CHAPTER 1: INTRODUCTION

The abundant supply of energy is such a common aspect of modern living that we have acquired a voracious appetite for it without worrying much of its sustainability. As we know, the industrialized society is now almost entirely depends on non-renewable fossil fuels, such as coal, petroleum and natural gas, as our primary energy resources for transportation, materials processing, secondary energy products and some stationary applications. These are a particularly important part of the global energy system, and burning these fossil fuels produces more than 81.56% of our energy.

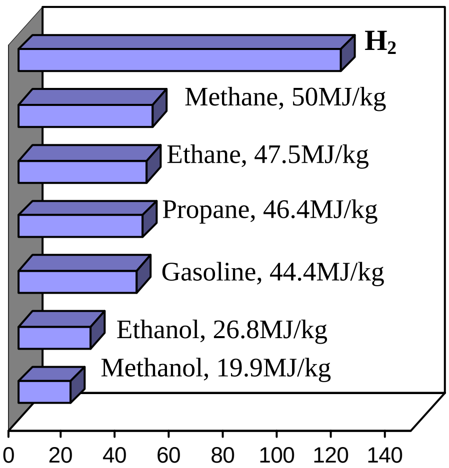

Figure 1.1 Heating energy content by weight of several common fuels **(**data source from Web 01, Alternative Fuels Data Centre, U.S.)

Although we cannot make an accurate prediction, it is clear that, if we do not search for a new source of energy supply, much of our fossil energy resources will become scarce and eventually be exhausted. In addition, there are a number of disadvantages of using fossil resources. CO_2 emission from burning such fuels is the main culprit for global warming. Vehicle-related air pollution is a significant and growing health hazard, directly linked to increases in asthma, bronchitis, emphysema and other diseases. There is now a considerable, social and economical drive to develop alternative/clean energy resources.

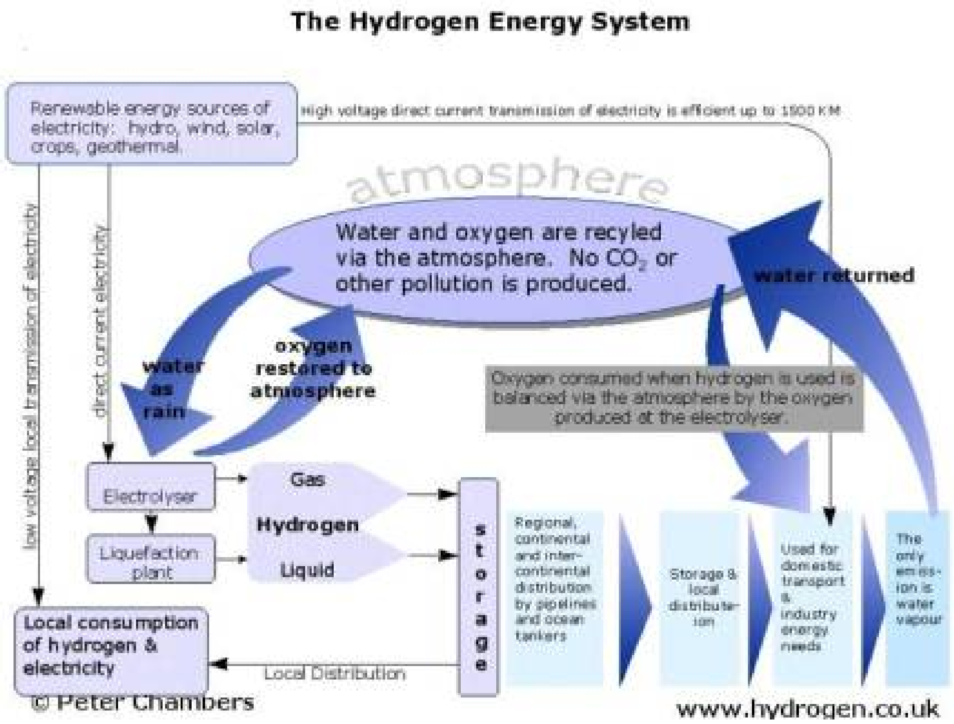

Figure 1.2 Cycle of hydrogen in a hydrogen economy that uses renewable energy sources [www.hydrogen.co.uk]

Hydrogen is a non-polluting renewable fuel, which can be easily produced from various energy resources. It has the highest energy density of all combustion fuels, about 120MJ/kg as shown in fig. 1.1. Its combustion essentially produces water vapour without releasing CO_2 or CO Fig. 1.2. Moreover, hydrogen is the most abundant element on the earth, it can be produced anywhere with a supply of water and electricity, biomass or solar energy. As a fuel, hydrogen can be employed to power three main types of energy conversion devices: fuel cells for producing electrical power; hydrogen steam turbines for electrical power; and internal combustion engines (ICE) for electrical or mechanical power. There is no doubt that hydrogen is the energy of the future. It is certainly one of the best alternatives to replace petroleum products as a clean energy carrier.

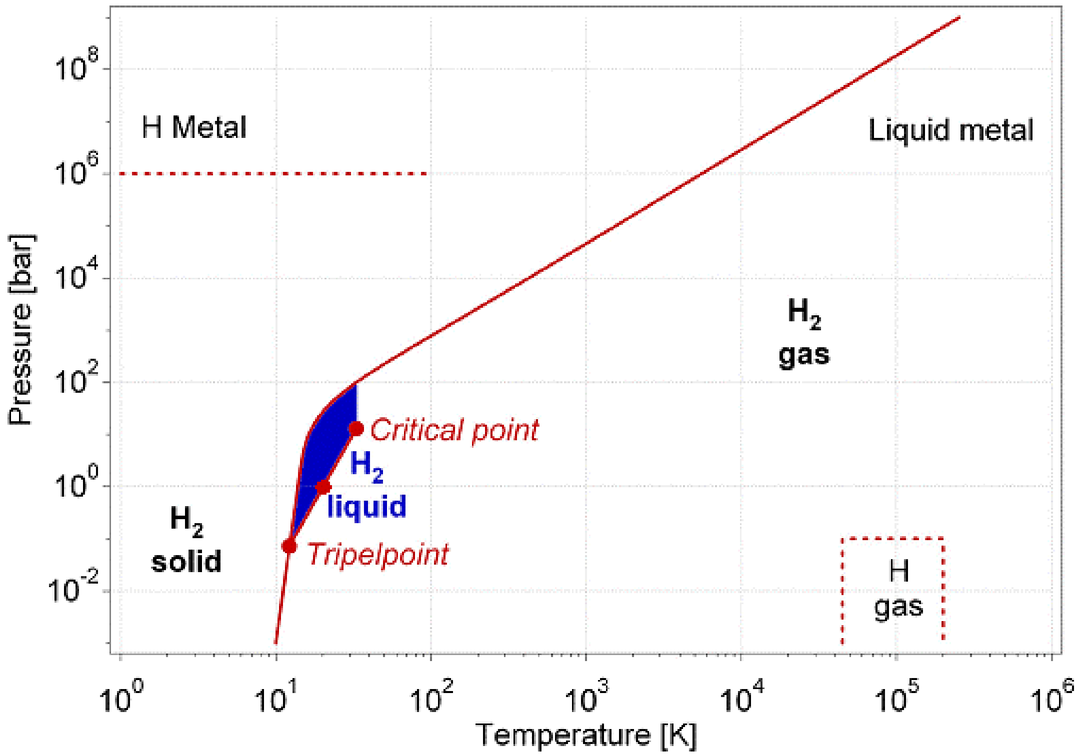

Figure 1.3 Primitive phase diagram of hydrogen [Leung et al.]

One of the major problems of using hydrogen is the difficulty of storing it in a safe and practical manner. Hydrogen can be stored in three states: gas, liquid, and in the form of a solid, e.g. a metallic or intermetallic hydride, a complex chemical hydride, and storage in carbon nano-structures. Gaseous storage gives a very low volume density, while heavy containers are required for the use of high pressures (200-300bar) fig. 1.3, the form of storage is also potentially dangerous, and any damage to the container would pose a risk of explosion. For liquid storage, a refrigeration system is required to keep the insulated bottles at -252.7^{o}C. In contrast, the form of solid state has a relatively large hydrogen storage density, it is capable of steadily absorbing and storing hydrogen several ten thousands times as much as its own volume before hydrogenation (under normal temperature and pressure).

There are presently three generic mechanisms known for storing hydrogen in materials: absorption, adsorption, and chemical reaction.

Absorption (fig. 1.4): 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.

Adsorption (fig. 1.5): 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. Sorptive 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.

Chemical reaction: The chemical reaction route for hydrogen storage involves displacive chemical reactions for both hydrogen generation and hydrogen storage. For reactions that may be reversible on-board a vehicle, hydrogen generation and hydrogen storage take place by a simple reversal of the chemical reaction as a result of modest changes in the temperature and pressure. Sodium alanate-based complex metal hydrides are an example. In many cases, the hydrogen generation reaction is not reversible under modest temperature/pressure changes. Therefore, although hydrogen can be generated on-board the vehicle, getting hydrogen back into the starting material must be done off-board. Sodium borohydride is an example.

Among them, hydrogen-absorbing metals and intermetallic compounds (hydrogen-metal system) have been studied for three decades, these are considered as one of the promising materials for safely and easily storing, keeping and transporting hydrogen as an energy source.

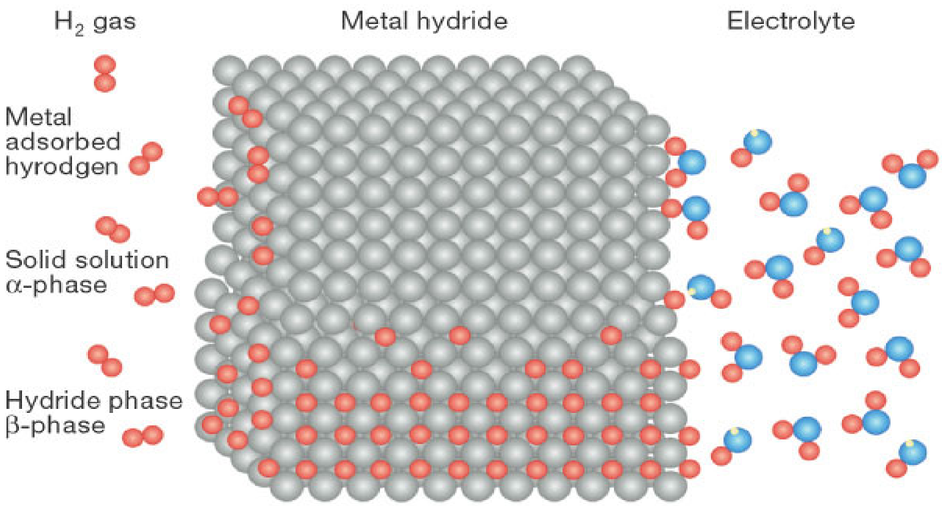

Figure 1.4 Schematic model of a metal structure with H atoms in the interstices between the metal atoms, and H2 molecules at the surface. Hydrogen atoms are from physisorbed hydrogen molecules on the left-hand side and from the dissociation of water molecules on the right-hand side. [Schlapbach & Züttel, 2001]

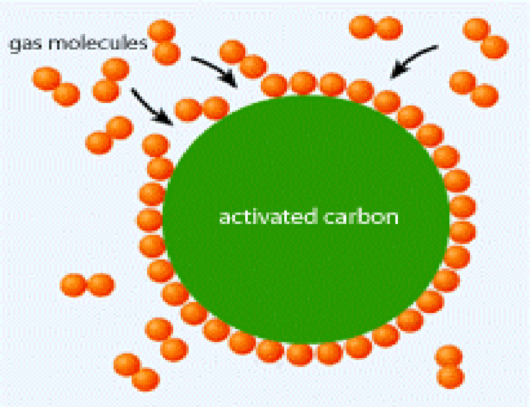

Figure 1.5 Adsorption of hydrogen on the material.

There are many advantages for using metal hydride as a hydrogen storage medium, such as: 1) high volumetric storage density; 2) provision of super-purity hydrogen delivery; 3) solid-state and safe storage; 4) reversible and no self-discharge; and 5) package flexibility - no need to use other assistant vessels to compress the hydrogen gas, hence it is easy to handle. In addition, metal hydrides have many possible practical applications, such as the negative electrodes for rechargeable NiMH batteries, hydrogen storage for heat energy, hydrogen-air fuel cells to power electric vehicles, heat pumps and hydrogen internal combustion engines, hydrogen purification and vacuum getters, and finally refrigeration application through the exothermic and endothermic reactions during hydrogen discharging and charging in metals.

Unfortunately, metal hydrides are still suffering from severe limitations. All hydrogen absorbing metals and intermetallic compounds except palladium, have an even greater affinity for oxygen than for hydrogen. These easily form a surface oxide layer, which may exist even after the metal has been cleaned by etching or mechanical polishing, and blocks the path of hydrogen atoms into the materials. The slow sorption kinetics presented in most hydrogen-metal systems is partially attributed to this surface passivation.

Most metal hydrides are thermodynamically very stable. The thermodynamic stability of a hydrogen-metal system actually describes how strong the attraction is for hydrogen to dissolve into the host metal and to form a hydride, and in which condition the reversible process could occur. The thermal stability can be evaluated through the hydride formation enthalpy or the equilibrium plateau pressure. Most metal hydrides have very low dissociation pressures at a temperature below 100°C and rather negative enthalpies of formation. Sufficient heat is required to activate the dissociation process. A relatively high temperature is required for dehydrogenation with 1 bar dissociation pressure. This hinders the practical application of the metal hydrides. Most metal hydrides are very heavy, and some are prohibitively expensive for hydrogen storage applications in practice.

New chemical approaches are needed to help achieve the 2010 and 2015 hydrogen storage targets. The concept of reacting lightweight metal hydrides such as LiH, NaH, and MgH2 with methanol and ethanol (alcoholysis) has been put forward. Alcoholysis reactions are said to lead to controlled and convenient hydrogen production at room temperature and below. However, as is the case with hydrolysis reactions, alcoholysis reaction products must be recycled off-board the vehicle. The alcohol must also be carried on-board the vehicle and this impacts system-level weight, volume, and complexity.

Another new chemical approach may be hydrogen generation from borazane by the following reactions:

$$NH_3BH_3 = NH_2BH_2 + H_2 = NHBH + H_2$$

The first reaction, which occurs at less than 120ºC releases 6.1-wt.% hydrogen, the second reaction that occurs at approximately 160ºC, releases 6.5-wt.% hydrogen.