CHAPTER II
LITERATURE REVIEW

2.1 Hydrogen Storage and Its Target

Hydrogen storage is an important topic to the hydrogen economy, particularly, storing hydrogen for vehicular applications or the fuel cell driven cars. The requirement of a hydrogen storage system for practical applications in both economic and environmental reasons including (Grochala and Edwards, 2004):

1) High storage capacity in both gravimetric and volumetric density.

2) Operating temperature in the range of 60–100°C, suitable for PEM (proton exchange membrane) fuel cell applications

3) Quick charging and recharging hydrogen

4) Low cost

5) Safe and reasonable cost

The hydrogen storage targets, which are fixed by the U.S. department of energy (DOE) for driving a car more than 500 km, are shown in Table 2.1.

Table 2.1 Targets of the U.S. DOE hydrogen storage system targets (Satyapal et al., 2007)

Storage parameter	Units	2010	2015
System gravimetric capacity	H_2/kg system	0.06	0.09
System volumetric capacity	H_2/L system	0.045	0.081
Storage System cost	$/L H_2	133	67
Life time charge-recharge cycle	Cycles	1000	1500
Operating temperature	°C	-40/85	-40/85

Currently, hydrogen can be stored in the forms of compressed hydrogen gas and hydrogen liquid. In addition, solid material storage like nanostructure materials and metal hydrides are being developed (Schlapbach and Züttel, 2001 ; Schlapbach, 2002).

2.1.1 Compressed Hydrogen Gas

Hydrogen is compressed in classical high-pressure tanks that are made of fairly cheap steel. Its advantages include simplicity of design and room temperature compressed gas storage. The drawbacks are high volume, high pressure, low density, and difficult to control pressure. Novel high pressure tanks made of carbon-fiber-reinforced composite material are being developed. The carbon-fiber-reinforced composite tank for 350 bar and 700 bar have already been used in the prototype hydrogen powered vehicles. However, at 700 bar, hydrogen can be stored in the tank about 3.1 kg of hydrogen and available for 270 km driving range, which still does not reach the DOE target. Moreover, the cost and safety are still the key challenges for compressed hydrogen gas tanks (Satyapal et al., 2007).

2.1.2 Liquid Hydrogen Storage (LH$_2$)

Hydrogen is condensed into liquid by liquefaction and stored in a cryogenic tank. This system can store more hydrogen in a given volume than compressed tanks since the volumetric of liquid hydrogen is 70.8 kg/m^3. However, the drawbacks are high cost for the liquefaction process (condensation temperature of hydrogen at 0.1 MPa is -252°C.) and heat transfer through the container leads to hydrogen loss (Satyapal et al., 2007).

2.1.3 Solid-state Hydrogen Storage

Hydrogen is stored in or on the materials by absorption or adsorption, while the materials can release hydrogen when they are heated. This system has been considered as an alternative method for on-board hydrogen storage. Major alternative solid-state storage technologies are based on the use of metal hydrides (more specifically alanates) and nanostructured materials (Orimo et al., 2007).

2.1.3.1 Nanostructured Materials

Nanostructure materials are a new class of materials with unique properties that stem from their reduced length scale ($1 < d < 100$ nm). The nanostructured materials considered for storing hydrogen are, for example, carbon nanostructure (carbon nanotubes, carbon nanofiber, and graphite nanofiber) and metal organic framework (MOF). Hydrogen can be stored by adsorbing

(physisorption) on the surface of these materials. Since physisorption is a non-activated process, fast kinetics and reversibility can be expected. These are the main favorable characteristics of physical absorbents. However, the major drawback is a very weak bond between hydrogen and adsorbent so hydrogen absorption can take place only in a cryogenic temperature. Moreover, a real value of hydrogen capacity by these materials is still contradicted, particularly for carbon nanotubes (science.energy.gov).

2.1.3.2 Metal Hydrides

Metal hydrides are a chemical compound of hydrogen and metal. They still give the sense of surface not bulk (chemisorption). Metal hydrides can store and retain hydrogen under specific temperature and pressure condition and release hydrogen and different conditions (increase temperature, decrease pressure). Hydrogen is located, either in the form of atom on interstitial sites of the host metal lattice (transition metal hydride) or the ionic-covalent bond with metal (light weight metal hydride). These materials have quite high capacity to store hydrogen, particularly light metal hydride such as LiH 12.7 wt%, MgH_2 7.6 wt%, $LiBH_4$ 8.6 wt%, $NaAlH_4$ 7.4 wt%. Thus, these materials are widely researched as a medium for hydrogen storage. However, the key issues of these materials are irreversibility, low kinetics, and too stable, which will need high temperature for hydrogen desorption (Orimo et al., 2007).

2.2 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:

$$M + \frac{x}{2}H_2 \leftrightarrow MH_x + heat \tag{2.1}$$

$$M + \frac{x}{2}H_2O + \frac{x}{2}e^- \leftrightarrow MH_x + \frac{x}{2}OH^- \tag{2.2}$$

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

$$\Delta G = \Delta H - T\Delta S \tag{2.3}$$

Hydrogen is absorbed if ΔG is less than zero and desorbed if ΔG 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 a H_2 gas, interface region and solid metal as shown in Figure 2.1. At the interface, the molecule is dissociated and dissolves into the metal phase. The metal phase is known as α phase at which some hydrogen is absorbed, the fully formed hydride is known as β phase.
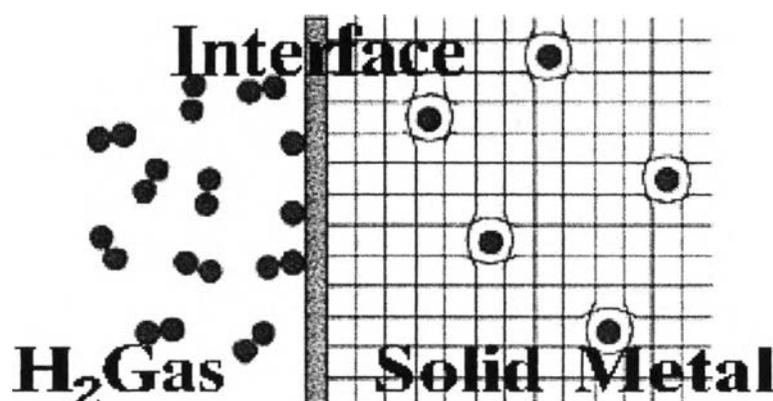
Figure 2.1 Model of the metal hydrides interaction
(http://www.ovonic-hydrogen.com/solutions/technology1.htm).

Figure 2.2 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 2.3). 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, 2003).
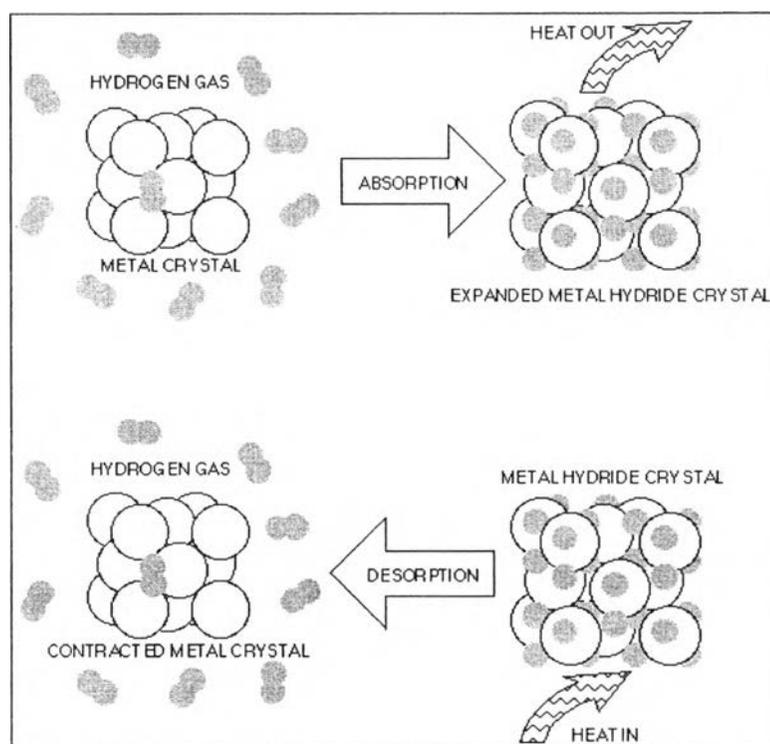
Figure 2.2 Absorption and desorption of metal hydrides.
(http://www.hydrogencomponents.com/hydride.html).

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, α-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 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, 2003).
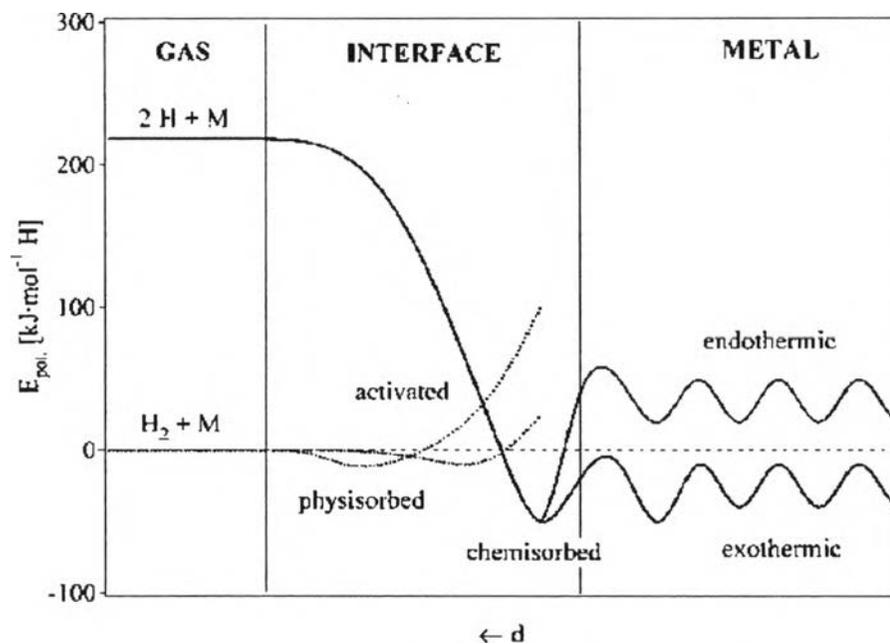
Figure 2.3 The potential energy of a hydrogen molecule and of two hydrogen atoms. (Züttel, 2003).

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 (β-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 α- and β-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 μm (Züttel, 2003).

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 (α + β 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 2.4.
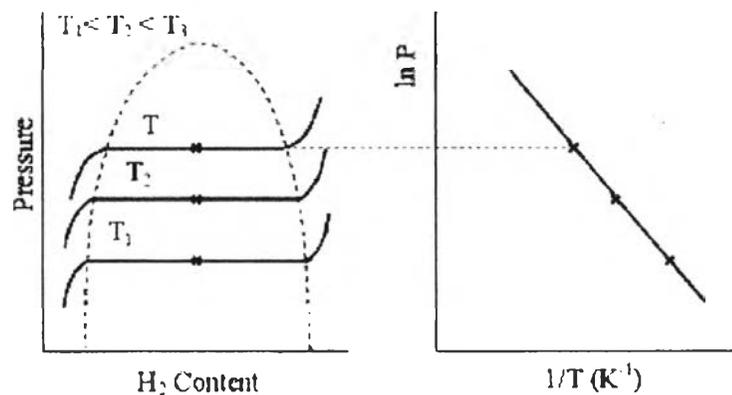
Figure 2.4 Pressure-concentration-temperature curve (PCT diagram) and Van't Hoff plot (Logarithm of the equilibrium against the reciprocal temperature) (http://www.ovonic-hydrogen.com/solutions/technology1.htm).

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

$$\ln P = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \tag{2.4}$$

where, ΔH and ΔS are the enthalpy and the entropy of the reaction, respectively, R is the gas constant and T is the temperature. The logarithm of pressure and one over

temperature (lnP vs 1/T) are plotted, called Van't Hoff plot, Figure 2.4. 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 separated 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 (aluminohydrides), 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 2.2, their theoretical total hydrogen capacities are high (from ~7 to 18 wt%).

Table 2.2 Theoretical hydrogen capacity of metal hydrides and complex hydrides

Hydrides	Hydrogen, wt%	Reversibility
MgH_2[1]	7.7	Yes (good)
LiH[2]	12.7	N/A
$NaAlH_4$[1]	5.6	Yes (good)
$LiAlH_4$[3]	10.6	No
$Mg(AlH_4)_2$[4]	9.3	No
$NaBH_4$[4]	10.7	No
$LiBH_4$[5]	18.5	Yes
$Mg(BH_4)_2$[4]	14.9	No
$LiNH_2$[6]	6.5	N/A
Li_3N[6]	10.4	Yes

[1]Sakintuna *et al.*, 2007; [2]Ichikawa *et al.*, 2005; [3]Blanchard *et al.*, 2004;
[4]Sandrock, 1999; [5]Jin *et al.*, 2008; [6]Isobe *et al.*, 2005.

b) Inter-metallic Metal Hydrides

Inter-metallic metal hydrides can perform many functions: (1) enhancing 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 classified on the basis of their crystal structures, such as AB2 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 2.3.

Table 2.3 Examples of inter-metallic compounds

		Maximum Hydrogen Capacity		
Type	**Intermetallic**	**H/M^a**	**wt%**	**Temperature (°C) for 1 atm P$_{desorption}$**
A_2B	Mg_2Ni	1.33	3.6	255
AB	TiFe	0.975	1.86	−10
AB	ZrNi	1.4	1.85	292
AB_2	$ZrMn_2$	1.2	1.77	167
AB_5	$LaNi_5$	1.08	1.49	12
AB_2	$TiV_{0.62}Mn_{1.5}$	1.14	2.15	−6

^{a} H/M is the hydrogen-to-metal atomic ratio in the compound (Sandrock, 1999)

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).

2.3 Hydrogen Storage in Metal Hydrides

Metal hydrides can be divided into two types: transition metal hydrides and light weight metal hydrides. Only light weight metal hydrides will be focused here. Light weight metal hydrides or alkali metal hydrides are divided into two parts: simple metal hydrides such as NaH, CaH_2, and LiH, and complex metal hydrides are group I and II salts of $[AlH_4]^-$, $[NH_2]^-$, and $[BH_4]^-$ (alanates, amides, and

borohydrides) such as $NaAlH_4$, $LiAlH_4$, and $LiBH_4$. Hydrogen is covalently bonded to the central atoms in complex anions (in contrast to interstitial hydrides).

The released hydrogen from complex metal hydrides can take place into two ways by a hydrolysis reaction and by heat decomposition (hydrogen desorption). The former method is not complex and can take place at ambient temperature but the regeneration process of product is very complex and cannot take place at the on-board applications. Examples of the hydrolysis reaction of complex metal hydride are shown in Table 2.4. Although the complex metal hydrides have high hydrogen capacity, most of them are too stable, which leads to the hydrogen desorption at a high temperature, low kinetics, or some of them is irreversibility. Therefore, the developments of complex hydride properties are needed in order to improve their properties to those of materials for hydrogen storage. Some complex metal hydrides show noticeable properties and their properties are shown in Table 2.5.

Table 2.4 Hydrolysis reaction of complex metal hydrides (Schüth *et al.*, 2004)

Hydrolysis reaction	wt% H_2
$LiH + H_2O \rightarrow LiOH + H_2$	7.7
$LiBH_4 + 4H_2O \rightarrow LiOH + H_3BO_3 + 4H_2$	8.6
$NaBH_4 + 4H_2O \rightarrow NaOH + H_3BO_3 + 4H_2$	7.3
$NaAlH_4 + 4H_2O \rightarrow NaOH + Al(OH)_3 + 4H_2$	6.4

Table 2.5 Examples of alkali metal hydride and their properties (Annemieke and Carlos, 2008)

Materials	Max. wt% H_2	T $_{decomposition}$, °C	Note
$NaBH_4$	13	400	Too stable, low kinetics
$LiBH_4$	19.6	380	Irreversible
$LiAlH_4$	10.54	190	Irreversible
$NaAlH_4$	7.4	180	Reversible with adding Ti
$LiBH_4 + MgH_2$	11.4	400	Low kinetics
$LiNH_2 + MgH_2$	5.35	200	Good reversibility
$LiNH_2 + LiH$	5.5	150	Reversible with adding

2.3.1 Lithium Aluminum Hydride (LiAlH₄)

Lithium alanate or lithium aluminum hydride (LiAlH₄) has high hydrogen capacity for complete decomposition (7.9 wt%). It has multiple steps for decomposition

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2 \tag{2.5}$$

$$Li_3AlH_6 \rightarrow 3LiH + Al + 3/2H_2 \tag{2.6}$$

The first step, Equation (2.5), takes place at 160 °C and releases 5.3 wt% hydrogen. The second step, Equation (2.6), releases 2.6 wt% hydrogen and occurs at about 200 °C. The unreleased part as LiH can be decomposed at a very high temperature, above 680 °C (Zaluski et al., 1999).

Suttisawat et al. (2007) investigated the catalytic effect of ZrCl₄ and HfCl₄ on hydrogen desorption/absorption of LiAlH₄ by different preparation method. LiAlH₄ doped with ZrCl₄ using a mortar and pestle showed the highest hydrogen released of 6 wt% at 150 °C. The addition of 4 mol% HfCl₄ decreased the desorption temperature by 40 °C compared with undoped LiAlH₄ while doping with 4 mol% ZrCl₄ improved the desorption kinetics of LiAlH₄. After that, all doped samples were

absorbed at 50 °C to 125 °C under 11 MPa hydrogen pressure for 12 hr. They found that all doped samples did not absorb hydrogen at all studied conditions.

Kumar *et al.* (2008) found that the dehydrogenation kinetics of $LiAlH_4$ were improved by adding CNFs co-doped with metal particles such as Ni and Cu because the particles increased the gain boundaries and provided a transition site for hydrogen transfer. The activation energy of dehydrogenation of this mixture was lowered. The re-hydrogenation capacity of this mixture achieved about 3.9 wt% hydrogen by adding 3 mol% VCl_3.

Sun *et al.* (2008) studied the effect of doping $NiCl_2$ on the dehydrogenation properties of $LiAlH_4$. Mixtures between $LiAlH_4$ and $NiCl_2$ were prepared by designed mixing and milling processes. $NiCl_2$ reduced the desorption temperature and enhanced the desorption kinetic behavior of $LiAlH_4$. $LiAlH_4$ doped with 2 mol% $NiCl_2$ by ball milling for 0.5 h released 4.2 wt% hydrogen at 100 °C within 3 h and decreased the desorption temperature by 50 °C. Active Ni species played a catalytic role in this system and the reaction between Cl^- and Li^+ may promote the dehydrogenation of $LiAlH_4$.

Xueping and Shenglin (2009) studied the hydrogen storage properties of $LiAlH_4$ by doping with 5 mol% Ti, Ni, $Ce(SO_4)_2$ and $LaCl_3$ by using ball milling. All the doped samples had lower desorption temperature and rate of hydrogen released in the first stage than the undoped one. Doping with $Ce(SO_4)_2$ decreased the desorption temperature by 38 °C compared with as-received $LiAlH_4$. In addition, the amount of hydrogen released was decreased by doping with Ti and $LaCl_3$. For absorption, doping with Ti showed the most promising results under 8 MPa at 180 °C for 2 h.

The effect of additives on the reversibility of $LiAlH_4$ was investigated by Xueping *et al.* (2009). Doping with 1 mol% Ti, Ni, Fe, and $Ce(SO_4)_2$ decreased the desorption temperature except doping with $LaCl_3$. The addition of Fe markedly decreased the hydrogen desorption temperature, 37 °C, while the amount of hydrogen released had decreased. Furthermore, the rate of hydrogen released was decreased regardless on dopants. $LiAlH_4$ doped with 1 mol% Ni exhibited the highest hydrogen absorption about 0.97 wt% at 180 °C under 8 MPa for 2 h.

Léon *et al.* (2009) investigated alanate mixtures (LiAlH$_4$+MgH$_2$) produced by reactive ball milling. They found that a milling speed and milling time were important parameters to the new hydride phase formation. For the sample ball-milled at 600 rpm, one or two new phases were observed, which showed the fast desorption kinetics. At 300 °C under 0.5 bar H$_2$, alanate mixtures released about 6.5 wt% hydrogen within 2,000 s during first cycle desorption, while only 2.5 wt% H$_2$ were released within 3,500 s during the second cycle desorption indicating that only MgH$_2$ was formed after the hydrogen uptake.

Liu *et al.* (2009) studied the effect of ball milling time on the hydrogen storage properties of 4 mol% TiF$_3$-doped LiAlH$_4$. When the ball milling time increased, the smaller crystallite sizes of LiAlH$_4$ were obtained and the changes in the desorption temperature was observed. An half hour ball milling of the sample doped with 4 mol% TiF$_3$ reduced the dehydrogenation temperature of LiAlH$_4$ to 80 °C, which is 70 °C lower than as-received LiAlH$_4$. They believed that the reaction between LiAlH$_4$ and TiF$_3$ formed catalyst, TiAl$_3$, which improved the desorption temperature. After complete dehydrogenation, all samples did not absorb hydrogen under 95 bar H$_2$ pressure at various temperatures: 20, 50, 100, 150 and 200 °C.

The dehydrogenation behaviors of both LiMg(AlH$_4$)$_3$ and LiAlH$_4$ were improved by adding graphite nanofibres (GNFs). Holical graphitic nanofibres (HGNFs) showed the favorable desorption kinetics and decreased the desorption temperature of both complex metal hydrides as well as the activation energy. HGNFs admixed LiMg(AlH$_4$)$_3$ and HGNFs admixed LiAlH$_4$ decreased the desorption temperature from 105 to ~70 °C and 159 to 128 °C, respectively, as compared to pristine LiAlH$_4$ phase. Moreover, the desorption rate of HGNFs admixed LiMg(AlH$_4$)$_3$ was higher than that of LiAlH$_4$. The activation energy of LiMg(AlH$_4$)$_3$ was reduced, with the addition of GNFs (Huson *et al.*, 2010).

The effects of NbF$_5$ addition on the hydrogen storage properties of LiAlH$_4$ were studied by Ismail *et al.* (2010). NbF$_5$ was mixed with LiAlH$_4$ by using ball milling. The addition of 0.5 and 1 mol% NbF$_5$ in LiAlH$_4$ decreased the desorption temperature of about 45-49 °C in the first state and about 27-29 °C in the second stage. The hydrogen capacities of all adding samples were reduced by adding NbF$_5$, especially for the 5 mol% added sample. The NbF$_5$ added LiAlH$_4$ improved

the hydrogen desorption rate 5-6 times faster than that of as-received $LiAlH_4$. The $LiAlH_4$ added with different weight ratios of NbF_5 (0.5, 1, 2 and 5 mol%) did not absorb hydrogen at 170 °C under 70 atm H_2 pressure.

2.4 Hydrogen Storage on Carbon Aerogels

Carbon aerogels compose of particles with sizes in the nanometer range, covalently bonded together. There are high porous materials consisting of a continuous rigid framework. Carbon aerogels can be used in many applications such as gas adsorption devices, for heavy metals and ions removal, purification of drinking water, electronic capacitors, fuel cell electrodes, parts for inertial confinement fusion targets, catalyst support and chromatographic packing (Somlok, 2009).

- Structure and properties of carbon aerogels

    Carbon aerogels represent attractive properties such as:
    - A high electrical conductivity (25-100 S/cm)
    - Controllable pore structure
    - Highly useable surface area (up to 1,100 m^2/g)
    - Biocompatibility
    - Anti corrosion by acid or base etc.

From many advantages, carbon aerogels were used as attractive materials for hydrogen storage applications.

Gross *et al.* (2008) used nanoporous carbon scaffolds to enhance hydrogen storage kinetics of $LiBH_4$ by filling a porous carbon aerogel medium with $LiBH_4$. They found that the dehydrogenation rate of $LiBH_4$ in a 13 nm carbon aerogel was increased by 50 times. It could reduce the activation energy and its desorption temperature was reduced by up to 75 °C. The hydrogen capacity over multiple sorption cycles was increased by nanostructured $LiBH_4$.

Tian *et al.* (2009) studied the enhancement of hydrogen storage capacity of carbon aerogels obtained by using KOH as a catalyst to accelerate the gelation, strengthening a cross-linking and solidifying the carbon network. The maximum

hydrogen uptake of this carbon aerogels reached 5.2 wt% at -196 °C and 3.5 MPa because of the high surface area and pore volume.

Zhu *et al.* (2010) studied the hydrogen storage properties of a Mg-Ni-C system prepared by mechanical milling and hydriding combustion synthesis. The presence of both Ni and carbon aerogels decreased the desorption temperature and improved the desorption behavior of MgH_2, while carbon aerogels prevented the conglomeration, bonding and welding of MgH_2 during the mechanical milling. The 90Mg-6Ni-4C (wt%) system absorbed hydrogen about 5.23 wt% within 68 s at 100 °C and desorbed hydrogen 3.74 wt% within 1,800 s at 250 °C. In addition, this ratio released hydrogen at 157 °C, which was lower than the 90Mg-10Ni and 90Mg-10C systems.