

## CHAPTER II

### BACKGROUND AND LITERATURE SURVEY

#### 2.1 Hydrogen Energy

The chemical energy per mass of hydrogen is about  $142 \text{ MJ kg}^{-1}$  (Schlapbach and Andreas, 2001). It is at least three times larger than that of other chemical fuels (for example, the equivalent value for liquid hydrocarbons is  $47 \text{ MJ kg}^{-1}$ ). The process of burning hydrogen can be done in an efficient and controlled way to liberate energy at a desirable rate. If hydrogen is used in an internal combustion engine, it is burnt rapidly with oxygen from air. The efficiency of the transformation from chemical to mechanical through thermal energy is slightly higher for hydrogen–air mixtures than for petrol–air mixtures. Hydrogen can electrochemically give off the energy when reacts with oxygen from air in a fuel cell, which produces electricity and also heat. The efficiency of the direct process of electron transfer from oxygen to hydrogen is not limited by the Carnot's law. It can reach upto 50–60%, which is twice as much as the thermal process.

Typically a four seats passenger car can be operated for a range of 500 km with about 24 kg of petrol in a combustion engine. To cover the same range, about 5 kg hydrogen is needed for an electric car with a fuel cell. However, at room temperature and atmospheric pressure, 4 kg of hydrogen occupies a volume of  $45 \text{ m}^3$ . This huge volume is not practical for a vehicle. So, there is a search for a technique to store hydrogen in a very high efficiency.

#### 2.2 Hydrogen Storage

Hydrogen is so difficult to store so that its use as a fuel has been limited. Even though hydrogen can be stored in a variety of ways, each with specific advantages and disadvantages. The criteria for choosing a storage method should be safety and ease of use. The following topics are the summary of different storage methods available today. However, some techniques are still in the research and development stage.

### 2.2.1 Compressed Hydrogen

Compressing hydrogen is similar to compressing natural gas, but the compressors need better seals since hydrogen is less dense. Hydrogen is normally compressed to between 200 and 250 bar for storage in cylindrical tanks of up to 50 litres. These tanks may be made from aluminium or carbon/graphite compounds and can be used for either small industrial projects or transportation. If the compressed hydrogen is to be used on a larger scale then pressures of 500-600 bar may be employed, though some of the largest compressed hydrogen tanks in the world (about 15,000 m<sup>3</sup>) use pressures of only 12-16 bar.

Compressing or liquefying the gas is expensive. Hydrogen can be compressed into high-pressure tanks where each additional cubic foot compressed into the same space requires another atmosphere of pressure of 14.7 psi. High-pressure tanks achieve 6,000 psi, and therefore must be periodically tested and inspected to ensure their safety.

### 2.2.2 Liquid Hydrogen

In order to reduce the volume required to store a useful amount of hydrogen - particularly for vehicles - liquefaction may be employed. Since hydrogen does not liquefy until it reaches -253°C (20 K), therefore the liquefy process is both long and energy intensive. Up to 40% of the energy content in the hydrogen can be lost. The advantage of liquid hydrogen is its high energy to mass ratio which is about three times that of gasoline. It is the most energy dense fuel in use (excluding nuclear reactions), which is why hydrogen is employed in all space programmes. The cooling and compressing process requires energy, resulting in a net loss of about 30% of the energy that the liquid hydrogen is storing. Moreover, combine the energy required for the process to get hydrogen into its liquid state and the tanks required to sustain the storage pressure and temperature and liquid hydrogen storage becomes very expensive comparing to other methods.

### 2.2.3 Glass Microspheres

Tiny hollow glass spheres can be used to safely store hydrogen. When the glass spheres are warmed, the permeability of their walls is increasing, and

then can be filled by hydrogen. The spheres are then cooled, locking the hydrogen inside of the glass balls. A subsequent increase in temperature will release the hydrogen trapped in the spheres. Microspheres have the potential to be very safe, resist contamination, and contain hydrogen at a low pressure increasing the margin of safety.

#### 2.2.4 Liquid Carrier

This is the technical term for the hydrogen being stored in the fossil fuels that are common in today's society. Whenever gasoline, natural gas, methanol, etc. is utilized as the source for hydrogen, the fossil fuel requires reforming. The reforming process removes the hydrogen from the original fossil fuel. The reformed hydrogen is then cleaned of excess carbon monoxide, which can poison certain types of fuel cells, and utilized by the fuel cell. Reformers are currently in the beta stage of their testing with many companies having operating prototypes in the field.

#### 2.2.5 Bonded Hydrogen

Metal hydrides are specific combinations of metallic alloys, which can store hydrogen similar to a sponge soaking up water. Metal hydrides possess the unique ability to absorb hydrogen and release it later, either at room temperature or through heating of the tank. The total amount of hydrogen absorbed is generally 1% - 2% of the total weight of the tank. Some metal hydrides are capable of storing 5% - 7% of their own weight, but only when heated to temperatures of 250 °C or higher. The percentage of gas absorbed to volume of the metal is still relatively low, but hydrides offer a valuable solution to hydrogen storage.

Metal hydrides offer the advantages of safely delivering hydrogen at a constant pressure. The life of a metal hydride storage tank is directly related to the purity of the hydrogen. The alloys act as a sponge, which absorbs hydrogen, but it also absorbs any impurities introduced into the tank by the hydrogen. The result is the hydrogen released from the tank is extremely pure, but the tank's lifetime and ability to store hydrogen is reduced as the impurities are left behind and fill the spaces in the metal that the hydrogen once occupied.

### 2.2.6 Carbon Nanotubes

Carbon nanotubes are carbon tubes having the diameter in nanometers (billionths of a meter). It has been suggested that carbon nanotubes can store hydrogen in the pores of the tubes and between the tube structures. The advantage of carbon nanotubes is the amount of hydrogen that they are able to store. Carbon nanotubes have been reported to be able to store anywhere from 4.2% to 6.5% of their own weight in hydrogen. Carbon nanotubes and their hydrogen storage capacity are still in the research and development stage. Research on this promising technology has focused on the areas of improving manufacturing techniques and reducing costs as carbon nanotubes move towards commercialization.

## 2.3 Hydrogen Storage in Carbon Nanotubes and Related Materials

Since carbon nanotubes were first synthesized by Iijima in 1991, their physical and chemical characteristics have been a subject of intensive research for many years. Carbon nanotubes, which have diameters of typically a few nanometers, should be able to draw up liquids by capillary force (Pederson and Broughton, 1992). Within the micropores (less than 2 nm) of a porous substance, gases can be adsorbed onto the solid surface. Due to the force of attraction between the solid and the gas, an adsorbed hydrogen phase will be much denser than the bulk gas phase. At high pressure, capillary condensation can lead to condensation of hydrogen at temperatures well above the standard condensation temperature, leading to enhanced storage density (Baumert and Epp, 1993).

Dillion *et al.* (1997) were the first to publish experimental data on hydrogen adsorption in single-walled carbon nanotubes (SWNT). Their experimental procedure, which they named Temperature Programmed Desorption, consists in measuring with a mass spectrometer the hydrogen desorbed by the carbon sample, 1 mg, during a heating run. They showed that gas could condense to high density inside narrow SWNT. They found that unpurified soot containing only 0.1-0.2 wt% of SWNT could also absorb about 5 to 10 weight % of H<sub>2</sub> at 133 K and 300 Torr. The rest of unpurified soot were consisted of a mixture of unidentified carbonaceous materials as well as a large fraction of cobalt catalyst particle (~20 wt%). With same

conditions, hydrogen does not induce adsorption within a standard mesoporous activated carbon. They also suggested that the high purity SWNT samples that have been recently produced, should be interesting candidates for evaluation.

Later, Ye and co-workers (1999) obtained 8.25 wt % of H<sub>2</sub> adsorption on high purity SWNT at 80 K and 100 atm. Liu *et al.* (1999) utilized constant volumetric method with 500 mg of sample and found that 4.2 wt%H<sub>2</sub> was obtained on SWNT with a large diameter of 1.85 nanometers at room temperature under modest high-pressure (about 10 megapascal). Moreover, 78.3 % of the adsorbed hydrogen could be released under ambient pressure at room temperature, while the release of the residual stored hydrogen required some heating of the sample.

Wu *et al.* (2000) synthesized multi-walled carbon nanotubes from the catalytic decomposition of CO and CH<sub>4</sub>. With TGA technique, the carbon nanotubes produced from CO were found to be able to uptake a certain amount of hydrogen under ambient conditions, whereas graphite powders were unable. They suggested the carbon nanotubes might be a promising material that could be used for hydrogen storage under ambient conditions.

Lee and co-worker (2000) performed density-functional calculations to search for hydrogen adsorption sites and predict maximum storage capacity in SWNT. They found two chemisorption sites at top site of the exterior and interior of the tube wall. They further observed that a form of H<sub>2</sub> molecule could exist in an empty space inside nanotubes. The storage capacity of hydrogen in an empty space increased linearly with tube diameter. The repulsive energies between H<sub>2</sub> molecules inside nanotubes limit the maximum storage capacity between H<sub>2</sub> molecules and the tube wall. They predicted that hydrogen storage capacity in (10,10) nanotube can exceed 14 wt%.

Zhu *et al.* (2001) showed that the bundles of aligned carbon nanotubes had a narrow pore distribution mainly in micro- and meso-pores, which were favorable for hydrogen uptake. The well-aligned carbon nanotube bundles had a hydrogen storage capacity over 3 wt% higher than randomly-ordered carbon nanotubes at room temperature and moderate pressure (3-10 MPa) determined by constant volumetric method. They also suggested that multi-walled carbon nanotubes were promising materials for hydrogen storage.

In addition, Chen *et al.* (1999) focused on alkali-doped carbon nanotubes and they found that lithium- or potassium-doped carbon nanotubes can absorb about 20 and 10 weight percent of hydrogen at moderate (200 to 400°C) and room temperatures, respectively, under ambient pressure. The carbon nanotubes used in the study were made from catalytic decomposition of CH<sub>4</sub>. After purification, almost all of the catalyst particles were removed. More than 90% of the product was in the form of MWNT, and 70% was in the diameter range of 25 to 35 nm. Hydrogen uptake was measured by thermogravimetry analysis (TGA).

However, Yang (2000) and co-worker revisited these data. They prepared the doped nanotubes following the same procedure and also measured the adsorption-desorption using a thermogravimetric analyzer. His conclusion was that special caution needed to be taken to remove any moisture contamination of the hydrogen in measuring the adsorption. Moisture, which drastically increased the weight gain, picked up and then put the results in error. So, for dry hydrogen, the adsorption is of 2.5 wt% for lithium-doped carbon nanotubes and of 1.8 wt% for potassium-doped carbon nanotubes. Results have recently been more confirmed by Pinkerton *et al.* (2000).

Recently, Tibbetts *et al.* (2001) have studied the sorption of hydrogen by nine different carbon materials at pressure up to 11 MPa (1600 psi) and temperatures from -80 to +500 degree Celsius. Their results were remarkably similar: very little hydrogen sorption. In fact, the sorption was so little. Careful attention must be paid to calibration to get reliable answers. Furthermore, their efforts to activate the materials by reduction at high temperatures and pressures were also futile. These results cast serious doubts on any claims so far for room temperature hydrogen sorption in carbon materials higher than 1 wt.%.

Furthermore, there were some studies of hydrogen sorption in other types of carbon materials. Activated carbon nanofibers and graphite were ones of candidate materials for hydrogen uptake. Carbon nanofibers consist of graphite platelets stacked together with respect to the fiber axis, giving rise to the assorted conformations. The nanofibers vary from 5 to 100 nm in diameter. Carbon nanofibers were discovered in 1970s, but it was not until recently that they were reported in having the potential to store up hydrogen.