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Authors
Burke, Andy
Gardiner, Monterey

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Andrew Burke

Monterey Gardiner

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Abstract

This report is concerned with the characterization and comparison of various technologies for hydrogen storage for light-duty vehicle applications. The storage technologies considered are compressed gas, cryogenic liquid, metallic and chemical hydrides, and activated carbon at 77 K. The technologies were evaluated in terms of weight and volume metrics - %wt H2/ system kg and gm H2/system and an energy intensity metric kJ/kg H2 for preparing the hydrogen fuel and placing it into storage for use on-board the vehicle. It was found that these metrics varied widely for the various hydrogen storage systems studied. The United States Department of Energy has presented a series of design targets/goals for hydrogen storage system development. Technologies that meet these design goals for hydrogen storage would permit the development of fuel cell powered vehicles that would meet consumer needs for vehicle performance, range, cost, and utility. The results of the present study were compared with the DOE goals in order to assess the present and projected state-of-the-art of the various hydrogen storage technologies. Special attention was given to systems using activated carbon as the storage medium as those systems have not been included in detail in past studies.

The near-term (2005-2010) DOE hydrogen storage goals are 6%wt/kg system and 45 gmH2/L system. The long-term (2010-2015) goals are 9% wt./kg system and 80 gm H2/ L system. Only liquid hydrogen (LH2) and high temperature hydrides (HTH) appear to have the potential to meet the combined near-term goals and none of the hydrogen storage technologies currently being developed seem to have the potential to meet the combined long-term goals. Both the LH2 and HTH technologies are energy intensive having energy intensities of 25-35 MJ/kg H2. Activated carbon storage has weight and volume metrics and an energy intensity close to those of compressed hydrogen (5%wt, 25 gm/L, and10 MJ/kg H2), but much less convenient from an operational point-of-view as the carbon must be maintained near 77 K and cooled and heated while the hydrogen is put into and removed from storage.

The objectives of the DOE hydrogen storage goals are to achieve the same range between refueling with fuel cell powered vehicle using hydrogen as is presently achieved in a conventional ICE vehicle using gasoline and not to reduce the utility of the vehicle due to the increased weight and volume of the H2 storage system. The results of the study indicate that

using available, known hydrogen storage technologies some reduction in vehicle range on hydrogen will likely be necessary in order to package the storage unit on board the vehicle. Volume constraints appear to be the most restrictive and could result in a reduction in the range to about 50% of that of the conventional ICE vehicle even if the effective fuel economy of the fuel cell vehicle is twice that of the conventional vehicle. This appears to be the case for all classes of vehicles from compact cars to standard size pickup trucks. High pressure (10kpsi) compressed gas seems to be the most satisfactory near term technology when all factors are considered including operational and energy intensity factors. The high temperature hydride materials using a catalyst to reduce the temperature required appear to offer some potential for achieving fuel cell vehicle ranges of about 75% of that of a conventional ICE gasoline vehicle. None of the hydrogen storage technologies appear to have the potential to reach less than $100 per kgH2 stored.

1.0 Introduction

There has been significant progress in developing fuel cell technology for vehicle applications in recent years. The California Fuel Cell Partnership is demonstrating prototype fuel cell powered vehicles from all the major auto manufacturers. Hence the prospects for fuel cells (FC) being a viable alternative to the gasoline engine in passenger cars in the future are becoming more favorable. Hydrogen is the most advantageous fuel for fuel cells. It could be produced from renewable energy sources in the future leading to a sustainable transportation system. Currently the three largest obstacles to a wide spread introduction of FCVs are the cost and reliability of fuel cells, a lack of a hydrogen fueling infrastructure, and a suitable technology for storage of hydrogen onboard the vehicle. The storage technology must be transparent to the consumer both in respect to utility (performance and range) and the cost of the vehicle and fuel.

At present time, the most promising hydrogen storage options are compressed hydrogen at 35 MPa (5kpsi) and 70MPa (10kpsi) and liquid hydrogen (LH_2 20 deg K). There are several other alternatives being pursued, such as metal and chemical hydrides and activated carbons. In this report, the various hydrogen storage technologies are examined in some depth and their characteristics compared for light duty vehicle applications. The characteristics of systems using compressed or liquid hydrogen are based primarily on information available in the literature or contacts with suppliers of those systems. The literature is also reviewed for metal and chemical hydrides. Less definitive information is available for the hydrides so their characteristics are less certain than for the compressed gas and liquid hydrogen systems. In a recent PhD thesis (Reference 1) at UC Davis, hydrogen storage using activated carbon was studied and a prototype unit assembled and laboratory tested. The characteristics given for activated carbon systems are based on the work reported in Reference 1. The characteristics of the various hydrogen storage systems are then compared with the Hydrogen Storage Program goals of the United States Department of Energy (DOE) and the prospects for meeting those goals are discussed.

2 Metrics and Storage System Parameters

Hydrogen storage systems are characterized in terms of various metrics similar to those

used for batteries. The basic definition of the metrics is not in all cases self-explanatory.
For example, weight percent is frequently used when comparing different storage technologies.
However, one must be clear if the value cited refers to the percent of hydrogen compared to the
weight of the material it is being stored in (material wt%) or system weight percent. Material
wt% is equal to the weight of the H_2 divided by the weight of the H_2 plus the weight of the
material that stores the hydrogen (Mat wt%=H_2/(H_2+Mat). Similarly, system wt% is equal to the
weight of the H_2 divided by the weight of the H_2 plus the weight of the entire system that stores
and dispenses the hydrogen (Syst wt%= H_2/(H_2+Syst). Obviously the system weighs much more
than just the material being used and will result in a much lower value for the metric.
Frequently press releases are not clear as to the material wt % and the system wt%, and if system
wt%, what components of the system are included. In addition to the wt% metric, the energy
storage characteristics of a material or system can be expressed in terms of its energy density
(kWh/kg) which is the ratio of the energy equivalent of the hydrogen stored in kilowatt hours
divided by the weight (kg) of the material or system (1 kg H2 = 33.33 kWh using the lower
heating value of hydrogen which is common in engine analysis). In citing, energy density one
should specify whether one is using the upper or lower heating value of hydrogen. Another
important set of metrics is concerned with the volume efficiency or packing density of the
storage material and system. As for wt%, the distinction must be made as to whether the value
of the metric refers to the material storing the H_2 or to the entire system required for storage and
release of the H_2. This metric is often presented as weight of the hydrogen per volume of the
material or weight of hydrogen per volume of the system (kgH_2/L or kWh/L where L is the
volume of material or the system in liters).

DOE has developed hydrogen storage system goals for fuel cell powered light duty
vehicles (Reference 2). These goals, which have been developed in consultation with auto
companies, are used by hydrogen storage technology developers as targets to be meet in their
programs. As is often the case in the development of new technologies, the goals become
increasingly demanding over a period of time. Current technical targets for On-Board Hydrogen
storage as of Fall 2003 for the years 2005, 2010 and 2015 are given in Table 1. The attribute
targets shown in the table are based on the need to store 5-6 kg of hydrogen in a passenger car to

attain a range of 300-350 miles with the ability to refuel in times comparable to conventional ICE vehicles.

Table 1: DOE Technical Targets: On Board Hydrogen Storage Systems[a, b, c]

Storage Parameter	Units	2005	2010	2015
Usable, specific-energy from H_2 (net useful energy/max system mass)[d]	kW·hr/kg (kg H_2/kg)	1.5 (0.045)	2 (0.06)	3 (0.09)
Usable energy density from H_2 (net useful energy/max system volume)	kW·hr/L (kg H_2/L)	1.2 (0.036)	1.5 (0.045)	2.7 (0.081)
Storage system cost [e]	$/kWe·hr net ($/kg H_2)	6 (200)	4 (133)	2 (67)
Fuel cost [f]	$ per gallon gasoline equivalent at pump	3	1.5	1.5
Operating ambient temperature[g]	°C	-20/50 (sun)	-30/50 (sun)	-40/60 (sun)
Cycle life (1/4 tank to full)[h]	Cycles	500	1000	1500
Cycle life variation[i]	% of mean (min) @ % confidence	N/A	90/90	99/90
Minimum and Maximum delivery temperature of H_2 from tank	°C	-20/100	-30/100	-40/100
Minimum full flow	(g/sec)/kW	0.02	0.02 FC 0.027 ICE	0.02 FC 0.033 ICE
Minimum delivery pressure of H_2 from tank FC=fuel cell, I=ICE	Atm (abs)	2.5 FC 10 ICE	2.5 FC 35 ICE	2 FC 35 ICE
Transient response 10%-90% and 90%-6[j]	Sec	0.5	0.5	0.5
Start time to full flow at 20°C	Sec	4	0.5	0.5
Start time to full flow at minimum ambient	Sec	8	4	2
Refueling rate[k]	kg H_2/min	0.5	1.5	2
Loss of useable hydrogen[l]	(g/hr)/kg H_2 stored	1	0.1	0.05
Permeation and leakage[m]	Scc/hr	Federal enclosed-area safety-standard		
Toxicity		Meets or exceeds applicable standards		
Safety		Meets or exceeds applicable standards		
Purity[n]		98%		

[a] Based on the lower heating value of hydrogen and a minimum of 300-mile vehicle range; targets are for complete system, including tank, material, valves, regulators, piping, mounting brackets, insulation, added cooling capacity, and/or other   balance-of-plant components.
[b] Unless otherwise indicated, all targets are for both internal combustion engine and for fuel cell use, based on the low likelihood of power-plant specific fuel being commercially viable.
[c] Systems must be energy efficient - for reversible systems, greater than 90% energy efficient; for systems generated off-board, greater than 70% life-cycle efficiency. Useful constants: 0.2778kWhr/MJ, ~33.3kWhr/gal gasoline equivalent.
[d] Generally the 'full' mass (including hydrogen) is used, for systems that gain weight, the highest mass during discharge is used.
[e] 2003 US$; total cost includes any component replacement if needed over 15 years or 150,000 mile life.
[f] 2001 US$; includes off-board costs such as liquefaction, compression, regeneration, etc; 2015 target based on H_2

production cost of $1.50/gasoline gallon equivalent untaxed.
[g] Stated ambient temperature plus full solar load
[h] Equivalent to 100,000; 200,000; and 300,000 miles respectively (current gasoline tank spec).
[i] All targets must be achieved at end of life
[j] At operating temperature.
[k] 2015 target is equivalent to 3-5 minutes refueling time.
[l] Total hydrogen lost from the storage system, including leaked or vented hydrogen; relates to loss of range.
[m] Total hydrogen lost into the environment as H_2; relates to hydrogen accumulation in enclosed spaces. Storage system must comply with CSA/NGV2 standards for vehicular tanks. This includes any coating or enclosure that incorporates the envelope of the storage system.
[n] For fuel cell systems: less than 10 ppb sulfur, 1ppm carbon monoxide, 1 ppm carbon dioxide, 1ppm ammonia, 100 ppm hydrocarbons, and water, oxygen, nitrogen and argon can't exceed 19000 ppm.

These metrics characterize hydrogen energy technologies (system) in terms of energy stored and the rates and efficiency at which the hydrogen can be loaded into and discharged from the system, leakage of hydrogen from the system during long periods of inactivity, and the costs of the system and hydrogen needed to fuel the system. These metrics will be discussed and compared with the DOE goals for a number of hydrogen storage technologies in the following sections of this report.

3. Hydrogen Storage System Parameters

3.1 Compressed Gas and Liquid Hydrogen Storage

As noted previously, there are a number of ways to store hydrogen. These technologies include liquid hydrogen, gaseous hydrogen, hydrides (metal/complex and chemical hydrides). Some of these options have moved beyond the laboratory stage into prototype vehicles. These are high-pressure storage at 34.5 MPa (5 kpsi) and 70 MPa (10 kpsi) in carbon fiber-composite tanks, liquid hydrogen in cryogenic tanks, low temperature metal hydrides with appropriate heat exchangers, and $NaBH_4$ using noble metal catalysts. Each option has advantages and disadvantages (References 3,4).

Compressed hydrogen gas (CHG) at 34.5 MPa (5 kpsi) has a density of 23.5 g/L. A storage of 6 kg would require a volume of 255 L (67.5 gallons) for the gas alone, not including the tank or supporting equipment. This additional volume over a 49 L (13 gallon) tank for conventional ICE vehicle would be difficult to package in a vehicle without compromising the utility of the vehicle. Compressing the hydrogen to 5kpsi (34.5 MPa) requires about 8.5% of the energy content of the hydrogen being compressed. Typically fill times are not a problem;

however, the fill rate must be monitored and regulated to reduce the temperature increase of the gas in the tank due to rapid filling (References 5, 6). At a pressure of 69 MPa (10kpsi), the density of the hydrogen is 38.7 g/L resulting in a tank volume of 155 L (41 gallons) which is still much larger than for the gasoline tank.

Liquid hydrogen (LH_2) has a density of 70.8 g/L, which requires much less volume for the same quantity of hydrogen than CHG. The 6 kg requires only 85 L or 22.4 gallons excluding the volume of the auxiliary systems to contain and fuel/refuel the cryogenic hydrogen. The main problem with LH_2 compared to other technologies is its energy intensity (efficiency) and the boil-off rate/dormancy. After a certain amount of time, some of the hydrogen will warm and change from its liquid state to a gaseous state. The time at which the vent pressure is reached and the gas cannot be contained within the LH_2 tank is called the dormancy or time to first venting. General Motors estimates a boil-off rate of 4% per day for a 4.6 kg tank; in this case, the hydrogen would last for 25 days (Reference 7). The second problem with LH_2 is its energy intensity. The energy required to produce LH_2 is more than 3 times the energy required to compress hydrogen gas to 70 MPa. Preparation of LH2 can use from 33-40% (depending on liquefaction plant size) of the energy content of the hydrogen (LHV).   Filling LH2 tanks from LH2 storage is not a major challenge; however, the transfer lines must be cooled to liquid hydrogen temperature and lines must be provided to capture vented gas during filling to reduce boil-off losses. Refueling of LH2 to CHG storage onboard the vehicle requires both heat exchangers and a compressor and is thus more difficult and expensive than from high pressure gas storage at the station. Stations for refueling hydrogen vehicles using both compressed and liquid hydrogen have been constructed and are in operation in a number of locations (Reference 8).

3.2 Hydride Hydrogen Storage

There are a number of reversible hydrides that have been studied for hydrogen storage. The hydrogen storage characteristics of the various materials being studied are summarized in Figure 1 taken from Reference (9).
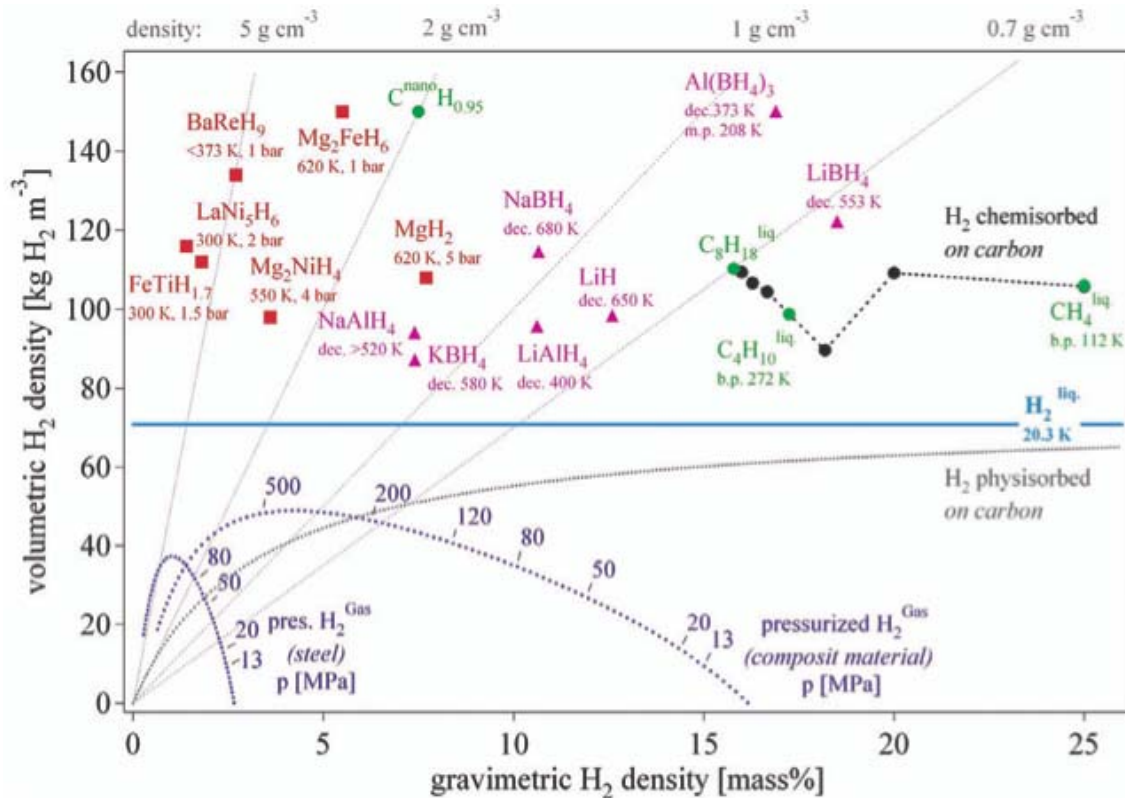
Figure 1: Mass and volume characteristics of various hydride materials

The simplest of the hydrides are the so-called metal or intermetallic hydrides such as LaNi and FeTi, which operate at relatively low temperatures near 100 deg C and moderate pressures less than 100 atm. These hydrides have high volumetric hydrogen storage density (0.10-0.12 kg H2/L), but store only a few percent (2-3wt%) hydrogen per unit weight of material. The result is relatively attractive system volumetric density and unattractive system gravimetric properties (kg H2/kg system). Hydrogen storage using an intermetallic hydride has been demonstrated in a hydrogen-fueled Prius by Texaco Ovonic (References 10-12). The unit stored 3 kg of hydrogen and weighed 190 kg and had a volume of about 70 L. The corresponding weight and volume metrics are 1.6 wt % and .042 kg H2/ L. Laboratory tests of the unit indicated a refueling (fill) time of about 10 minutes and that the hydrogen capacity could be desorbed in 90 minutes at a steady rate and at relatively high transient rates permitting the

Prius to be tested on the Federal Urban and Highway driving cycles. The driving range of the hydrogen-fueled Prius was about 150 miles.

Higher gravimetric and volumetric storage densities can be attained using high temperature hydrides (References 13-15) such as MgH_2 and $MgNiH_2$ which operate at 300-350 deg C and at pressures as low as 5-10 atm. The metrics on a material basis for the high temperature hydrides are 3-8 wt.% and 0.13-0.15 kg H2/L. These metrics, specially the wt %, are significantly better than the low temperature hydrides, but the high temperature requirement probably precludes their use in light-duty vehicles. In principle, higher wt % with hydrides can be attained using the alanates (Reference 16, 17), which are combinations of alkali metals and aluminum. These are high temperature hydrides operating at 300-400 deg C and relatively low pressures (less than 10 atm). At these conditions, the metrics for the alanates are 5-12 wt % and .08-12 kg H2/L. The most studied of the alanates for hydrogen storage is $NaAlH_4$. It has been found that by doping it with a catalyst (Reference 17) containing Ti and Zn compounds, the operating temperature of $NaAlH_4$ can be reduced to about 100 deg C comparable to that of the low temperature hydrides. The pressures are low being less than 10 atm. The metrics for the $NaAlH_4$ is 4-5wt% and .08 kgH2/L. This material with the catalyst has been cycled (hydrogen adsorbed and desorbed) at relatively fast rates and cycle time is not thought to be a problem. $NaAlH_4$ is considered to be one of the most promising hydrides because its wt% is 2 to 3 times higher than typical low temperature hydrides. The volumetric hydrogen storage (kg H2/L) of $NaAlH_4$ is lower than that of the low temperature hydrides, but in an acceptable range. It is also a relatively low cost material.

Another class of hydrides for storing hydrogen is the chemical hydrides, such as sodium borohydride ($NaBH_4$). These hydrides undergo a chemical reaction to release the hydrogen. In the case of $NaBH_4$, the hydride is mixed in solution with water and pumped through a chamber containing a catalyst to release the hydrogen (Reference 18). The reaction is exothermic generating about 35 kJ/ gm H2. This corresponds to 35 MJ/kg H2 which is 29% of the energy content of the hydrogen and indicates that cooling the reaction chamber will not be a simple matter. The $NaBH_4$ chemical contains 10 wt% hydrogen and in solution with water about 7 wt%. The rate of hydrogen release is controlled by the flow rate of the $NaBH_4$ /water solution through

the reaction chamber. Refueling involves removing the spent $NaBH_4$ as $NaBO_2$ and returning it to a processing plant to produce more $NaBH_4$. Providing a recycling infrastructure is one of the serious disadvantages of this approach to storing hydrogen. In addition, the reprocesses of the spent fuel is energy intensive as indicated by the high heat release when the $NaBH_4$ is reacted with the water to release the hydrogen. The round-trip efficiency of the formation/H2 release processes will be less than 70%. The $NaBH_4$ system has been demonstrated by Millennium Cell (References 18, 19) in two hydrogen fueled ICE vehicles and three fuel cell vehicles. This indicates that the system is technically feasible as far as operation in a vehicle is concerned.

3.3 Activated Carbon Hydrogen Storage

The activated carbon storage system operates at 77 deg K and a pressure of 50-100 atm. The temperature is close to that of liquid N2, which is one of the attractive features of this approach. The system consists of a cryogenic tank filled with the carbon and auxiliary components to control the release of the hydrogen. Liquid N2 can be used to cool the hydrogen during the filling process. The hydrogen is stored as a liquid in the micropores of the carbon and as a low temperature gas in the macropores between the carbon particles. The hydrogen storage capacity of carbon is dependent on its surface area and pore size distribution and the extent to which the carbon particulates are compacted prior to loading into the cryogenic tank. Studies (References 20-22) of the storage capacity of carbons have indicated that a surface area of at least 2000 m2/gm is needed to get 5-6% hydrogen storage in the micropores of the activated carbon. Higher wt % may be possible in nanotube carbon, but data to date makes that possibility uncertain (Reference 23, 24).

For a carbon density of .3 gm/cm3, the weight metrics are 7.6% at 50 atm and 9.5% at 100 atm (Reference 1, 25). The corresponding values for .7 gm/cm3 carbon are 4.2% and 4.8%. The volumetric metrics for the .3 gm/cm3 carbon are .025 kg H2/L at 50 atm and .031 kg H2/L at 100 atm. The corresponding values for .7 gm/cm3 carbon are .031 kg H2/L and .0355 kgH2/L, respectively. The information above indicates that the best approach is to use a carbon density of .3 gm/cm3 and a pressure of 100 atm (1500 psi). The material metrics for that

combination are 9.5% and .031 kg H2/L. These metrics compare favorably with compressed hydrogen, especially at 5000 psi, but are significantly less favorable than liquid H2.

The hydrogen is stored in the pores of the carbon by a physisorption process (References 26, 27). The heat of desorption for the carbon is relatively low being 2.5 kJ/gm H2 compared to 10-20 kJ/gm H2 for metal hydrides and 35 kJ/gm H2 for $NaBH_4$. Hence the energy intensity of the hydrogen/carbon storage is much less than the metal and chemical hydrides. The energy intensity of compressing hydrogen to 5000-10000 psi is 9-12 kJ/gm H2 and liquefying it to 20 deg K is 30-35 kJ/gm. These energy requirements are much higher than that for the absorption of hydrogen in carbon. Hence one of the advantages of the storing hydrogen in carbon is the relatively high overall efficiency of the storage/delivery processes.

Another energy related aspect of comparing hydrogen storage as LH2 and in activated carbon is that of dormancy and subsequent rate of boil-off of the stored hydrogen (Reference 1, 28). Both approaches utilize cryogenic temperatures, 20 deg K in the case of LH2 and 77 deg K for the activated carbon. Heat leakage into the systems from the environment will result in boil-off of the stored hydrogen after a period of time. This time, referred to as the dormancy time, depends on the magnitude of the heat leak and the energy required to evaporate or desorb the hydrogen and then increase its pressure to the level required to begin its venting. The energy required to increase the temperature of the LH2 system from 20K to 40K is 667kJ/kg. For the activated carbon system, the energy to increase the temperature from 80K to 180K is 4167 kJ/kg H2. The energy in both cases is that needed to completely discharge all the hydrogen in the system. Note that the dormancy of the carbon system is 6 times the LH2 system for the same heat leak rate. This is one of the key advantages of the carbon system relative to the LH2 system. Hence in comparing hydrogen storage systems one should consider energy aspects of the system in addition to their weight and volumetric metrics.

4. Hydrogen Storage System Operational Considerations

Operational considerations include metrics external to hydrogen storage system itself, such as fill times and efficiencies related to hydrogen production and fueling. Fill times for compressed hydrogen gas and LH_2 are not an issue, but they can be for hydride and carbon based

systems. This section of the report deals with the external metrics and how they are different for the various hydrogen storage systems.

4.1 Compressed Gas and Liquid Hydrogen Storage

Fueling efficiency is one of the more important external metrics. It is defined as the ratio of the energy content of the hydrogen dispensed to the vehicle from the storage unit to the total energy needed to fuel the vehicle starting with gaseous hydrogen at standard conditions. In the case of compressed and liquefied hydrogen it includes the energy needed to compress the gas to the storage pressure and the energy needed to prepare liquid hydrogen at 20 deg K.

Compressed H2

Calculation of the work (energy) need to compress the hydrogen to the high storage pressure is complicated by at least two factors (Reference 29). First, hydrogen is not an ideal gas at the high pressures and second, the compression process is done in multiple stages with cooling between stages. Fortunately the calculations can be done on the computer with available software (Reference 30). The results of such calculations are shown in Figure 2 and Table 2. The energy required for compression varies between 8.5% (10.2 MJ/kg) of the energy content of the hydrogen at 5000 psi and 9.5% (11.4 MJ/kg) at 10000 psi. This relatively small difference between the work at 5000 psi and 10000 psi results from the process being close to isothermal with the work varying as the natural log (Ln) of the pressure ratio.
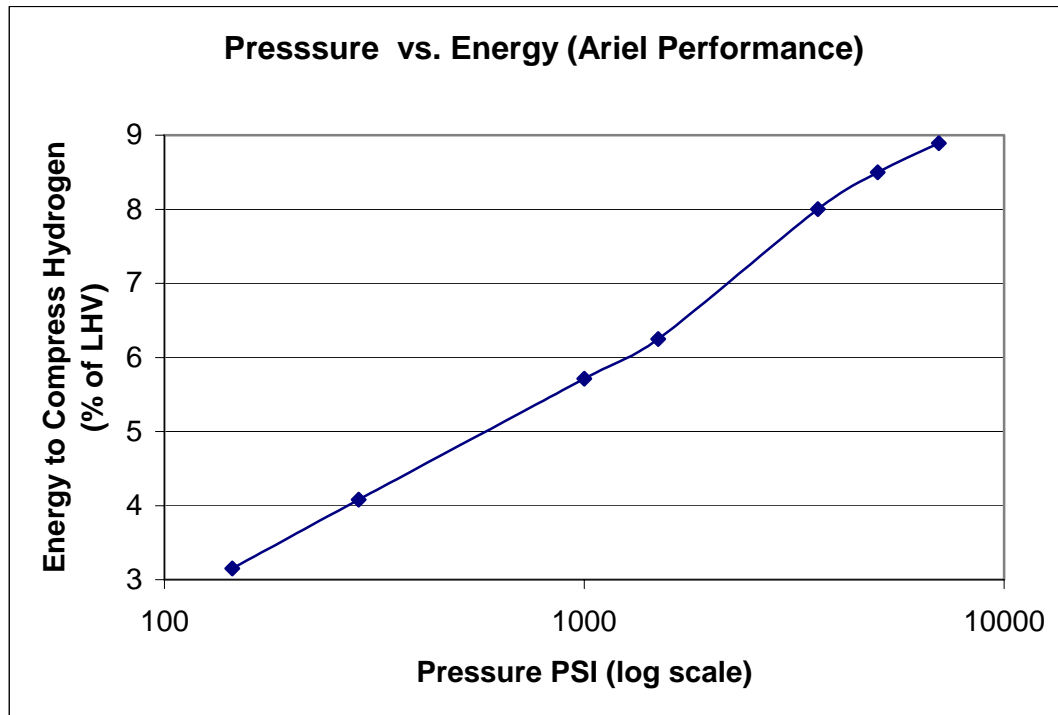
Figure 2: Plot of Compression Energy

Table 2: Compressor Energy, Ariel Software Frame JGK/6 (dry H$_2$ (0%H$_2$0) 6 stages, 5psig Inlet Suction, and spec gravity of 0.0696)

Bar	psi	kW	kg/hr	kwhr/kg	% of LHV(32.9 kWh)
689.48	10000				~9.5
482	6991	1767	604.0	2.93	8.89
344.74	5000	1867	667.8	2.8	8.50
248.21	3600	1765	670.5	2.63	8.00
103.4214	1500	1335	649.6	2.06	6.25
68.95	1000	1228	653. 5	1.88	5.71
20	290	921	686.2	1.34	4.08
10	145	716	691.0	1.04	3.15
Ideal work T1(S1-S2)-(h1-h2)					
689.48	10000		NA	2.39	7.26
344.74	5000		NA	2.08	6.32
248.21	3600		NA	1.93	5.87
68.95	1000		NA	1.46	4.44

Liquefied hydrogen (LH2)

The liquefaction requires cooling the hydrogen to 20 deg K. The processes developed are quite complex and difficult to analysis. A good discussion of the processes is given in Reference 31. The results given in Reference 31 for the calculation of the minimum energy required to liquefy various gases leave little doubt that liquefying hydrogen is very energy intensive (see Table 3).

Table 3: Ideal liquefaction energies for various gases

| Gas	Temperature (deg K)	Cooling (kJ/kg)	Min. work(kJ/kg)	Total (kJ/kg)
Nitrogen	77.8	197	580	777
Methane	111.8	277	870	1147
Hydrogen	20.4	6100	6090	12190
Helium	4.2	6901	1488	8389

As indicated in Table 4, large operating hydrogen liquefaction plants (Reference 32) use even more energy than shown in the Table 3. The plant cited uses 39 MJ/kgH2 which is 32% of the energy content of the hydrogen.   This large expenditure of energy is one of the biggest obstacles to using liquid hydrogen as an automobile fuel.

Table 4: Irreversible component losses of large-scale hydrogen liquefiers (Reference 32)

W_i =3.92 kWh/kg W =10.8 kWh/kg	$W-W_i$ =6.88 kWh/kg
Cycle Compressor	29.35%
Feed Compressor	8.61%
Turbines	12.96%
Heat Exchanger	12.65%
O-P Conversion	4.08%
LN_2 –Refrigerator	25.02%
Other Losses	7.33%
TOTAL	100.00%

A NREL report (Reference 33) places the energy intensity between 28.8 MJ/kg H2 and 45 MJ/kg H2. The ideal liquefaction cycle is about 14 MJ/kg H2. (12% of the energy content of the hydrogen). The Temperature-Entropy Diagram for the ideal path is shown below in figure 3.

Figure 1: Ideal Liquefaction Temperature-Entropy Diagram
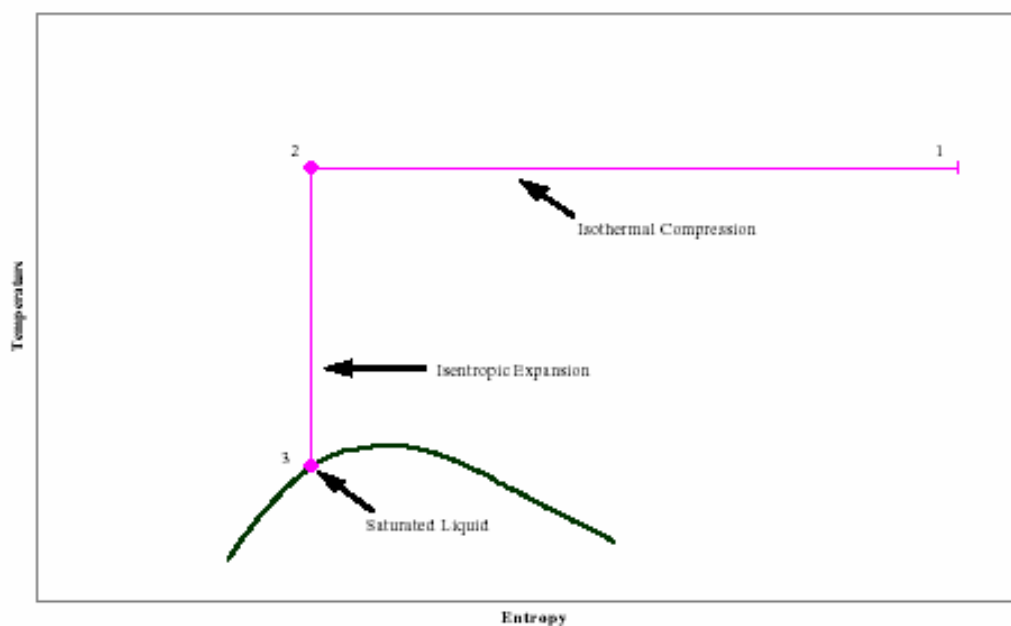
Once LH2 is available, refueling a vehicle has proven to be relatively straightforward and fast (Reference 8). There can be some boil-off at the refueling station, but that resultant energy loss is small compared to the energy intensity of producing the LH2 .

4.2 Hydride-Based Hydrogen Storage

As discussed in Section 3.2, all the hydrides release heat (exothermic reactions) when hydrogen is loaded into the storage unit during refueling. For the metal hydrides, the heat of absorption is 10-20 kJ/gm. This makes rapid refueling difficult as the required rate of heat removal is high. For example, if a 5 kg H2 unit of the low temperature hydride (100 deg C and 12 kJ/gmH2) is refueled in 10 minutes, the required heat removal rate would be 100 kW. For a high temperature hydride having a heat of absorption of 20 kJ/gm H2, the heat removal for 10 minute refueling would be 166 kW. Desorbing the hydrogen to fuel the vehicle during driving will be done over several hours so the rate at which heat must be supplied to the storage unit is much lower than during refueling. For example, for a vehicle that gets 50 mi/kgH2 at 60 mph, the heating rates for the two cases above would be 4 kW for the low temperature hydride and 6.6 kW for the high temperature hydride. The quantity of heat (MJ) for desorbing would be comparable to that released during fueling and if the heat for fueling is not waste heat, the effect on the efficiency of the vehicle of supplying this heat energy will be large. Hence for hydrides, the effect of the magnitude of the heat of absorption on the vehicle operation and efficiency can be a critical consideration in assessing the attractiveness of hydrides for hydrogen storage. Most of the operational aspects of using sodium borohydride (NaBH$_4$) were discussed in Section 3.2. It was noted that the process of releasing the hydrogen is exothermic with a heat of reaction of 35 kJ/gm H2 and that the spent fuel must be collected from the vehicle at the time of a refill and transported to a central processing plant to be re-hydrided before returning it to the filling station. There is no problem with heat removal during refueling of the NaBH$_4$ because the fuel as delivered to the vehicle is stable and unreacted. There is heat release during vehicle operation as the hydride is reacted with water to generate hydrogen. For vehicle speeds of 60-65 mph, the cooling required would be equivalent to 10-15 kW which is manageable, but not low. During

periods of acceleration, the heat release would be higher, but the thermal mass of the system would absorb much of that heat.

Demonstration vehicles have been operated using both sodium borohydride (References 18, 19) and low temperature intermetallic hydrides (references 10-12) to generate hydrogen without significant difficulty. Hence it appears from a vehicle operation point-of-view, these hydrides for hydrogen storage are feasible.

4.3 Activated Carbon Based Hydrogen Storage

The energy required to store the hydrogen in the cryogenic tank containing the activated carbon consists of two parts (References 1, 28). First the hydrogen must be compressed to the pressure of the storage and then cooled to 77 deg K. Second, the heat generated by the adsorption of the hydrogen in the carbon must be removed to maintain the temperature in the tank at 77 deg K. It is assumed that both the cooling of the hydrogen and the heat removal is done using liquid nitrogen (LN2). Hence the energy required for the cooling is then equal to the energy needed to liquefy the nitrogen. This can be estimated once the quantity (kg) of LN2 is known. The first step in the calculation is to determine the cooling (MJ/kg) required. To cool the hydrogen from 300 deg K to 77 deg K requires 3.5 kJ/gm. The heat of adsorption in the carbon is 3 kJ/gm. The total cooling is then 6.5 kJ/gm H2. The energy needed to compress the hydrogen before it is cooled is 3.8 kJ/gm H2 for compression to 100 atm and 2.4 kJ/gm to 20 atm assuming an ideal isothermal process. The corresponding quantity of LN2 needed to cool the hydrogen is then the cooling energy required divide by the latent heat of LN2. Hence for a pressure of 100 atm., the LN2 required is 6.5/.2 = 32.5 gm N2/gm H2.

The energy needed to liquefy the nitrogen from the vapor state at 100 deg K can be estimated by assuming isothermal compression to 100 atm and a Joule-Thompson expansion to a liquid at 77 deg K. The pressure at the end of the expansion is 1 atm. Assuming ideal processes for both the compression and expansion, the energy required is 140 J/gm N2. The latent heat of nitrogen at 77 deg K and 1 atm is 200 J/gm. The corresponding energy required to liquefy the nitrogen used as a coolant is 32.5 x .14 = 4.55 kJ/gm H2. Adding the energy for cooling and that for compressing the hydrogen to 100 atm, the total energy required is 8.35 kJ/gm H2 or 6.95% of

the energy content of the hydrogen. The processes considered were all ideal and thus the actual energy requirements will be larger, but it seems likely they will be relatively low compared to liquid hydrogen and high temperature hydrides.

A more detailed breakdown of the cooling requirements for the various system components in a 5 kg hydrogen unit is shown in Table 5. It was assumed in this calculation that the hydrogen and the tank materials were initially at 300 deg K. The energy per unit hydrogen stored is 7.0 kJ/kg H2, which compares closely to the 6.5 kJ/kg H2 calculated in the previous paragraph starting with the unit at 77 deg K.

Table 5: Breakdown of the cooling energy required for a 5 kg H2 unit

5 kg of H2	Weight (g)	Energy kJ/g	Energy kJ	% of LHV	kg of LN2	L LN2
Aluminum	31130	0.18	5465.53	0.91	27.56	34.07
Carbon	45000	0.09	4057.09	0.68	20.46	25.29
Hydrogen HoA	5000	2.98	14880.95	2.48	75.04	92.77
Hydrogen Cp	5000	3.10	15500.00	2.59	78.16	96.63
Ortho to Para	5000	0.69	3450.00	0.58	17.40	21.51
SUM:	91130	7.03	43353.57	7.23	218.63	270.28
LLV H2 120 kJ/g	% of LHV	7.23				

This table shows that the thermal mass of the hydrogen and the exothermic heat of adsorption of the hydrogen dominate the cooling energy required. The Cp of aluminum and carbon at low temperatures is calculated by integrating the kJ/kg*K curve over the desired temperature range (300-80K). The calculated energy requirements indicate that the use of liquid nitrogen (LN2) for cooling the hydrogen during fueling the carbon is feasible and not energy intensive compared to other storage alternatives.

5. Comparisons of the Various Technologies

The general characteristics of the various hydrogen storage approaches have been discussed in previous sections. In this section, the various design features of the approaches will be compared in more detail. The previous comparisons are summarized in Table 6 using the format and metrics utilized by DOE in Table 1 (Hydrogen Storage System goals). A special feature of the present comparisons will be to include the activated carbon system with the other better known approaches.

Table 6: Hydrogen Storage Technology Comparison

Chemical Interaction	Conventional Hydrogen Storage			Advanced Storage Methods				
	No Bonding Occurs			Chemical Bonding, Covalent, Ionic, Physisorption				
Approach	CHG 35 MPa, (5 kpsi)	CHG 70MPa (10 kpsi)	LH2	Low Temp MH	High Temp MH MgH2	Complex Hydrides Alanates	Chemical Hydrides NaBH4, LiH	High Surface Area Activated Carbon .7 & .3g/cc
Companies	Quntum, Lincoln	Quntum, Lincoln	Linde	Ovonics/ECD	Ovonics /ECD	LLNL/Sand ia NL	Millennium Cell, Hydrogenics	Hydrogen Research Institute, Air
Temp. of H2 ©	Ambient	Ambient	-253	<100	300	Variable	Variable	-196 to -123
Pressure MPa	35	70	1	1-10	1	Variable	1	3-10
Material Wt% H2	NA	NA	NA	2	7	8	7-36	5.2/9.8
System Wt% H2	5.7/6.3	4.5/5.7	5.3/6	1.6	5.5	3.5	7.7/36.7	6
Material Vol eff. (g H2/ L)	23.22	39.1	70.8	70	110	70	77	37.9/29.5
System Vol eff. (g H2/ L of system)	21	35	36.6/48	60	47.62	50	42	30.32
Efficiency %LLH	5.9	6.7	33-40	5.5	6	5.5	88	13
Fill Time kg/min	1	1	1	0.3	0.87	~3	1	.009/.5
Dormancy days /Boil-off%	0.0005	0.0005	30 days/4%	NA	NA	NA	NA	.7 g/cc 200/1 .3g/cc 150 /2
Lifetime	15K-45K	15K-45K	unknown	unknown	650	unknown	unknown	unknown
System Cost $/kWh	12	16	6	12	16	16	8	100/60
Safety Neg/Pos	High Pr	High Pr	Cryogenic 20K	High Temp /Low Pr	High Temp /Low Pr	Very Reactive/ Low Pr	Very Basic /Low Pr	Cryogenic 80K /Low Pr
Infrastructure Requirements	X	XX	XXX	XXX	XXXX	X	XXXX	XXXX
Conformability	XX	X	X	XX	X	XX	XXXX	XX

[27] B. D. James, C.E. Thomas, et.al., *Comparison of Onboard Hydrogen Storage for Fuel Cell Vehicles*, Ford Motor Company, DOE, DE-AC02-94CE50389 p. 4-8, 4-30
[28] D.L. Anton, D.A. Mosher, C. Read, *A Review of On-Board Hydrogen Storage Alternatives for Fuel Cell Powered Automotive Applications*, Nation Hydrogen Association, April 2004

5.1 Weight and volume comparisons

Figure 2 illustrates the weight and volume of the tanks needed to store 6 kg of hydrogen as a compressed gas (5000 psi), a liquid (20 deg K), and adsorbent on activated carbon (77 deg K). The weights and volumes shown are for the tanks alone and do not include the balance of plant for any of the systems (Reference 34).
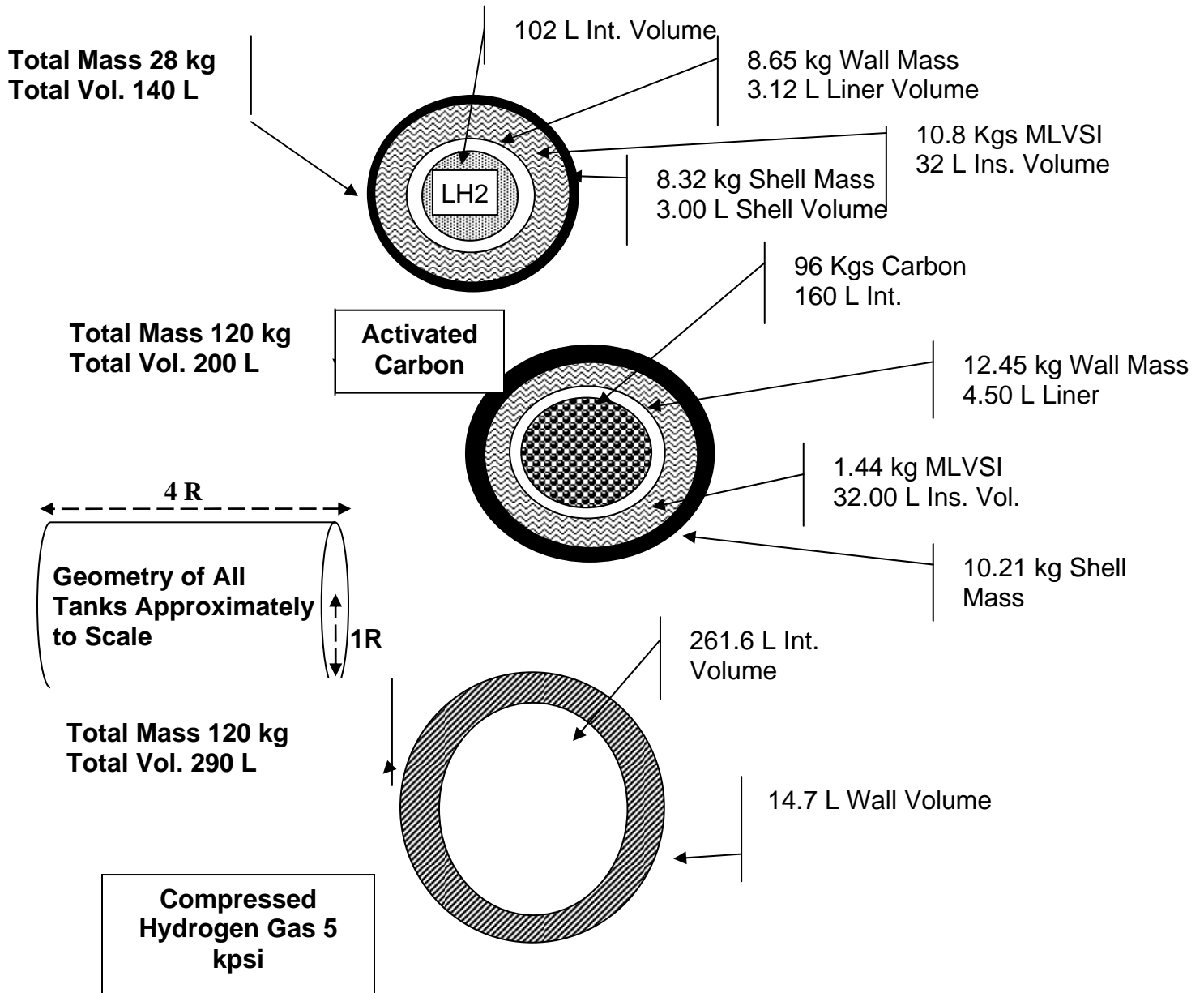
102 L Int. Volume

Total Mass 28 kg
Total Vol. 140 L

8.65 kg Wall Mass
3.12 L Liner Volume

10.8 Kgs MLVSI
32 L Ins. Volume

LH2

8.32 kg Shell Mass
3.00 L Shell Volume

96 Kgs Carbon
160 L Int.

Total Mass 120 kg
Total Vol. 200 L

Activated Carbon

12.45 kg Wall Mass
4.50 L Liner

1.44 kg MLVSI
32.00 L Ins. Vol.

4 R

Geometry of All Tanks Approximately to Scale

1R

10.21 kg Shell Mass

261.6 L Int. Volume

Total Mass 120 kg
Total Vol. 290 L

14.7 L Wall Volume

Compressed Hydrogen Gas 5 kpsi

Figure 2: Sketches of tanks for compressed hydrogen gas, liquid hydrogen, and cryogenic hydrogen physisorbed on activated carbon (6 kg of Hydrogen)

The significant advantage of storing the hydrogen as a liquid is evident from Figure 2.   Storing hydrogen in activated carbon (AC) provides an intermediate choice between CHG (5000 psi) and LH$_2$ as shown by 20 kg weight advantage and nearly 100 L volume advantage of activated carbon (AC) over CHG. If the hydrogen had been stored at 10000 psi, the tank would have been smaller and heavier. Such tanks are presently being developed.   The volume of the 10000 psi hydrogen tank would be comparable to that of the AC system, but the weight of the CNG system would be significantly greater.

The key factor in determining tank weight and to a lesser extent the volume is the wall thickness. For the LH2 and AC storage systems, the wall construction is complicated because the wall is both a structural element and a thermal barrier. The contributions of the various sections of the wall to the system weight and volume are shown in Figure 3. Even though the AC tank consists of a liner, MLVSI material, and an outer shell, the total wall volume is less than twice the wall volume of the CHG tank because the tank is much smaller. .
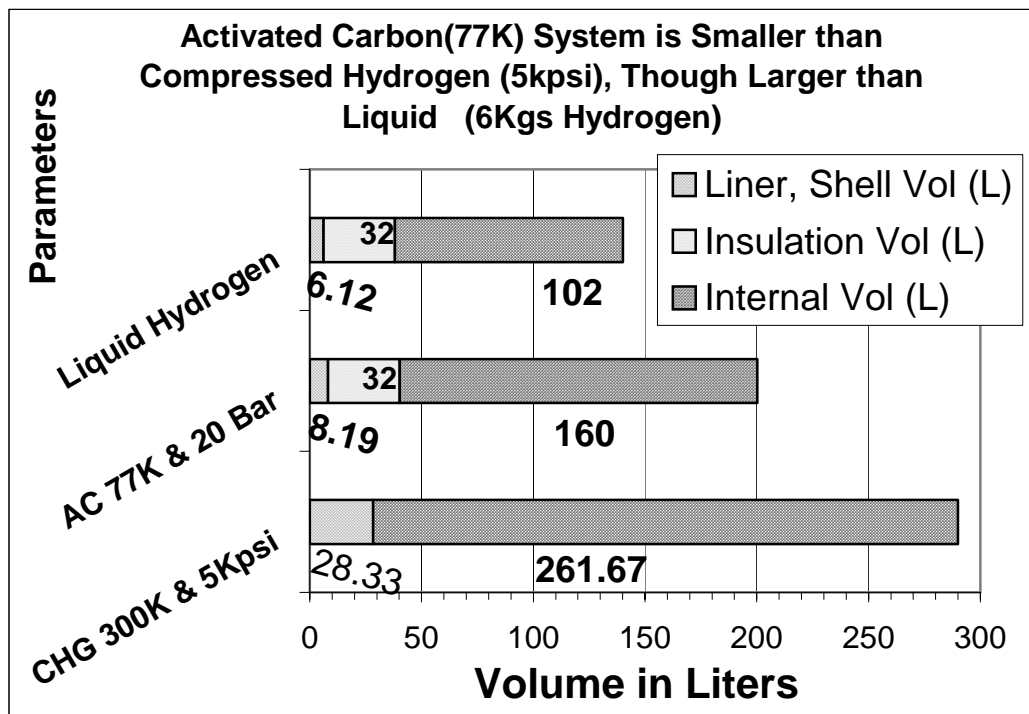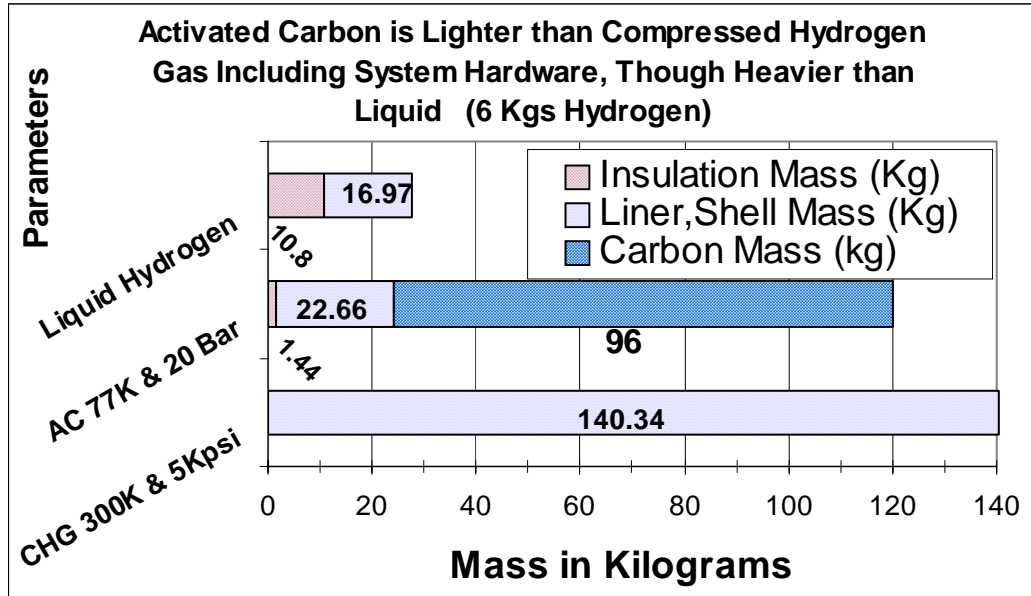
**Figure 3: System Volume & Weight: Compressed hydrogen gas,
liquid hydrogen, and activated carbon for 6 kg of hydrogen**

Detailed designs of metal hydride systems were not performed as part of this study, but the tank weights and volumes for the hydride system can be inferred from the work done on the other hydrogen storage systems and from the low temperature hydride unit assembled and tested by Texaco/Ovonic (References 10-12). The Texaco/Ovonic unit stored 3 kg of hydrogen, weighed 190 kg, and had a volume of about 70L. The weight and volume of the hydride alone was 136 kg and 27L, respectively. Hence the packaging factors for the Texaco/Ovonic unit were .715 for the weight and .385 for the volume. These packaging factors are much lower than those for the activated carbon system described in Figure 2 especially for the volume. If the volumetric packaging factor for the hydride systems were improved to .6 and the gravimetric factor to .8, the hydride system weights and volume would be the following for storing 6 kg H2:

Low temperature hydride (AB$_2$)	**340 kg**	**90L**
High temperature hydride (MgH2/NaAl)	**110 kg**	**112L**

Comparison of the projected hydride system characteristics with those for the other systems in Figure 3 indicate that from the point-of-view of system weight and volume

hydrogen storage in LH2 is by far the most favorable with the high temperature hydride being the most favorable of the other systems. Hydrogen storage in activated carbon seems competitive with the high temperature hydride in terms of volume, but not weight. The compressed gas systems are heavier and larger in volume even at 10 kpsi pressure.

5.2 Dormancy and energy intensity comparisons

Comparisons of hydrogen storage systems involve more than just comparing system volume and weight. Convenience of operation, including dormancy, and energy intensity, including overall efficiency, must being considered. Some of these factors for the various energy storage approaches have been discussed in previous sections. Dormancy for the activated carbon (AC) and LH2 systems will be discussed in this section before summarizing all the energy related aspects of the different hydrogen storage technologies.

Dormancy of the LH2 and activated carbon systems

In the discussion of dormancy, it is convenient to consider the LH2 and AC systems together as both are cryogenic systems which will tend to heat up due to heat leakage into the units from the ambient environment (Reference 1, 28).

In LH_2 system, some portion of the heat leak goes into the tank walls, heater and a few other components within the system. However, a significant portion of the heat leak vaporizes the LH2; in the case of AC, a significant portion of the heat leakage desorbs the hydrogen and heats the carbon.   In the case of the LH2 unit, the interior of the tank has small heat capacity, except for maybe the small internal pressure regulator. Heat leakage into the tank from the ambient environment will cause hydrogen gas to vent depending on the lock-up pressure set for the tank and the effective capacity of the H2 unit will be less than its rated value. Both dormancy (time to first venting), and the boil-off rate are a function of heat leak (HL) into the system and how that heat is dissipated within the system.

The boil-off rate of the AC and LH_2 systems may be calculated based on a few simple assumptions and factors. It is assumed that all the hydrogen will be desorbed

from the carbon as it changes from 80K to 180K at 6 atm (88.2 psi) and that all the LH$_2$ will be vaporized during the temperature transition from 20K to 40K at 1 atm(14.7 psi).   For LH$_2$, this includes the heat of vaporization (445.59 J/g), the heat capacity (Cp) of the gas integrated from 20K to 40K(216.53 J/g), and the specific heat (Cp) of the aluminum liner (integrated from 20K to 40K .3039 J/g). For AC unit, this includes the heat of desorption for the carbon (2.48 kJ/g), and the thermal mass (Cp) of the carbon in the tank (22.29 J/g). Due to the higher temperature, the thermal masses of the aluminum liner (56 J/g), and hydrogen gas (1210 J/g) are higher in the AC system than in the LH2 system. The aluminum liner is larger in the AC system because of its greater volume and pressure required by the carbon: 7.72 kg for the 102L LH2 tank and 12.45 kg for the 160L AC tank. Table 7 summarizes the thermal characteristics of the LH2 and AC systems. The boil-off rates for several rates of heat leak (HL) are given in Table 8.

Table 7: Energy (kJ) required to evolve all the hydrogen in LH2 and activated carbon systems storing 6 kg of hydrogen

LH2 20K to 40K	kJ	AC 80K to 180K	kJ
Lat. Heat of Vaporization	2673.5	Heat of Adsorption 5kJ/mol	14880.95
Specific Heat, Gas	1299.18	Specific Heat, Gas	7260.00
Specific Heat, Tank	2.63	Specific Heat, Tank	706.19
		Specific Heat, Carbon	2139.23
Total kJ	3975.35	Total kJ	24986.37

Table 8: Heat leak and resulting boil-off rates for LH2 and activated carbon systems storing 6 kg of hydrogen

Watts, Heat Leak	LH2 20K to 40K		AC 80K to 180K	
	Days	Boil-off Rate, % per day	Days	Boil-off Rate, % per day
0.5	90	1	580	0.2
1	50	2	290	0.4
2	25	4	145	0.7

Comparisons of Energy Intensity

The energy required to place the hydrogen in storage varies between the various energy storage approaches. The energy intensity values (MJ/kg H2) are shown in Table 9.

Table 9: Energy Intensity of various hydrogen storage approaches

Hydrogen Storage Approaches	Energy Intensity (MJ/kg)
Compressed gas	
5000 psi	10.2
10000 psi	11.4
Liquid (LH2)	28-45
Activated carbon (77 deg K)	8-10
Hydrides	
Low temperature (< 100 deg C)	10-12
High temperature (>300 deg C)	20-25

6. Hydrogen Storage in Vehicle Applications

6.1 Analysis of Hydrogen Storage Vehicle Requirements and Relationship to System Metrics and DOE Goals

Hydrogen storage is needed onboard the vehicle and at distribution and refueling stations. The onboard vehicle application is difficult. This is due to the fact that hydrogen is a low molecular weight gas and is difficult to contain in tanks due to its tendency to diffuse through metals. Both of these characteristics contrast markedly with gasoline which is a liquid fuel and is easy to contain at ambient conditions in a simple metal tank. The main requirement for acceptance of hydrogen as a fuel is that it be transparent to the consumer in terms of vehicle utility and range and refueling cost and time. Meeting these requirements is difficult due to the low volumetric energy density of hydrogen and the resultant need to storage the hydrogen at conditions far different than ambient.

As indicated in Table 1, DOE has set goals for the development of hydrogen storage systems. Primary consideration is given to the weight and volume of the systems to store sufficient hydrogen for a vehicle range approaching that of conventional ICE vehicles using gasoline. The weight and volume of the hydrogen storage system must be such that it does not adversely affect the design, performance, and utility of the vehicle. There is, of course, considerable judgment involved in setting the limits for acceptable weight and volume for the hydrogen storage systems. In this section, an approach to estimating the envelope characteristics for storage for a number of vehicle classes is discussed and the system metrics determined compared to the DOE design goals.

Increased weight and volume beyond that of the gasoline tank adversely affects the vehicle design in a number of ways. Added weight decreases fuel economy causing the hydrogen storage system to be larger for the same vehicle range, increases the power required to achieve specified acceleration times which results in a larger fuel cell and electric driveline components, increases the total vehicle weight by greater than the added fuel storage system weight due to the impact on the vehicle design as a whole, and finally all these factors result in higher vehicle cost. The direct effects of the increased volume of the fuel storage system are changes in the packaging of all the components of the vehicle. In fact, if the increase is large enough, it makes packaging impossible and the mass of the hydrogen stored on the vehicle must be reduced with the resultant decrease in vehicle range. Hence in any analysis of hydrogen storage onboard vehicles, it is convenient to reference their weight and volume limits in terms of the weight fraction of a conventional ICE vehicle and the space available under the vehicle to store hydrogen.

The maximum volume available for the hydrogen storage was calculated from the following relationship:

Maximum volume available for hydrogen storage:

9 inches X the wheelbase X the width of the vehicle X 0.25

It is assumed that a storage unit of this volume could be packaged under the vehicle with without significantly affecting overall design of the vehicle. The maximum weight allowed for the hydrogen storage unit was taken to be 10% of the curb weight of a comparable ICE vehicle. This increase in weight for fuel storage can be accommodated without a significant effect on the power of the electric driveline components. The

amount (kg) of hydrogen to be stored was based on a doubling of the energy efficiency of the fuel cell vehicles compared to comparable ICE vehicles and the fact that 1 kg of hydrogen is approximately equal to 1 gallon of gasoline. Hence the number of kg of hydrogen required is set equal to half the gallon capacity of the gasoline tank. The range of the fuel cell and ICE vehicles would then be equal for each vehicle type.

An analysis of hydrogen storage requirements has been performed for eight classes of vehicles – compact, mid-size, and full-size cars, small, mid-size, and large SUVs, and compact and standard-size pickup trucks. The compact size car is based on the Honda Civic, the mid-size car is based on the V6 Honda Accord, the full-size car is based on the Dodge Intrepid, the small SUV is based on the Ford Escape, the mid-size SUV vehicle is based on the Toyota Highlander, the large SUV is based on the Toyota Sequoia, the compact pickup truck is based on the Chevrolet S-10 and the standard-size pickup on the Ford F-150. The characteristics of the baseline vehicles (Reference 35), which are given in Table 10, have been used in the calculations of hydrogen storage system requirements presented in Table 11. Note from Table 11 that the storage requirements in the form of the system metrics do not vary significantly with vehicle class.

Table 10: Baseline vehicle characteristics

Vehicle Class	curb Wgt. kg	W_B inches	Width inches	F. E. mpg	Fuel tank Gal.	Range miles
Cars						
Compact	1136	102	67	34	13	442
Mid-size	1409	108	72	28	17	476
Full-size	1590	113	75	25	18.5	462
SUVs						
Small	1455	103	70	22	15	330
Mid-size	1682	107	72	21	20	420
Large	2364	118	78	16	28	448
Pickup						

Trucks						
Compact	1455	118	69	20	18	360
standard	1910	138	80	18	26	468

Table 11: Hydrogen storage characteristics and attributes

Vehicle Class	kg H2 Stored (1)	Wgt. kg (2)	Volume Liter (3)	Volume Liter (4)	% wt. H2 sys.	gm H2/L sys. (3)	gm H2/L sys. (4)	Range Miles
Cars								
Compact	6.5	114	255	99	5.7	26	66	442
Mid-size	8.5	141	285	130	6.0	30	65	476
Full-size	9.85	159	314	141	5.8	30	65	462
SUVs								
Small	7.5	145	265	115	5.2	28	65	330
Mid-size	10	168	283	153	6.0	35	65	420
Large	14	236	340	214	5.9	41	65	448
Pickup Trucks								
Compact	9	145	300	137	6.2	30	66	360
Standard	13	191	407	198	6.8	32	66	468

(1) kg H2 needed in fuel cell vehicle to get the same range as a comparable ICE vehicle assuming the fuel cell vehicle is two times as efficient as the ICE vehicle.

(2) Weight of the H2 storage system assuming it weighs 10% that of the vehicle. The system includes the tank and all balance of plant components.

(3) Volume of the H2 storage system if its volume is given by

W_B x width x 9" x .25

(4) Volume of the H2 storage system if it is twice the volume of the gasoline tank in the ICE vehicle.

6.2 Hydrogen storage option assessment for vehicle applications

It is of interest to compare the hydrogen storage system design attributes given in Table 11 with the DOE goals (Table 1) and the projected capabilities of the various hydrogen storage technologies. Note that the values given in Table 11 were calculated assuming that the hydrogen fuel cell and gasoline ICE vehicles would have the same range. The calculated values are proportional to the desired range of the fuel cell vehicles.

First, consider the weight of the hydrogen storage system. If the storage system is to weigh less than 10 % of the vehicle curb weight, the specific weight metric of the system should be about 6 wt% H2/kg system. The storage tank characteristics shown in Figures 7 and 8 indicate that the weight metric of the LH2 system would be less than the 6% requirement even including the weights of the balance of plant, but that of the weights of the other systems will be significantly heavier. The tank weights of systems using activated carbon and high temperature hydrides and compressed hydrogen at 5 kpsi result in are in a weight metric in the range of 4-5% so the complete system weights will be significantly heavier than 10% of vehicle curb weight. The tank weight metrics for compressed hydrogen at 10 kpsi is likely to be in the range of 3-4% and low temperature hydrides in the range of 2-3%. The use of these latter technologies would require the range of the fuel cell vehicle to be significantly reduced from that of the ICE gasoline fueled vehicle. The DOE goal for the specific weight metric is 6% by 2010 and is 9% by 2015. The 2015 goal would reduce the weight fraction of H2 storage system to about 7% of the vehicle curb weight. The corresponding weight for gasoline fueled vehicles is about 4% using a metal fuel tank.

Next consider the volume of the H2 storage system. If the volume is to be set by the space assumed to be available under the vehicle, the volume metric requirement is 30-40 gm H2/liter system. If the volume of the H2 storage is limited to two times the volume of the gasoline tank, then the requirement is 66 gm H2/liter system. From Figures 7 and 8, it appears that all the storage tanks except compressed hydrogen storage at 5 kpsi can meet the 30-40 gm H2/liter system requirement, but that only the hydrides appears to have a reasonable chance of meeting the 66 gmH2/liter system requirement. Compressed hydrogen at 10 kpsi is likely to have an energy density of 30-35 gmH2/liter system. In the case of volume, there is a more direct relationship between tank/materials

and system characteristics than is the case for weight. In addition, some of the balance of plant components can be packaged remote from the storage tank. The DOE goals for the volume metric are 45 gmH2/liter system in 2010 and 81 gmH2/liter in 2015. Hence it is not until 2015 that the DOE goal requires a storage volume less than twice the volume of the gasoline tank in a comparable ICE vehicle.

When one considers the combined storage requirement of 6% wt. H2/kg system and either 30 gmH2 or 66 gm H2/liter system, the difficulty of the hydrogen storage problem becomes apparent even when one considers only the tank alone. Only the LH2 system satisfies both the 6% and 30 gmH2/liter requirement.   Only the high temperature hydride comes close to the 6% weight requirement and can satisfy the 66 gm H2/liter requirement. Most of the storage technologies seem to have a chance to meet the absolute weight and volume requirements (kg and liter) for the vehicles if the acceptable range is reduced by about a factor of two. Such a reduction in the vehicle range makes the requirements for fast and convenient refueling very important for consumer acceptance of hydrogen fueled vehicles. Reducing the weight (kg) of hydrogen stored on board the vehicle will also reduce the cost of the hydrogen storage unit for the vehicle.

The system metrics for the various hydrogen storage technologies are summarized in Table 12 and compared with the DOE goals for 2010. The numbers shown for the system values are based on the results of this study and discussions with tank and system developers/suppliers concerning the effect of balance of plant on the system metrics.

Table 12: Comparisons of the system metrics for various technologies and DOE goals (2005-2015)

Hydrogen Storage Approaches	Wt%H2/ tank	kg System *DOE goal: 6-9 wt.%/kg*	gm H2/ tank	Liter sys. System *DOE goal: 45-80 gm H2/L*
Compressed gas				
5000 psi	6	4-5	20	15
10000 psi	5	3-4	32	25
Liquid (LH2)	20	15	63	52
Activated carbon (77 deg K)	6	5	30	25
Hydrides				
Low temperature (< 100 deg C)	2	1.8	105	70
High temperature (>300 deg C)	7	5.5	90	55

It is of interest to compare the energy storage characteristics of the various hydrogen storage technologies with the corresponding characteristics of batteries. This is done in Table 13 in terms of Wh/kg and Wh/L. Note that the energy densities of hydrogen storage technologies are a factor of at least 10 greater that those of even the lithium-ion batteries. The energy density of gasoline is about the same factor greater than that of the hydrogen storage systems.

**Table 13: Comparisons of the energy densities of
battery and hydrogen storage technologies**

Storage Tech.	Wh/kg	Wh/L
Batteries		
Lead-acid	30	70
NiMtHydride	70	175
Lithium-ion	100	200
Compressed H2		
5000psi	2000	700
10000psi	1666	1165
Liquid H2	1885	1400
Metal Hydrides		
100 C	535	2000
300 C	1880	1600
Activated carbon	2000	1000
Gasoline	11660	8750

6.3 Future Projections and Possibilities

As noted in Table 12, none of the presently available hydrogen storage
technologies meet the DOE long-term goals and thus result in vehicle designs that
completely meet consumer needs and expectations. In addition, the storage conditions
are far from ambient. Hence some new approaches to hydrogen storage are needed.
Some of these approaches are discussed briefly in this section.

Long-term options include such things as carbon nanotubes, metal-organic
frameworks, and glass microspheres. Carbon nanotubes have been a research area of
great interest for a number of years since Baker and Rodriguez (Reference 36) reported
upwards of 75wt%. Since then, no one has reproduced those results, and there have been
conflicting evidence of what can be stored on carbon nanotubes (Reference 23, 24, 37).
Relatively large adsorption quantities have been reached at low temperatures and
pressures, 6.4wt% at 2 bar (Reference 38). Single walled nanotubes are difficult to
purify, and multiwalled nanotubes do not show any strong adsorption characteristics.

Recently metal-organic frameworks were reported in a Science magazine article (Reference 39) which claimed 4.5 wt% at less than 1bar. BASF is working on developing the material and their estimated timeline is 2 to 5 years (Reference 40). The materials are attractive because they can be made from low-cost raw materials such as zinc oxide, and terephthalate (plastic in bottles), and be able to reach 6 wt%. There was a review paper at the 15th WHEC on glass micro-spheres (GMS). The major finding of the paper (Reference 41) was that GMS is one of the few technologies with the potential to break 9 wt%. Currently the major challenges are to reduce the operating temperature (200C-400C), the high pressures required and the associated compression energy (60 MPa), and finally the relatively low density by volume (20 g/L).

7. Economic Considerations

Cost comparisons of hydrogen storage technologies are difficult to make and any cost projections are very uncertain for a number of reasons. The storage systems are not finalized, mass production will bring the costs down, and raw material costs depend greatly on volume. This section will cover the activated carbon system, high pressure tank components, LH2 tanks, and a brief consideration of metal and chemical hydrides. The time frame considered is approximately the first 10 years after commercial (private consumer/fleet) hydrogen vehicles are offered.

The only hydrogen storage system for vehicles that can presently be purchased as a near standard product is a compressed gas system at a pressure of 5 kpsi. The tanks in those systems are fabricated from carbon composites. Storage units for buses that store about 40 kg H2 cost about $1000/kg H2. Smaller systems for light-duty vehicles, especially those at a pressure of 10 kpsi, can be expected to cost considerably more on a $/kg H2 basis. The costs of the compressed gas systems will decrease markedly with increased volume of sales, but it seems unlikely they will approach the DOE cost target of 100-200 $/kg H2 for light-duty vehicles.

The more advanced hydrogen storage system that use activated carbon or hydrides are still in the prototype and laboratory stages of development so detailed cost projections are not possible. First consider costs associated with the activated carbon hydrogen storage system. Currently the cost of high surface area carbon is high in small quantities (less than a few kg); 3000 m^2/g is $246/kg, 2500 m^2/g is $237/kg, and 2000

m^2/g is \$228/kg (Reference 42). The activated carbon cost from Kansai Coke and Chemical for material (not shipping) for 10 kg or more is 18000 Yen/kg (~153\$/kg) and >100 kg is 15000 Yen/kg (~127\$/kg).   This cost would be significantly reduced if the demand for the special activated carbons greatly increased. Conventional activated carbons for water treatment are only \$0.41/kg (\$0.91/lb) with 400 million pounds consumed in 2002. It is not likely that the special carbons for hydrogen storage will be this cheap, but a reduction in cost to \$5-\$10/kg might be possible.

The multi-layer vacuum super insulation (MLVSI) is more costly than either a cryolite blanket or perlite. The perlite material is inexpensive (\$12/ft^3) and simple to place into the tank. However, the material is prone to settling. Another drawback is that its performance is not as good as some other materials for blocking all forms of heat transfer. For applications where cost is of primary importance perlite is a good option. The MLVSI is expensive (\$71/kg), and labor intensive to install.   Aluminum is relatively inexpensive for lining the tanks and is not subject to hydrogen embrittlement. The 6061 alloy is least expensive; however, the T7075 alloy is more easily welded without loss of strength.

The carbon fiber is the highest cost material component of high pressure compressed gas tanks. The material is ~ \$80/kg and accounts for more than half the cost of the tanks. By comparison LH2 tanks are much lower cost due to their low pressure. However, the air-liquifaction/heat exchangers used by Linde are expensive and they are planning on installing a liquid/gaseous hydrogen compressor in parallel with their system to compress boil-off gas.

In general the system costs are reasonably low for chemical hydrides; however, there are problems with the lifetime of the catalysts and the materials are expensive to regenerate. In contrast, metal (complex) hydrides in high temperature systems have higher system costs due to the higher pressures and temperatures required. Magnesium based hydrides have low material costs (~\$7/kg)

This overview of costs is intended to indicate what materials and components are most expensive and how much they are relative to other components. Detailed cost projections must awaited the detailed design and testing of the advanced hydrogen storage systems.

8. Summary and conclusions

This report is concerned with the characterization and comparison of various technologies for hydrogen storage for light-duty vehicle applications. The storage technologies considered are compressed gas, cryogenic liquid, metallic and chemical hydrides, and activated carbon at 77 K. The technologies were evaluated in terms of weight and volume metrics - %wt H2/ system kg and gm H2/system and an energy intensity metric kJ/kg H2 for preparing the hydrogen fuel and placing it into storage for use on-board the vehicle. It was found that these metrics varied widely for the various hydrogen storage systems studied. The United States Department of Energy has presented a series of design targets/goals for hydrogen storage system development. Technologies that meet these design goals for hydrogen storage would permit the development of fuel cell powered vehicles that would meet consumer needs for vehicle performance, range, cost, and utility. The results of the present study were compared with the DOE goals in order to assess the present and projected state-of-the-art of the various hydrogen storage technologies. Special attention was given to systems using activated carbon as the storage medium as those systems have not been included in detail in past studies.

The near-term (2005-2010) DOE hydrogen storage goals are 6%wt/kg system and 45 gmH2/L system. The long-term (2010-2015) goals are 9% wt./kg system and 80 gm H2/ L system. Only liquid hydrogen (LH2) and high temperature hydrides (HTH) appear to have the potential to meet the combined near-term goals and none of the hydrogen storage technologies currently being developed seem to have the potential to meet the combined long-term goals. Both the LH2 and HTH technologies are energy intensive having energy intensities of 25-35 MJ/kg H2. Activated carbon storage has weight and volume metrics and an energy intensity close to those of compressed hydrogen (5%wt, 25 gm/L, and10 MJ/kg H2), but much less convenient from an operational point-of-view as the carbon must be maintained near 77 K and cooled and heated while the hydrogen is put into and removed from storage.

The objectives of the DOE hydrogen storage goals are to achieve the same range between refueling with fuel cell powered vehicle using hydrogen as is presently achieved

in a conventional ICE vehicle using gasoline and not to reduce the utility of the vehicle due to the increased weight and volume of the H2 storage system. The results of the study indicate that using available, known hydrogen storage technologies some reduction in vehicle range on hydrogen will likely be necessary in order to package the storage unit on board the vehicle. Volume constraints appear to be the most restrictive and could result in a reduction in the range to about 50% of that of the conventional ICE vehicle even if the effective fuel economy of the fuel cell vehicle is twice that of the conventional vehicle. This appears to be the case for all classes of vehicles from compact cars to standard size pickup trucks. High pressure (10kpsi) compressed gas seems to be the most satisfactory near term technology when all factors are considered including operational and energy intensity factors. The high temperature hydride materials using a catalyst to reduce the temperature required appear to offer some potential for achieving fuel cell vehicle ranges of about 75% of that of a conventional ICE gasoline vehicle. None of the hydrogen storage technologies appear to have the potential to reach less than $100 per kgH2 stored.

References

1. Gardiner, M.R., Investigation of Cryogenic Hydrogen Storage with High Surface Area Carbon: Theory, Experiments, and System Design, Ph. D. Thesis in Transportation Technology and Policy, University of California-Davis, September 2004

2. Bouza, A., Read, C.J., Satyapal, S., and Milliken, J., 2004 Annual DOE Hydrogen Program Review, Hydrogen Storage, Office of Hydrogen, Fuel Cells, and Infrastructure Technologies, 2004

3. Gardiner, M., Cunningham, J., etals., Compressed Hydrogen Storage for Fuel Cell Vehicles, SAE paper 2001-01-2531, August 2001

4. Ijaz, M., Hydrogen Solutions for Future FCVs, paper presented at the 17th International Electric Vehicle Symposium, Montreal, Canada, October 2000

5. Richards, M.E., Liss, W.E., etals, Development and Validation Testing of Hydrogen Fast-Fill Fueling Alogrithms, 15th World Hydrogen Energy Conference, Yokohama, Japan, June 2004

6. Herrmann, M.M. and Meusinger, J., Hydrogen Storage Systems for Mobile Applications, General Motors, September 4, 2003

7. Arnold, G., Advanced Hydrogen Storage Technologies, General Motors Hydrogen Storage and Refueling, Global Alternative Propulsion Center.

8. California Hydrogen Fueling Station Guidelines, Report to the California Energy Commission by TIAX LLC, Technical Report TR-03-163a, November 2003

9. Schlapbach, L. and Zuttel, A., Hydrogen-Storage Materials for Mobile Applications, Nature, Insight review articles, Vol 414, 15 November, 2001

10. Young, R., Current Status of Solid Hydrogen Storage, Texaco Ovonic Hydrogen Systems presentation at the Hydrogen: Fueling the Clean Air Future, Palm Desert, California, August 2004.

11. Young, R., Chao, B., Myasnikov, V., Huang, B., and Ovshinsky, S.R., A Hydrogen ICE Vehicle Powered by Ovonic Metal Hydride Storage, SAE paper 04-606

12. Chao, B.S., Ferro, P.D., Zelinsky, M., and Stetson, N., Solid Hydrogen Storage Systems for Portable Power Application, paper from Texaco Ovonic Hydrogen Systems, Rochester Hills, Michigan 48309

13. Anton, D.L., Mosher, D.A., and Read, C., A Review of On-Board Hydrogen Storage Alternatives for Fuel Cell Powered Automotive Applications, paper presented at the NHA 2004, Los Angeles, California, April 2004

14. Zuttel, A., Materials for Hydrogen Storage, Materials Today, September 2003

15. Oelerich, w., Klassen, T., Eigen, N., and Bormann, R., Nanocrystalline Metal Hydrides for Hydrogen Storage, published in "Functional Materials", Wiley-VCH, 2000

16. Bogdanovic, B. and Schwickardi, M., Ti-doped NaAlH4 as a hydrogen-storage material-preparation by Ti-catalyzed hydrogenation of Aluminum powder in conjunction with sodium hydride, Applied Physics, A 72, 221-223, 2001

17. Jensen, C.M. and Gross, K.J., Development of catalyically enhanced sodium aluminum hydride as a hydrogen-storage material, Applied Physics, A 72, 213-219, 2001

18. Amendola, S., etals., A safe, portable, hydrogen gas generator using aqueous borohydride solution and Ru catalyst, International Journal of Hydrogen Energy, Vol. 25, p.969-975, 2000

19. Mohring, R.M. and Luzader, R.E., A Sodium borohydride On-board Hydrogen Generator for Powering Fuel Cell and Internal Combustion Engine Vehicles, SAE paper 2001-01-2529, 2001

20. Schwarz, A., Hydrogen storage on activated carbon, NY State Energy Research and Development Authority, Report Number 94-20, November 1994

21. Dillion, A.C., Parilla, P.A., etals., Hydrogen Storage in Carbon-based Materials, National Renewable Energy Laboratory presentation at Rochester Institute of Technology, Rochester, N,Y., May 26, 2004

22. Nijkamp, M.G., Van Dillen,A.J., etals., Hydrogen Storage using Physisorption-Material demands, Applied Physics, A 72, 619-623, 2001

23. Poirier, E., etals., Storage of Hydrogen on single-walled Nanotubes and other carbon structures, Applied Physics, A 78, p 961-967, 2004

24. Cheng, H., Pez, G.P., and Cooper, A.C., Mechanism of hydrogen sorption in single-walled carbon nanotubes, Journal of the American Chemical Society, 123, pp 5845-5846, 2001

25. Gardiner, M., and Bradley, K., Hydrogen Storage for Fuel Cell Vehicles: Advantages and Insights regarding a Cryo-adsorption system, NHA 14th Annual U.S. conference, Washington, D.C., March 2003

26. Weber, S.E., Talapatra, S., etals., Determination of the binding energy of Methane on single-walled carbon nanotube bundles. Physical Review B, Vol. 61, Number 19, 2000

27. Masel, R.I., Principles of Adsorption and Reaction on Solid Surfaces, John Wiley & Sons, 1996

28. Gardiner, M., Michelsen, J., etals., Hydrogen Storage Test-Bed: Physisorption on Pelletized Carbon at Cryogenic Temperatures and Moderate Pressures, 15th World Hydrogen Energy Conference, Yokohama, Japan, June 2004

29. Gardiner, M.. Cunningham, J., etals., Compressed Hydrogen Storage for Fuel Cell Vehicles, SAE paper FFT-2001-01-2531, Future Transportation Conference, August 2001

30. Ariel Compressor Software, Ariel Performance Program, Ver. 7.1.3, 2002

31. Bett, Rowlinson, and Saville, "Thermodynamics for Chemical Engineers, MIT Press, 1975

32. Peschka, W., Liquid Hydrogen, Fuel of the Future, Springer-Verlag Press, NY, 1992

33. Amos, W.A., Costs of Storing and Transporting Hydrogen, NREL/TP-570-25106, 1998

34. Abele, A., Current Status of Hydrogen Storage, Quantum Technologies presentation at the Hydrogen: Fueling the Clean Air Future, Desert Palms, California, August 2004

35. Consumer Guide-Car and Truck Test (Buying Guide), June 2003

36. Chambers, A., Park, C., and Rodriguez, N.M., …., Journal of Physical Chemistry, B, 102,4253,1998

37. Ritschel, M., Uhlemann, M., etals., Hydrogen Storage in Different Carbon Nanostructures, Applied Physics Letters, Vol. 80, No. 16, pg 2987, 2002

38. Pradhan, B.K., etals., Large cryogenic storage of hydrogen in carbon nanotubes at low pressure, Journal of Materials Research Society, Vol. 17,No. 9, p 2209-2216, Sept 2002

39. Rosi, N.L., Eckert, J., etals., Hydrogen Storage in Microporous Metal-Organic Frameworks, Science, Vol. 300, May 16, 2003

40. Smalley,E., Hydrogen Storage Eased, Technology Research News, May 21, 2003

41. Herr, M., Lercher, J. A., and Lang, M., New Methods for the Storage of Hydrogen in Microspheres, 15th World Hydrogen Energy Conference, Yokohama, Japan, June 2004

42. correspondence from Kansai Netsu Kagaku Seizo, Amagasaki, Japan