

## OVERVIEW OF HYDROGEN STORAGE TECHNOLOGIES

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Hydrogen is becoming increasingly acknowledged as the energy carrier of choice for the twenty first century. Clean and inexhaustible, substitution of hydrogen for petroleum for use as an automotive fuel would largely eliminate smog in inner cities and health concerns related to air born particulates, and would reduce dependence on foreign oil reserves. Coupled with the high efficiency of Proton Exchange Membrane (PEM) fuel cells as an automotive power plant, simultaneous significant increases in vehicle fuel economy can be made. Indeed, the recent flurry of strategic alliances in the automotive fuel cell world (Ford/Daimler-Benz/Ballard/dbb, General Motors/Toyota) attests to the seriousness with which the automotive industry views fuel cell propulsion, and since fuel cells fundamentally depend on hydrogen fuel, attests to the increasing importance and prominence of hydrogen production, storage, and distribution for the future.

Clearly the hydrogen star is rising. What is less certain is whether the hydrogen bulk supplier community will be able to accommodate the increased consumer demand for hydrogen in the near, mid and far term time frames. The use of liquid hydrocarbons (gasoline, methanol, DME) in onboard reformer fuel cell vehicles is under active development as an interim step to a full hydrogen economy. Such onboard chemical reformation plants capable of converting widely available fuels (gasoline) into a hydrogen rich reformat stream for use by the fuel cell have the major advantage of not requiring major fuel infrastructure alternations. However, creating a load following, highly efficient, compact, low cost reformer is technically challenging and necessarily compromises vehicle system performance compared to a pure hydrogen system. For this reason, onboard hydrocarbon reformation is viewed as an interim link between today's gasoline internal combustion engine automobiles and tomorrows pure hydrogen fuel cell vehicles.

Whether for vehicular onboard storage or stationary bulk storage, the storage of hydrogen has been problematic due to hydrogen's low volumetric density and resulting high cost. This presentation will outline current hydrogen storage techniques for both vehicular and stationary storage and will discuss future hydrogen research trends.

The following methods of hydrogen storage are of interest:

- Liquid hydrogen (LH2)- Liquid hydrogen storage is currently the bulk hydrogen storage medium of choice and has a very impressive safety record. The hydrogen is typically liquefied at the production site in large quantities (10-30 tons per day) and then trucked cross-country in 11,000 gal LH2 tankers with no boil-off losses. Unfortunately, the energy requirements of liquefaction are high, typically 30% of the hydrogen's heating value, leading to relatively high hydrogen cost as compared to gaseous hydrogen. LH2 will likely remain the main technique of bulk, stationary hydrogen storage for the foreseeable future.

Vehicular LH2 systems have the highest H2 mass fractions and one of the lowest system volumes, along with near zero development risk, good fast fill capability, and acceptable safety characteristics. They would appear to be an excellent choice except for two adverse factors: dormancy and infrastructure impact. Dormancy concerns arise due to boil-off losses that will inevitably concern the average car owner, although daily use or proper planning for route or fleet applications can remove most if not all dormancy concerns. Infrastructure impacts are three fold: first, the liquefaction process is costly, second, small scale LH2 production is impractical, and third, low volume distribution/dispensing of LH2 is expensive. Consequently, LH2 systems will not easily support a transition from anemic start-up to a robust H2 economy. Overall, LH2 storage is a most appropriate for a mature H2 economy where the inherent difficulties (and high cost) of large scale remote LH2 production and very small scale LH2 dispensing are least encountered.

- Compressed Gaseous Hydrogen (GH2)- Vehicular compressed hydrogen systems consisting of 34.5 MPa (5,000 psi) gaseous hydrogen in metal or plastic lined, carbon fiber wound pressure vessels offer simplicity of design and use, high H2 fraction,

rapid refueling capability, excellent dormancy characteristics, minimal infrastructure impact, high safety due to the inherent strength of the pressure vessel, and little to no development risk. The disadvantages are system volume and use of high pressure. Integrating the moderate-to-large system volume will clearly challenge the automotive designer, but such a tank volume can be packaged into a "clean sheet" vehicle. In our opinion, the many advantageous features of compressed gas storage outweigh its larger volume. Compressed gas storage is supportable by small-scale H<sub>2</sub> production facilities (on-site natural gas reforming plants, partial oxidation burners, and electrolysis stations) as well larger scale LH<sub>2</sub> production facilities. Thus a plausible H<sub>2</sub> infrastructure transition pathway exists. For these reasons, room temperature compressed gas storage is viewed as the most appropriate fuel storage system for PEM fuel cell vehicles.

For stationary hydrogen storage, GH<sub>2</sub> also offers the advantages of simplicity and stable storage (no boil-off losses) but at a considerably greater volume than LH<sub>2</sub>. Even accounting for compression costs, high pressure gaseous hydrogen is cheaper than LH<sub>2</sub>. However, except of pipeline transmission, GH<sub>2</sub> lacks the bulk transportability of LH<sub>2</sub>. Consequently, GH<sub>2</sub> will mostly be employed for storage of limited hydrogen quantities, for long term storage, or when the cost of liquefaction is prohibitive. Remaining issues for GH<sub>2</sub> include its safety perception, and the current high cost of the pressure vessels and hydrogen compressors.

- **Metal Hydrides**-Metal hydrides can be subdivided into two categories: low dissociation temperature hydrides and high dissociation temperature hydrides. The low temperature hydrides suffer from low H<sub>2</sub> fraction (~2%). The high temperature hydrides require a heat source to generate the high temperature of dissociation (~300°C). Both systems offer fairly dense H<sub>2</sub> storage and good safety characteristics. Indeed it is the bad characteristics of dissociation (high temperature, high energy input) that create the good safety characteristics (no or slow H<sub>2</sub> release in a crash). Overall for vehicular hydrogen storage, metal hydrides are either very much too heavy or their operating requirements are poorly matched to PEM vehicle systems. Without a dramatic breakthrough achieving high weight fraction, low temperature, low dissociation energy, and fast charge time, metal hydrides will not be an effective storage medium for PEM fuel cell vehicles. For stationary storage, the high weight of metal hydride system is not an adverse factor. Consequently, their attributes of high volumetric storage density and stability make them quite attractive. Improving resistance to gaseous contaminants and increasing system cycle life remain as obstacles to overcome.
- **Carbon Adsorption**- Gaseous hydrogen can be adsorbed onto the surface of carbon to attain storage volumetric densities greater than liquid hydrogen. Adhesion capacity is greatly increased by low temperature (particularly cryogenic temperatures) and by high pressure. Indeed significant fractions of the hydrogen contained in carbon adsorbent systems is actually held in gaseous form within the interstitial volume of the carbon adsorbent. Carbon nanofibers are a special type of carbon adsorbent systems which may exploit a fundamentally different mechanism of hydrogen storage and thereby achieve dramatically improved storage capability. However, development and evaluation of nanofibers is at an early stage of development and system characterization is speculative.
- **Microspheres**- Microsphere hydrogen storage systems consists of hollow glass spheres that are "charged" with hydrogen (300°C-500°C, 27-62 MPa for an hour), and discharged by heating (200°C-250°C) and reducing pressure. The microspheres can be pumped or poured from one tank to another, making them viable for vehicular hydrogen storage. Overall, system characterization is immature. Microsphere shelf life remains a concern.

In summary, multiple techniques of hydrogen storage are viable for both vehicular storage and bulk stationary storage. However, no one storage mechanism is ideal. As demand for hydrogen grows, industry must respond by supplying (and storing) hydrogen in ways suitable for the new class of consumers and must educate the public in its safe use.