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Technical Evaluation of Current Hydrogen Storage Technologies for Vehicles

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Abstract: With the decline of global fossil fuel reserve and the increasing demand for energy, there is a sincere need to develop alternative fuels for automobiles. Hydrogen is an environmentally friendly and renewable energy source. It has been considered an ideal fuel for replacing fossil fuels. Currently, Liquid Hydrogen (LH2) system (with a density of 51 kg m^{-3} and 14 wt.%) is close to practical use. However, the cost of using LH2 as a transportation fuel is nearly twice that of Gaseous Hydrogen (GH2), due to the liquefaction process, increased fuel transportation costs and more complex manipulation of the fuel. If the intention is to use hydrogen on a large scale, storage is a key problem. Researchers have shown that hydrogen could be stored as: compressed gas, cryogenic hydrogen and metal hydrides. However, the number of alternative methods is growing, including the use of carbon novel materials, chemical hydrides and glass microspheres. This are also being considered. The present is study reviews the different solutions for hydrogen storage and highlights the promising technology for vehicle use.

Key words: Hydrogen storage, cryogenic, hydrides, compressed gas

INTRODUCTION

Currently fossil fuels on which most automobiles run are declining, which puts a tremendous pressure on the automotive industry to develop alternative fuels which can meet the demands of the industry. Some of the alternative fuels which are being considered include LPG, LNG, bio-diesel, methanol, ethanol and hydrogen. Table 1, compares the energy contents of various fuels. Of these hydrogen offers the highest energy per unit mass (141.9 MJ kg^{-1}) making it most suitable for automotive applications as discussed by Robert and Setlock. (2004), Banyay (2006), Gopalan (2006) and Ryu (2006). It can thus be seen that hydrogen contains about 2.75 times more energy per unit mass than gasoline. Many properties of hydrogen make it a unique and very promising fuel suited for automotive use. Of these properties: a very high flame speed and a wide range of flammability limit as mentioned by MatWeb (2006), DIAB (2006) and Das (1996). Many problems are associated with the use of hydrogen as an automotive fuel. These problems are associated with its production, distribution and storage. Out of these, storage is the key problem since hydrogen has a very low density (0.0899 kg m^{-3} at STP) and also a low volumetric energy density (0.013 GJ m^{-3}) as discussed by Tiwari *et al.* (2005). Due to this low volumetric energy density, hydrogen has to be stored at a higher pressure in the range 20-80 Mpa in regular sized tanks as mentioned by Zuttel (2006). Hydrogen-powered vehicles are required to provide the same driving distance as today's gasoline-powered vehicles. As per the targets set by the US Department of Energy, storage system for onboard vehicular application must ideally provide a mass efficiency of 6.5 weight percentage of hydrogen for weight and size appropriateness and to facilitate a fuel cell car to drive a distance of 560 km (350 miles).

Table 1: Energy content for various fuels

Fuel	Chemical formula	State	Energy unit^{-1} mass (MJ kg^{-1})	Energy unit^{-1} volume (MJ m^{-3})
Gasoline	$C_{5-10}H_{12-22}$	liquid	47.4	34.900
LPG	$C_{3-4}H_{8-10}$	liquid	48.8	24.400
LNG	$\sim CH_4$	liquid	50.0	~ 230.000
Methanol	CH_3OH	liquid	22.3	18.100
Ethanol	C_2H_5OH	liquid	29.9	23.600
Liquid hydrogen	H_2	liquid	141.9	10.100
Hydrogen	H_2	Gaseous	141.9	0.013
Natural gas	$\sim CH_4$	Gaseous	50.0	0.040

HYDROGEN STORAGE TECHNOLOGIES

Storage is the key drawback in utilizing hydrogen-powered vehicle technologies, since hydrogen has a low density (0.0899 kg m^{-3} at STP) and a low volumetric energy density (0.013 GJ m^{-3}) as discussed by Tiwari *et al.* (2005). Due to this, 1 kg of hydrogen at ambient temperature and atmospheric pressure occupies a volume of 11 m^3 as mentioned by Zuttel (2006). Thus hydrogen has to be stored at high pressure limit of 69 to 103 Mpa (10000-15000 psi) in regular sized tanks as mentioned by Zuttel (2006).

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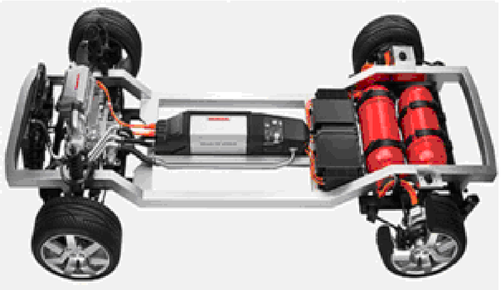

Fig. 1: Honda FCX fuel cell car showing the hydrogen storage tanks

Hydrogen powered vehicles should provide the same driving distance as today's gasoline powered vehicles without consuming much of passenger space as discussed by Tiwari *et al.* (2005).

Hydrogen storage in compressed gaseous form: This is the simplest and most straight-forward method of hydrogen storage. According to the National Renewable Energy Laboratory (NREL), compressed hydrogen storage method is the simplest and least expensive method of on-board hydrogen storage. The most common hydrogen storage systems can withstand a pressure of 20 Mpa, while light weight composite cylinders can withstand a pressure up to 80 Mpa as mentioned by Zuttel (2006). When hydrogen is stored at such high pressures, very thick wall tank has to be used. These tanks are mounted on-board occupying a considerable fraction of the needed passenger space, (generally in the trunk of the car). The proposed Honda FCX Fuel cell car, which uses one of the concepts of an on-board hydrogen storage, is shown in Fig. 1 and 2. As shown in Fig. 1, the hydrogen storage tanks are cylinders mounted at the rear of the car between the wheels. This car has a range of 560 km (350 miles) on a 5 kg (11 lbs) tank of hydrogen at 35 Mpa (5150 psi). The current FCX has a range of 305 km (190 miles).

From Fig. 3, it is clear that the storage space is lost due to the placement of the bulky tanks below the trunk. Some of the major disadvantages of compressed hydrogen storage systems are; higher volume and weight of tank, high cost of compression and safety issues due to higher pressures.

Cryogenic hydrogen storage (LH2): Hydrogen can be stored in the liquid form at a very low temperature of about 20 K and ambient pressure. Due to this low temperature the storage system must be perfectly insulated. In this method, hydrogen is transformed into liquid state and is stored inside the super-insulated tanks made up of rigid, closed-cell porous material; also called Dewars or cryostals, Das (1996). Zuttel (2006) has used hydrogen in the liquid form as a principal fuel in the space programs due to its high volumetric density (70.8 kg m^{-3}). However, the main challenge in utilizing this method is finding energy and cost-efficient methods for the liquefaction of hydrogen and the difficulty in thermally insulating the cryogenic storage vessels to reduce boil-off of the hydrogen (Das, 1996).

Fig. 2: Outer styling of the Honda FCX

Table 2: Assessment of metal hydride storage capacity

Fuel materials and storage	Energy storage density (MJ kg^{-1})	Storage of 3 kg (360 MJ) H_2 (kg)	Storage of 10 kg (1200 MJ) H_2 (kg)
Gasoline	43.0	8.3	28.0
H_2 liquid	120.0	3.0	10.0
FeTiH	1.8	200.0	665.0
MgH_2	8.7	41.3	138.0

Metal hydrides: On-board hydrogen storage can be achieved through reversible metal hydrides. Metal hydrides are essentially metallic alloys which have the ability to absorb hydrogen molecules within their structure and release it later either by heating or at room temperature. Metal hydrides provide a compact and safe hydrogen storage method as compared to compressed gas storage. However, when compared with liquid hydrogen storage, they do not provide as good volumetric energy density as hydrogen storage in liquefied form. As seen in Table 2, storing of 3 kg of hydrogen requires 200 kg of FeTiH (0.9% H_2 weight percent) and 41.3 kg of MgH_2 (7.7% H_2 weight percent); which is considerably high. Most of the hydrides absorb 2-5% of their weight of hydrogen, while the best hydride is known to absorb 12.7% of its weight of hydrogen Das (1996). This low weight percent of hydrogen makes the tank heavier, which is undesirable for on-board application, Das (1996). Besides these metal hydrides, research is currently been undertaken for chemical hydrides and complex metal hydride. Some of these complex metal hydrides such as alanate (AlH_4) have the potential of holding a higher weight percent of hydrogen. These alanates store and release hydrogen as illustrated by the following two-step displacive reaction for sodium alanate with catalyst as titanium dopants.

Here, the first reaction step releases 3.7 weight% of hydrogen at 33°C and the second reaction step releases 1.8 weight% of hydrogen at 110°C at atmospheric pressure. Thus the maximum hydrogen sodium alanate can hold 5.5 weight% of hydrogen, which is below the 2010 DOE target of 6.5 weight%. It should be noted that this 5.5 weight% of hydrogen is just the material capacity and not the system capacity. Lithium amide has been developed recently to represent a complex hydride system which can store 6.5 weight% of hydrogen reversibly using the displacement reaction at 285°C and at 1 atmospheric pressure using the following reversible reaction, NREL (2006). It has the potential of storing 10 weight% of hydrogen but the operating temperature of 285°C is too high for its use in a vehicle.

Hydrogen storage in carbon nano-tubes: Carbon nano-tubes and carbon nanofibers are carbon nanomaterials with diameter size less than 100 nm. Some researchers are trying to develop these materials to be suitable to be used for vehicular application of hydrogen storage. The conditions vary with temperature between 77 K to room temperature and pressure between atmospheric pressure to 148 bar. The results of H_2 uptake vary from 0.11 to 6.3 wt% depending on the pressure and temperature conditions as well as type of material used as an adsorbent. SEM imaging of sample is shown in Fig. 3a-c. The highest uptake was recorded with H_2 uptake of 6.3 wt% with purified multiwall nanotube (MWNT) as adsorbent using volumetric measurement at 148 bar and 298 K (Hou *et al*., 2003). Regardless of what type of measurement that a researcher decides to take up in hydrogen adsorption experiment, careful procedures need to be taken into consideration since the amount of hydrogen adsorbed on carbon materials is much smaller include apparatus leakage, temperature control, time for equilibration of pressure, gas purity and amount of sample than that of other gases like methane. These measures used as the adsorbent (Takagi *et al*., 2004). Limited studies have been carried out in measuring H_2 adsorption onto CNTs and CNFs by gravimetric measurement technique that is using magnetic suspension balance or MSB. Measurement of the hydrogen adsorption was done by volumetric measurement and few of them use gravimetric measurement. Generally, CNTs can store 4.2-6.5 weight% of hydrogen, however no significant progress has been made yet. As known while the nanotubes are obtained by the arc discharge method, the produced on the electrodes surface deposition contains, besides nanotubes a lot of impurities including metal particles such particles of amorphous carbon and nanographite (Ströbel *et al*., 1999). That is why attestation and establishment of structural characteristics of nanocarbon materials obtained by different methods just as the development of purification methods and investigation of influence of these methods on the structure of nanocarbon materials are urgent tasks, I. Ovsiyenko. Figure 4, shows the hydrogen isotherms for carbon fibers at room temperature. It is obvious that post synthesis treatment has a significant impact on hydrogen uptake. The increase in surface area correlates with the hydrogen uptake. Preliminarily measurements of hydrogen adsorption at 77 K for post synthesis treated samples also has shown that the hydrogen uptake can be improved considerably.

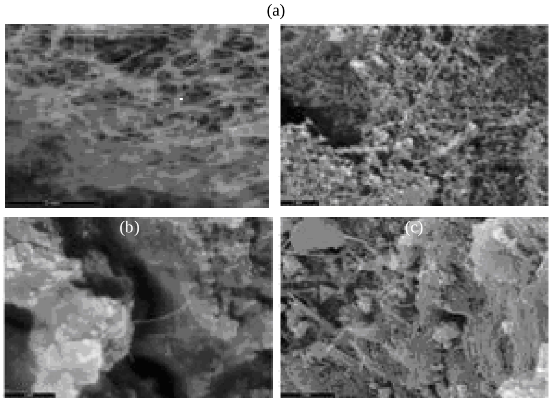

Fig. 3: SEM imaging of sample: (a) surface (b) the raw material and (c) the purified material

Hydrogen permeability and sorption: Every fluid has the ability to transmit through any material. Measurement of this ability is known as its permeability. The intrinsic permeability of any porous material can be measured according to the following equation (Lueking, 2005):

$$k_T = C.d^2$$

where, k_T is the intrinsic permeability [L2], C is a dimensionless constant that is related to the configuration of the flow-paths. d is the average, or effective pore.

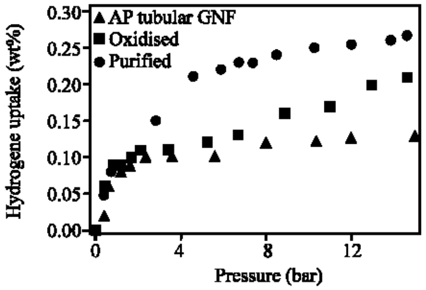

Fig. 4: Hydrogen uptake on different carbon fibers at 300 K

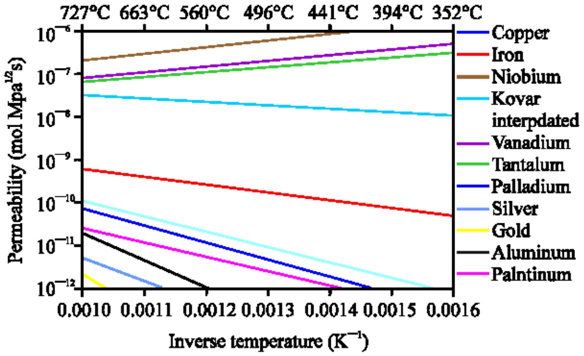

Fig. 5: Hydrogen permeability in metals at various temperatures

Thus, hydrogen permeability provides the measure for the ability of the hydrogen to transmit through the layers of various metals, alloys or polymers. This is an important phenomenon in determining flow characteristics of the hydrogen gas reservoirs.

Hydrogen permeability changes with change in temperature and is different for every material as shown in Fig. 5. The inter-related term sorption is a common parameter used in place of the adsorption and absorption. Adsorption is a physical phenomenon operating through the surface while the absorption is in a whole sole process in which the incorporation of the substances between two different states takes place. Thus, sorption of hydrogen refers to either the adsorption or absorption of hydrogen to the various metals, alloys and polymers. The hydrogen permeability and its sorption represent the ability of a substance to adsorb or absorb the hydrogen. In other words, it is the measure of its affinity towards the hydrogen. Hydrogen permeation and sorption eventually causes hydrogen embrittlement in the substance. This entire phenomenon is related to the environmental conditions like temperature, pressure, exposure time, nature of material and its thickness (Buxbaum, 2006).

CONCLUSION

There are many problems associated with the use of hydrogen as an automotive fuel, these include production, distribution and storage. Out of these storage is a key problem due to the low volumetric density and low volumetric energy density of hydrogen. Adsorptive storage employing carbon nanotubes can be considered the most efficient and promising technology for actual vehicle use but a significant progress in terms of storage capacity is required for this technology to be suitable for practical use.

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