sub> and SiO<sub>2</sub>-powder (25:75mass%) exhibited that the first hydrogen desorption started at 200°C, the amount of released hydrogen reached up to 9 mass% below 400°C, and the second desorption was observed at 453°C, as described in the following schematics:

1. Structural transition at 108°C



2. First hydrogen desorption started at 200°C



3. Second hydrogen desorption started at 453°C



## 2.9 Li–Al–B–H System

Jin *et al.* (2008) investigated the LiBH<sub>4</sub>/Al system. Composite powder, a mixture of LiBH<sub>4</sub> and LiAlH<sub>4</sub> together with 3 mol% TiF<sub>3</sub>, was prepared by ball milling. LiAlH<sub>4</sub>, instead of Al powder, was mixed with LiBH<sub>4</sub> in order to produce fine and surface oxide-free Al by an in situ decomposition of LiAlH<sub>4</sub> during milling or dehydrogenation processes. The powder started to decompose between 177°C and 247°C and the weight loss reached up to 7.2 wt% at 387°C. The formation of AlB<sub>2</sub> was clearly observed after desorption at 400°C for 4 h. It was also confirmed that de-

hydrogenated product can be hydrogenated to about 5.1 wt% H<sub>2</sub> at 350°C for 6 h under 70 bar of hydrogen. They clearly confirmed that the following reaction:



was reversible at moderate temperature and pressure conditions, although the reaction kinetics seems to be rather slow. Besides, it was confirmed that the use of transition metal halide as a catalyst precursor enhanced the dehydrogenation reaction kinetics significantly.

Mao *et al.* (2009) investigated the hydrogen storage properties of the LiAlH<sub>4</sub>-LiBH<sub>4</sub>, both undoped and doped with TiF<sub>3</sub> and TiO<sub>2</sub> as catalysts. The samples were mixed by ball milling. The systems exhibited 2 steps of hydrogen release—the first step started at about 118°C whereas the second step started at about 300°C. LiAlH<sub>4</sub> + 2LiBH<sub>4</sub> doped with 5 mol% TiF<sub>3</sub> showed the best hydrogen storage properties, the onset temperature of the first and second dehydrogenation steps were decreased by 64 and 150°C, respectively. Moreover, it could absorb 3.76 wt% and 4.78 wt% in 1 h and 14 h, respectively, at 600°C and under 4 MPa of hydrogen, while doping with 5 mol% TiO<sub>2</sub> decreased the temperature of the first and second decomposition steps by 27 and 50°C, respectively. Furthermore, it was observed from X-ray diffraction analysis that after heating to 150°C, Li<sub>3</sub>AlH<sub>6</sub>, Al, and LiH were formed, no LiAlH<sub>4</sub> was presented but LiBH<sub>4</sub>. After heating to 300°C, Al, LiH, AlB<sub>2</sub>, and some LiBH<sub>4</sub>, were observed. After heating to 600°C, no LiBH<sub>4</sub> was found but LiAl.