

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Hydrogen

A large amount of hydrogen is formed as H_2O . Less than 1% is formed as hydrogen gas, H_2 , and some is in liquid or gaseous hydrocarbons. The hydrogen atom is interesting because its electron is followed by only one proton, the best ratio of valence electrons to protons of all the elements in the periodic table; and the energy gain is very high (Schlapbach and Züttel, 2001).

Hydrogen is produced in many ways, such as from water or from fossil fuel. At ambient temperature and atmospheric pressure, one kilogram of hydrogen gas has a volume of 11 m^3 (Züttel, 2003). The methods for storing hydrogen gas are the next steps to be considered.

2.2 Hydrogen Storage

2.2.1 Compressed Hydrogen Gas

There is a common storage system, operating at a very high pressure of about 200-300 bar to store hydrogen gas in cylindrical tanks. This method is not safe as the tanks must be made and sealed carefully, and the energy consumption is quite intensive. The energy required for compressing hydrogen gas is about 30-40% of the low heating value (LHV) of hydrogen (Heung, 2003).

2.2.2 Liquid Hydrogen Storage

Liquid Form

In the liquid storage system, hydrogen is condensed and stored in cryogenic tanks at 21.2 K and ambient pressure. The energy required to cool hydrogen to the liquid state is considerable. But the actual required energy is even more because liquid hydrogen needs to evaporate and warm up before using. The total energy required to liquefy one kilogram of hydrogen is about 42% of the low heating value of hydrogen (Heung, 2003). The advantage of liquid hydrogen is its high energy-to-

mass ratio. But the disadvantage of this process is that it is both long and energy intensive (Züttel, 2003).

Hydrocarbons

After hydrocarbons have burnt completely by oxidation, carbon in the form of carbon-dioxide (CO_2) and hydrogen in the form of water (H_2O) are given off. Some hydrocarbons can be considered as liquid storage for hydrogen. For example, tetralin ($\text{C}_{10}\text{H}_{12}$) desorbs four hydrogen atoms and forms naphthalene (C_{10}H_8), called a hydrogenation/dehydrogenation reaction (Hodoshima *et al.*, 2005).

2.2.3 Solid-Stage Storage

Gas-on-Solid

The important part of the gas-on-solid method is adsorption. Hydrogen adsorption on a solid with a large surface area depends on the applied pressure and temperature. The interaction of hydrogen with the surface of a solid can be of two types, physisorptions and chemisorptions. The gas-on-solid method focuses on physisorption because the energy used ($E_{\text{Phy}} \approx 10 \text{ kJ/mol}$) is lower than that for chemisorption ($E_{\text{Chem}} \approx 50 \text{ kJ/mol-H}$) (Züttel, 2003). The advantages of physisorption for hydrogen storage are its low operating temperature and pressure, which are related to the low cost of consumption and materials. Materials that are often used in this method are carbon species because they are inexpensive, have high porosity, and tend to have high capacity adsorption.

Metal Hydrides

When metal reacts with hydrogen under suitable conditions, a metal-hydrogen bond occurs, the results of which are called metal hydride. This reaction is exothermic and reversible. When temperature decreases, the hydrogen is absorbed and heat removal during rehydriding becomes the controlling factor on rehydriding time (Heung, 2003). The metal-hydrogen bond has certain advantages, such as high hydrogen density at moderate pressure, safe handling (Schlapbach and Züttel, 2001), and the system requires the least amount of energy to operate, compared with the methods mentioned above. But most metal hydrides are heavy compared with the amount of hydrogen that is contained, which is a disadvantage. The advantages and disadvantages of all the methods are shown in Table 2.1.

Table 2.1 Comparison of available types of hydrogen storage

Method	Carrier	Advantage	Disadvantage
Gas H ₂	- High-pressure gas cylindrical tanks	- Not complex	- Not safe - Intensive energy consumption - Large space in vehicle
Liquid H ₂	- Cryogenic tanks	- High energy-to-mass ratio - Suitable for use in air and space travel	- Intensive energy consumption
Hydrocarbons	- Liquid / Gas hydrocarbons	- Easy to find the carriers	- Require high temperature - Long start-up duration
Gas-on-Solid	- Activated carbons - Carbon nanotubes - Graphite	- Low cost - High porosity - Less energy consumption	- Does not reach the target 6.5 wt%
Metal/ Chemical Hydrides	- NaAlH ₄ - LiNH ₂ /LiH	- High hydrogen density - Safe handling - Less energy consumption	- Does not reach the target 6.5 wt%

2.3 Metal Hydrides

This type of hydride is focused on the combination between hydride ions and metals. The reaction of hydrogen with a metal can be written as follows:



Whether hydrogen is released or absorbed depends on the value of the Gibbs energy at the reaction conditions:

$$\Delta G = \Delta H - T\Delta S \quad (2.2)$$

Hydrogen is absorbed if ΔG is less than zero and desorbed if ΔG is greater than zero.

The suitable metals, which can be metal hydrides, must react and release hydrogen at moderate pressure and temperature and must be stable to maintain its reactivity and capacity. The moderate pressure mentioned above means the hydrogen supply pressure is less than 27 bar and the discharge pressure is higher than 2 bar. Moderate temperature means the temperature for absorption is not colder than 283 K (10°C) and the temperature for desorption is not higher than 373 K (100°C) (Heung, 2003).

Using a metal hydride to store hydrogen requires two steps, absorption and desorption. 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).

A metal-hydrogen system consists of H₂ gas, an 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 the α phase and the hydride is known as the β phase.

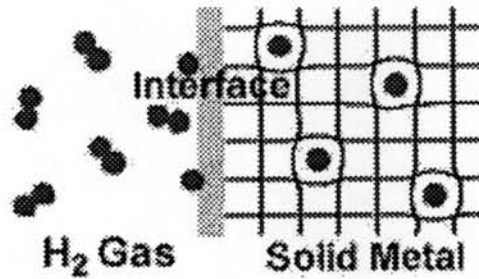


Figure 2.1 Model of the metal hydrides interaction.

(http://folk.uio.no/ravi/activity/hydride/hyd_tutorial.html).

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.

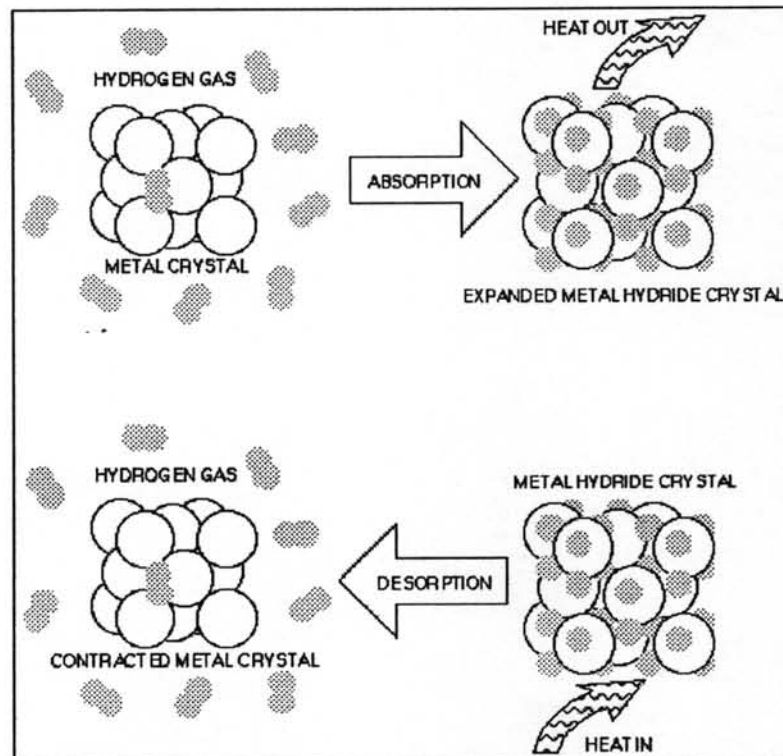


Figure 2.2 Absorption and desorption of metal hydrides.

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

The stages that are of interest in this system are physisorption and chemisorption. The interaction between the hydrogen molecule and the metal surface in the

in the physisorbed state is the Van der Waals force. The physisorption energy is about 10 kJ/mol. When hydrogen is close to the surface, the hydrogen has to overcome an activation barrier of dissociation, and the energy of the activation barrier depends on the surface elements. The hydrogen-metal bond is formed. Hydrogen atoms share their electrons with the metal atoms in the chemisorbed state. The chemisorption energy is about 50 kJ/mol-H. The chemisorbed hydrogen atoms have high surface mobility, interact with each other, and form surface phases with high coverage (Züttel, 2003). In the next stage, the chemisorbed hydrogen atom diffuses on the interstitial sites of the host metal lattice. Figure 2.3 shows a simplified one-dimensional potential energy curve.

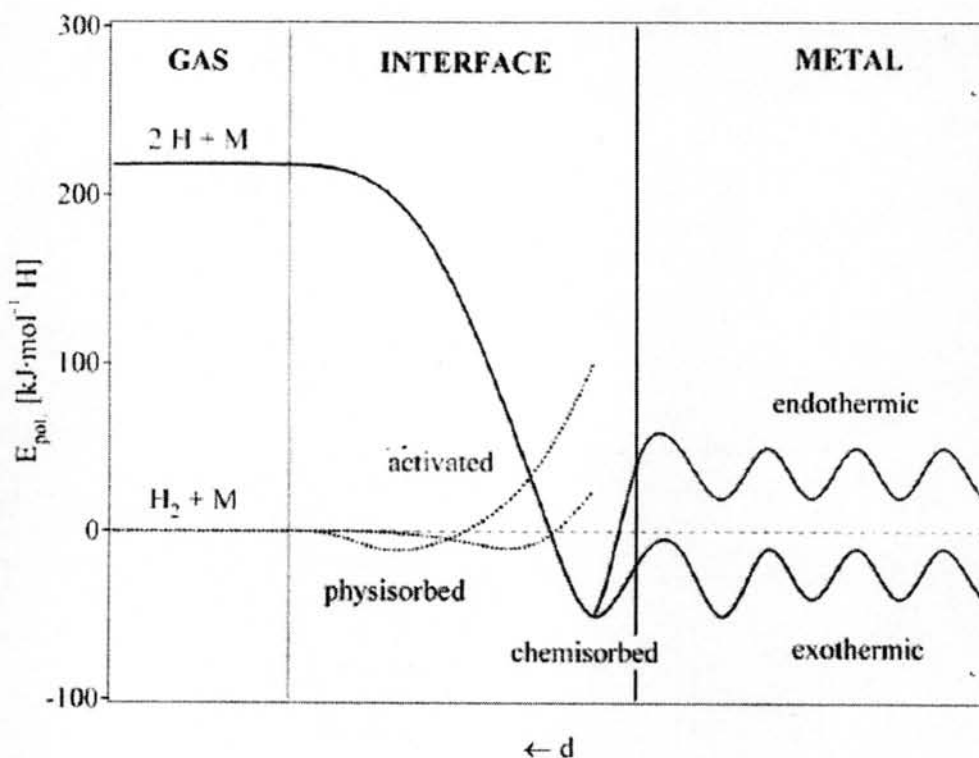


Figure 2.3 Potential energy of a hydrogen molecule and of two hydrogen atoms. (Züttel, 2003).

The hydrogen molecule approaches the metal atom by Van der Waals forces and forms a physisorbed state. Before diffusion into the metal, the hydrogen molecule must overcome the activation barrier and dissociates to form a chemisorbed state (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 the solid solution and hydride phase region ($\alpha + \beta$ phase), the pressure change is small and the size of the region depends on the amount of 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). Hydrogen absorption on metal is represented by a PCT diagram as shown in Figure 2.4.

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

$$\ln P = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (2.3)$$

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 the inverse of temperature ($\ln P$ vs $1/T$) are plotted, called the 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 change term gives information about the stability of the metal hydrogen bond and the entropy change term gives information about the change from hydrogen gas molecule to dissolved hydrogen (Schlapbach and Züttel, 2001).

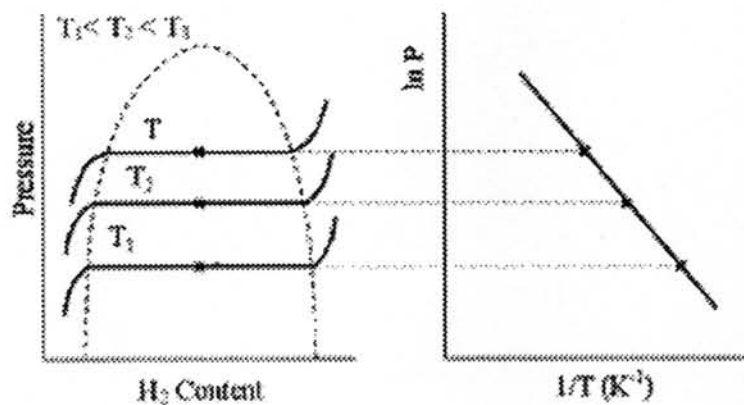


Figure 2.4 Pressure-concentration-temperature curve (PCT diagram) and Van't Hoff plot (Logarithm of the equilibrium against the reciprocal temperature).
(<http://www.ovonic-hydrogen.com/solutions/technology1.htm>).

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

2.3.1 Alkali Metal Hydrides

Some examples and their properties are shown in Table 2.2.

Table 2.2 Examples of alkali metal hydrides and their properties

Material	Practical wt%	Kinetic reversibility	Temperature desorption (°C)	Notes
NaH	4.2	good	425	Low wt%, High temperature desorption
NaAlH ₄	5.5	good	125	Not reach 6.5 wt%
LiBH ₄	19.6	irreversible	380	Too stable
LiH/LiNH ₂ *	5.5	good	150-250	Not reach 6.5 wt%

(*LiH/LiNH₂ with TiCl₃)

(Grochala and Edwards, 2004)

2.3.2 Inter-Metallic Metal Hydrides

Inter-metallic metal hydrides can perform several 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. Some families of inter-metallic compounds are listed in Table 2.3.

Table 2.3 Inter-metallic compounds (Züttel, 2003)

Composition	A	B	Inter-metallic compounds
AB	Ti, Zr	Fe, Ni	TiNi, TiFe, ZrNi
AB ₂	Ti, Zr	Mn, V	TiMn ₂ , ZrMn ₂ , ZrV ₂
AB ₃	Ce, Y	Fe, Ni	CeNi ₃ , YFe ₃
AB ₅	La, Rare earth	Cu, Ni	LaNi ₅ , LaCu ₅
A ₂ B	Mg, Zr	Fe, Ni	Mg ₂ Ni, Zr ₂ Fe
A ₂ B ₇	Th, Y	Fe, Ni	Th ₂ Fe ₇ , Y ₂ Ni ₇

Metal Hydride Development

Factors to develop metal hydrides for practical and economic hydrogen storage systems are:

1. Weight
2. Operating temperature
3. Capacity and amount of usable hydrogen
4. Rate of absorption/desorption
5. Cyclic stability
6. Cost and availability

2.4 Li-N-H and Li-Al-N-H System

The Li-N-H system has high hydrogen-absorption potential (percentage of desorption hydrogen is 6.5 wt%) and its weight is quite low. However, it requires a high temperature for dehydrogenation and a high pressure for rehydriding. The reaction is as follows:

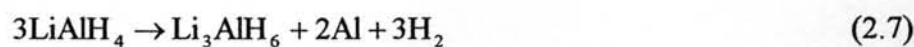


The assumption of suitable elementary reactions for reaction (2.4) is as follows:



where the enthalpy change of reactions (2.5) and (2.6) could be calculated at +84 kJ/mol NH₃ and -42 kJ/mol H₂, respectively. For the acceleration of this reaction, the ball milling treatment was performed (Ichikawa *et al.*, 2005).

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



The first step (Eq. (2.7)) takes place at 160°C and releases 5.3 wt% hydrogen. The second step (Eq. (2.8)) releases 2.6 wt% hydrogen and occurs at temperature about 200°C. The unreleased part as bond of LiH which can be decomposed at very high temperature, above 680°C (Zaluski *et al.*, 1999).

The dehydrogenation reaction of the LiNH_2/LiH mixture was accelerated by the addition of 1 mol% Ti(III) species and the prolonged ball-milling time (16h) for an enhanced reaction rate. The results indicated that the Ti(III) additives change the hydrogen desorption reaction mechanism of the LiNH_2/LiH (Matsumoto *et al.*, 2006).

The mixture contains 1 mol% of TiCl_3 as a catalyst, leading to lower activation energy for the reaction (temperature desorption is in range from 150 to 250°C). The reaction can desorb 5.5 wt% hydrogen and does not desorb ammonia (Ichikawa *et al.*, 2004a).

High-energy ball milling on the reaction of LiNH_2 and LiH mixture results in finer particle, better mixing of reactants and reduction in the activation energy. The peak temperature for releasing H_2 can be reduced by 100°C. (Shaw *et al.*, 2006)

Yoshihiro *et al.* (2006) studied the hydrogen desorbing behavior of the hydrides in rare earth elements and measured them by temperature swing column chromatography. It was found that the hydrogen-desorbing profiles of the rare earth hydrides, except Eu, had two peaks. The first peaks were located at lower temperature, around 600-700 K, and the second peaks were located at around 700-900 K.

Leng *et al.* (2005) designed a new family of metal-N-H hydrogen storage systems and synthesized the metal amide $\text{M}(\text{NH}_2)_x$. The results, measured by gas chromatographic examination and X-ray diffraction, indicated that the kinetics of these reactions with gaseous NH_3 is faster, in the order of $\text{NaH} > \text{LiH} > \text{CaH}_2 > \text{MgH}_2$. For decomposition, both $\text{Mg}(\text{NH}_2)_2$ and $\text{Ca}(\text{NH}_2)_2$ decomposed and emitted NH_3 at lower temperature than LiNH_2 .

Meisner *et al.* (2005) observed the reaction of hydrogen and lithium nitride. The results reported more than 7 wt% hydrogen gas uptake at 160°C, no observable hydrogen release into a vacuum, and about 5.2 wt% cyclable hydrogen sorption at 240°C with a reversible lithium amide/lithium imide reaction. The plateau pressure for the amide/imide reaction is quite low.

Pinkerton (2005) studied the kinetic behavior of lithium amide decomposition for hydrogen storage. LiNH_2 is a primary component of the hydride state in Li-N-H storage materials based on Li_3N or Li_2NH . It was obtained by ball milling for 10 or 20 min and was detected by using thermo-gravimetric analysis (TGA). The reac-

tion rate was found to depend on the sample size, as large samples produce a high concentration of NH_3 .

Isobe *et al.* (2005) studied the efficiency of different Ti forms for the Li-N-H system. The TDS profiles show a hydrogen desorption curve and the results from TDS and XRD indicated that the Ti^{nano} , TiCl_3 and $\text{TiO}_2^{\text{nano}}$ disperse in the nanoscale and act as an effective catalyst in the reaction of hydrogen desorption. The additive particle size is an important factor for improving the kinetics of hydrogen storage, and TiO_2 in nano-scale should be a better additive because of its light weight, low cost and easy treatment.

Luo (2004) developed a new storage material, which is from the partial substitution of lithium by magnesium. The mixtures between LiNH_2 and MgH_2 with 2:1.1 mol ratios were examined. The plateau pressure of the new Mg-substituted system is about 30 bar, and the temperature is 200°C . The amount of hydrogen desorbed is 4.5 wt% and possibly higher because the theoretical capacity is 5.35 wt%. The difference between the theoretical and experimental capacities may result from isolated islands of the two solid reactants, and better sample mixing may improve its desorption efficiency.

Lu and Fang (2005) investigated dehydrogenation properties of the mixture of LiAlH_4 and LiNH_2 (2 $\text{LiAlH}_4/\text{LiNH}_2$). Thermogravimetric analysis indicated that a large amount of hydrogen (~ 8.1 wt%) can be released between 358 and 593 K.

The dehydrogenation/rehydrogenation reactions of a combined system of Li_3AlH_6 and LiNH_2 were studied. Thermogravimetric analysis (TGA) of $\text{Li}_3\text{AlH}_6/3\text{LiNH}_2/4$ wt% $\text{TiCl}_3\text{-}\frac{1}{3}\text{AlCl}_3$ mixtures indicated that a large amount of hydrogen (≈ 7.1 wt%) can be released between 150 and 300°C under a heating rate of $5^\circ\text{C}/\text{min}$ in two dehydrogenation reaction steps (Lu *et al.* 2006).

The power characteristics of lithium hydride (LiH) as a function of high-energy ball milling condition were investigated via quantitative X-ray diffraction (XRD) analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and specific surface area (SSA) analyses. The results indicated that ball milling at room temperature was effective in obtaining nano-crystalline LiH power. The crystal size reduction proceeded rapidly at the early stage of ball milling, the size reduction rate decreased beyond 90 min of ball milling (Ortiz *et al.*, 2007).

Blanchard *et al.* (2004) studied the thermal decomposition temperature of ball milling of LiAlH_4 doped with additives. The results were measured by using thermal desorption spectroscopy and X-ray diffraction and found that LiAlH_4 in the presence of VCl_3 or $\text{TiCl}_3 \cdot \frac{1}{3}(\text{AlCl}_3)$ can reduce its thermal decomposition temperature by 60 and 50°C, respectively.

Temperature-programmed desorption scans of the Li-Al-N-H system, which is the mixture of Li_3AlH_6 and LiNH_2 with 1:2 mol ratio, indicated that a theoretical amount of hydrogen is about 6.9 wt% and it can be released between 370 and 773 K. The desorption/absorption capacities of the Li-Al-N-H system with a nano-Ni catalyst exhibited 3-4 wt% at 473-573 K, while the capacities of the system without the catalyst were 1-2 wt% (Kojima *et al.*, 2006)