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Hydrogen Storage for Vehicular Applications: Technology Status and Key Development Areas (U)

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HYDROGEN STORAGE FOR VEHICULAR APPLICATIONS: TECHNOLOGY STATUS AND KEY DEVELOPMENT AREAS

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Abstract

The state-of-the-art of hydrogen storage technology is reviewed, including gaseous, liquid, hydride, surface adsorbed media, glass microsphere, chemical reaction, and liquid chemical technologies. The review of each technology includes a discussion of advantages, disadvantages, likelihood of success, and key research and development activities. A preferred technological path for the development of effective near-term hydrogen storage includes both current DOT qualified and advanced compressed storage for down-sized highly efficient but moderate range vehicles, and liquid storage for fleet vehicle applications. Adsorbate media are also suitable for fleet applications but not for intermittent uses. Volume-optimized transition metal hydride beds are also viable for short range applications. Long-term development of coated nanoparticulate or metal matrix high conductivity magnesium alloy, is recommended. In addition, a room temperature adsorbate medium should be developed to avoid cryogenic storage requirements. Chemical storage and oxidative schemes present serious obstacles which must be addressed for these technologies to have a future role.

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EXECUTIVE SUMMARY

The state-of-the-art of bulk hydrogen storage for vehicular applications is reviewed. The intent is to identify key development needs and desirable technologies to support near-term (less than 10 years) and far-term (15 years and beyond) hydrogen storage requirements for a spectrum of vehicular applications. We consider the hydrogen storage options of storage as high pressure gas (including microspheres and cryogenic gas), storage as liquid, storage as metal hydrides, storage on adsorbate media, and others such as chemical reaction. The various technologies are compared to the Department of Energy storage goals, which are a weight efficiency of 7 wt % hydrogen and a volumetric density of 70 kg hydrogen/cubic meter.

In defining the preferred research paths, and therefore the supporting or enabling technology development tasks, the discriminating factors were the following:

Is the technology appropriate for near or far term payoff?

What are the prospects of technical success?
(achieving weight and volume density, dormancy)

What are the prospects for economic success?

How does the technology fit with volume and weight sensitive applications?

What must be done to assure both safety, and the perception of safety?

In the near term, compressed gas storage using either current Department of Transportation vessels or advanced pressurized storage is viable for highly efficient, down-sized commuter or town vehicles. Compressed gas storage may also afford interim support of large fleet-type vehicles such as buses. For fleet applications, cryogenic compressed gas also offers advantages, although its utility in personal vehicles will be limited unless highly efficient cooling, insulation, and control devices are developed. Advanced hydride bed designs with improved volume efficiency (to about 50% that of the bulk hydride) may also support highly efficient, down-sized commuter or town vehicles. Transition metal hydrides are capable of supplying hydrogen in improved beds today, provided a high efficiency (miles per gallon) vehicular standard is achieved. Liquid hydrogen storage is suitable today for fleet-type, professionally maintained vehicles. Glass microsphere storage, which suffers from low volumetric storage density, may be useful to volume-insensitive vehicles. However, other technologies may be more suitable. Adsorbate media are unsuitable today for personal vehicles because of the cryogenic requirements, the need for a pressure vessel, and the lack of dormancy, but may be usable for fleet applications today. Chemical storage media have many difficulties, including the need to recycle masses of material, and the heavy, costly reforming equipment. The highest hydrogen density carrier, liquid ammonia, is toxic in low concentrations and therefore unacceptable.

In the future, nanoparticulate coated magnesium hydride, or coated metal matrix high conductivity hydride, having reduced absorption and release temperatures, offers safety, weight and volume efficiency provided the many technical obstacles can be overcome. Superabsorbent carbon needs development so that near room temperature absorption occurs, otherwise the cryogenic cooling and control requirements will hinder its acceptance in private vehicles. These hindrances may be acceptable in fleet vehicles. Microsphere technology should address stronger, more perfect spheres to allow and increase in storage pressure. Currently considered hydrogen-bearing media, or chemical reaction media, are deficient. Clearly breakthroughs are needed, making this a long-term option at best.

Introduction

Hydrogen is currently being investigated in the USA, Japan and Germany for use in alternatively fueled vehicles. For the USA, hydrogen offers the potential for (a) freedom from pollution, including greenhouse gases, (b) independence from foreign fuel sources, and (c) potential system efficiencies in excess of those currently realized. The candidate hydrogen-using power sources include, hydrogen-air fuel cells, hydrogen-burning internal combustion engines, and internal combustion engines using hydrogen-natural gas blends such as hythane (5% hydrogen in methane).

While it is unlikely that hydrogen will serve as a large-scale commercial vehicular fuel in this century, there are additional opportunities for the application of hydrogen on a significant scale. Some of these applications are as a vehicular fuel, although many are not. The space station, space shuttle, and advanced discrete monitoring devices all require hydrogen storage. Self-monitoring ("smart") containers for high value cargo may also use hydrogen storage. Unmanned undersea vehicles have requirements which mate well with hydrogen use, and advanced hydrogen storage technology also has application to battery packs used in satellites, etc. which require high power, long life and very high reliability. The dual-use nature of developments in hydrogen storage technology may be of benefit to the United States Department of Energy/Defense Programs (USDOE/DP), National Aeronautics and Space Administration (NASA) and Department of Defense (DoD). Therefore, although this paper concerns hydrogen storage technologies in terms of vehicular applications, many of these technologies would support a variety of possible end-use options.

Numerous system level reviews have been published recently [1-4] and in the near past [5-7] concerning hydrogen storage options. The dominant hydrogen storage issues are:

Storage parameters

Weight efficiency (%hydrogen to total weight), volume density (kg hydrogen/unit volume) and dormancy, that is, time until energy is required to maintain storage.

Safety

We assume that no lessening of current safety standards is acceptable.

Fuel-cycle costs

This includes generation cost, and parasitic energy loss or energy cost such as material recycling.

System costs

System costs are driven by the complexity of the charge/discharge cycle, materials, and other technology costs.

These issues will be treated in turn for each of the currently known hydrogen storage technologies. The specific technology will be introduced and its advantages and disadvantages discussed. The requirements for full development of the technology to the point of utility and the development opportunities will then be considered.

Systems analysts have also attempted to match requirements to vehicular characteristics, including weight, duty cycle, carrying capacity or payload, etc. Several different hydrogen storage technologies will likely be required to address the unique requirements of both light-duty and heavy-duty vehicles, since weight and volume sensitivity vary considerably. For example, the sensitivity to weight and volume of a variety of vehicular applications has been portrayed [4] as shown in Figure 1. It is apparent from the figure that no single storage medium is necessarily

appropriate for all applications, and research and development on several technologies may be appropriate. Technologies deemed unsuitable for use in personal vehicles may prove suitable for heavy-duty fleet-type commercial vehicles, such as a storage mode having poor dormancy, but having a continuous and high fuel demand. Use of LH₂ (liquid hydrogen) in buses would be such an example.

In addition to the weight and volume sensitivity of vehicular applications portrayed in Figure 1, the additional factor of technological advances in vehicles must be considered. As an example, Lovins[8] has postulated a revolution in vehicle construction techniques which would incorporate vehicle downsizing to subcompact dimensions, the use of lightweight composite materials instead of steel as structural and body materials, and the implementation of series-hybrid electric-drive power plants sized to average rather than peak power demands. Peaking power would be provided by high power-density batteries. Such a power plant would use an internal combustion engine of about 10-20 kW capacity, in a point-tuned optimized engine, running a generator. Propulsion would be by switched-reluctance electric motors at the drive wheels. Lovins asserts that, application of "state of the shelf" technology is capable of producing fully satisfactory automobiles which consume 0.4 MJ/km (~ 600 BTU/mile), which is less than the 2 MJ/km (3000 BTU/mile) common today (approximately 30 mpg) in compact and subcompact automobiles. Lovins' prognostications are more optimistic than the targets recently set by the administration, its National Laboratories and commercial partners in the US Car alliance. Their goal is an 82 mpg (0.725 MJ/km) consumer-acceptable four-person vehicle. Leaving aside the questions of safety, manufacturing, the need for a hydrogen infrastructure, and compatibility with existing vehicles, hydrogen as a fuel becomes a more viable option for such a highly efficient vehicle since the fuel storage requirement is greatly diminished. Rather than storing 7 kg of hydrogen to achieve a 550 km (340 miles) range, as identified in the DOE Hydrogen Plan [9], it would be necessary only to store 2.8 kg or less of hydrogen to achieve that range in an 82 mpg-equivalent vehicle. In this scenario, many of the decision points for choosing an appropriate hydrogen storage technology would shift dramatically.

In this review, we consider the hydrogen storage options of storage as high pressure gas (including microspheres and cryogenic gas), storage as liquid, storage as metal hydrides, storage on adsorbate media, and others such as chemical reaction. In the remainder of this report, the storage goals are reviewed, hydrogen storage technologies are evaluated, and potential high pay-off research and development activities are identified. We also attempt to chart desirable development pathways for both the near future and more distant technologies. The appendix contains a detailed description of each storage technology, a listing of advantages and disadvantages, and a discussion of key development activities.

Hydrogen Storage Goals

The primary technological limitation which has been repeatedly identified in hydrogen utilization is the storage of adequate quantities of hydrogen (enabling significant vehicle ranges, etc.). The storage concern arises since, while hydrogen is energy-rich on a weight basis, it is relatively energy-poor on a volumetric basis (by comparison for example with gasoline). The Department of Energy has established a goal [9] under the Matsunaga Hydrogen Implementation Act for efficiency of hydrogen storage of a volumetric density of 70 kg H₂/m³ (4 lbs H₂/ft³) and 7 wt % gravimetric density. It should be noted that the volumetric density goal is approximately 70% of the highest hydrogen density found in nature, for example in methanol and liquefied ammonia.

Hydrogen Storage Options: State-of-the-Art

The current hydrogen storage options discussed are high pressure gas, liquid hydrogen, hydrides, activated carbon, glass microspheres, and chemical reaction and liquid chemical storage. Table I summarizes our view of the advantages and disadvantages of each storage method. Figure 2(A and

B) provides a comparison of volumetric and gravimetric densities for the various hydrogen storage options, with the system volume normalized to 1 kg of hydrogen. The effects on mass and volume of appropriate safety factors, system controls, etc. are included in these estimates of system performance.

High Pressure Gaseous Storage

High pressure gaseous storage is a relatively simple technology on the surface, offering dormancy, easy filling and requiring only appropriate valving and metering to supply product. It has the disadvantages of low volumetric densities and the perception of being excessively hazardous. For this reason, it is often seen as a transitional stage of hydrogen storage development. However, the excellent safety record of Compressed Natural Gas (CNG) vehicles should mitigate some of the perception of hazard associated with compressed gaseous fuels. Moreover, storage and handling are required for any hydrogen system, indicating a need for handling technology development and standardization.

The design and qualification of highly efficient storage containers to meet all foreseeable environmental, structural and safety requirements is not straight forward. A number of issues need to be dealt with. Both vessels and distribution system must be hydrogen embrittlement-resistant (see a related white paper [10]). There is an upper bound in the practical or useful pressure imposed by hydrogen embrittlement, fatigue effects, structural material limits and construction quality, and pumping efficiency losses (which rise rapidly above 55 MPa or 8000 psi). Detailed design and analysis work is required to assess the materials-manufacturing quality-pressure-costs tradeoffs. Questions such as on-board pressurization vs. station-based pressurization must be addressed. Department of Transportation (DOT)-qualified vessels are probably necessary to address both perceptual risk problems and hypothetical hazards. However, DOT does not at present own the regulatory problem of hydrogen fuel storage for vehicular propulsion. Ballard Power Systems of Vancouver Canada is using DOT-qualified natural gas vessels to fuel its fuel-cell powered bus. Frank Lynch and Associates of Denver CO are reportedly operating vehicles on hythane, also stored in DOT-qualified natural gas vessels. Further demonstrations would be valuable.

Hydrogen density is known to increase greatly with decreasing temperature as shown in Figure 3, suggesting that cryogenic hydrogen technologies deserve exploration. A related concept of high pressure plus liquid storage was originally advanced by Kuhn[3] which is discussed later. A more detailed assessment of the potential for cryogenic compressed gas storage should be performed.

Technology Assessment

Some storage of compressed gas may be necessary for all hydrogen technologies. Safe hydrogen gas handling equipment and infrastructure will be mandatory but from a consumer perspective is not yet developed. The potential for achieving high storage densities by using pressures of 20.7-69 MPa (3000-10,000 psi) is limited by the compressibility of the gas, fatigue, hydrogen embrittlement, and mechanical energy and safety considerations. Never the less, if highly efficient hydrogen-using vehicles become available, gas storage is viable for at least short- to moderate range applications. Cryogenic gas storage has the potential of 50-100% increases in storage densities, but it must be compared to liquid hydrogen.

Key Recommendations

- Assess the cost-materials-construction quality-pressure tradeoff for a conceptual design delivery system for compressed gas storage, integrating metallurgical, manufacturing, and non-destructive test data bases.
- Assess methane (natural gas) - qualified DOT vessels for hydrogen storage use.

- Develop a DOT-qualified advanced composite high pressure gaseous hydrogen vessel, using improved textile-based polymer matrix composite technology and improved matrix toughening technology. Analyze and verify long-term structural performance.
- Investigate the effects of hydrogen exposure on composite liner materials.
- Develop conceptual cryogenic gas storage designs and perform cost and technical trade-off analyses.

Liquid Storage

Liquid hydrogen has been extensively demonstrated as a motor vehicle fuel by Los Alamos National Laboratory, BMW, Nissan and others. An often-raised primary objection is that greater than 30% of the fuel energy (12.5 kWhr/kg) is required to liquefy hydrogen, decreasing system efficiency significantly. (Research into magnetic liquefaction technology may diminish this cost.) This energy penalty may be acceptable given the potentially high efficiency of hydrogen-using engines or fuel cells, the possibility of recovering some of the liquefaction energy, and the anticipated environmental and public health improvements resulting from decreased pollution accompanying a switch to hydrogen fuel. Liquid storage offers moderately high storage weight densities, although the volume is more than triple that of gasoline for equivalent BTU content. Some automotive analysts believe that the volume represents a safety concern, although BMW successfully demonstrated 130 liter tankage in a large automobile, which endured collisions without releasing hydrogen [10]. Dormancy is poor since the boil-off rate even with superior insulation is unacceptably high (ca. 1.8%/day). Venting of an expensive fuel is possibly unacceptable, and would require catalytic combustion/flaring to avoid hazardous accumulations. Fractional losses are inversely related to the tankage size, and so light vehicles are at a disadvantage. Recent advances in thermal design and shielding using boil-off gases may greatly improve the performance of even small tanks. Systems for collecting the boil-off add greatly to the complexity, weight and cost of the system. However, they would be needed to obtain long dormancy periods. High-pressure dewars to contain the boil-off have been suggested[3], but these only extend the "lockup" time to about 10 days, at the cost of a very strong, high pressure tank with extensive and costly insulation and highly reliable valving. Finally, consumer-oriented liquid hydrogen use would entail cryogenic hazards requiring safety education, intelligent error-resistant refueling stations, and robust systems. The rigorous training of operators and the detailed handling of liquid during transport and delivery of merchant liquid hydrogen stands as testimony to these requirements [10]. Liquid hydrogen is appropriate to regularly scheduled, professionally maintained vehicle applications. BMW's automated filling station [26] facilitates the fueling step. However, using liquid hydrogen extensively in the family automobile still presents serious technical and social obstacles.

Technology Assessment

Commercial experience in handling and delivering large volumes of liquid hydrogen has been good, although it relies upon careful training and strict procedures. It is doubtful that this level of rigor could be transferred en masse to the driving public. Furthermore, dormancy of the containment is inadequate for infrequently used vehicles, releases are unacceptable, catalytic burning technology has not been demonstrated, and the acceptability of flaring and expensive fuel gas has yet to be demonstrated. Fleet applications would be most suitable. Adequate ruggedness and resistance to failure of vehicular LH₂ containers have been demonstrated.

Key Recommendations

- Investigate techniques for extending dormancy; develop and demonstrate equipment.
- Develop a safe and easy to use refueling capability.
- Investigate techniques for improving weight and volume storage efficiencies.

Hydride Storage

Hydride storage of hydrogen has been demonstrated in vehicles by both Mercedes-Benz and Mazda, although their vehicle ranges were severely limited because of volume and weight inefficiencies associated with existing or current hydride state-of-the-art technology. Hydride storage avoids high pressure concerns since hydrides are stable with relatively low gas overpressures. The theoretical volume density of the materials themselves is high, and they exhibit unlimited dormancy provided the necessary temperature and overpressure are maintained. However, it is anticipated that hydrides will be readily poisoned by impure gas (oxygen) altering the kinetics and losing capacity. In addition, certain hydrides may be pyrophoric or at least oxidize rapidly in an accidental release. The ideal hydride absorbs and desorbs hydrogen near room temperature, has an equilibrium pressure slightly above atmospheric pressure, is lightweight, but is highly dense in hydrogen. Unfortunately, light hydrides bond ionically and require high temperatures, while the covalently bonded hydrides which hydride and dehydride near ambient temperatures are heavy and are generally transition metals. A combination of these traits is sought in laboratories worldwide. Now, a significant opportunity exists to advance the state of the art, combining low temperatures and overpressures with light weight. Superficial coatings applied to magnesium would facilitate low temperature charging and discharging (by permitting hydrogen sorption and dissociation at low temperatures) and would decrease the negative aspects of poisoning and pyrophoricity. Improved safety is expected with such a system due to the low temperature and pressure and the coating which should be less air-reactive than the magnesium alone. Never the less, safety will need to be demonstrated.

In addition, a significant effort to improve hydride bed design should be undertaken, using computational models of heat and mass transfer, and confirmation through experiment. Storage bed design efforts should include powdered metal hydride beds and porous metal matrix hydride beds with superior heat transfer properties. The primary purpose of this work would be to achieve improved volume density, up to 50% of the density of monolithic hydride. This work would have applicability not just to hydrogen storage for fuels, but also to hydride heat pumps, which could play a role as CFC-free air conditioning devices, as hydrogen storage media in advanced batteries, and as hydrogen compressors.

Technology Assessment

Low temperature (transition metal) hydrides are too heavy for efficient vehicular use, and light hydrides generally require unsuitably high temperatures for functioning. The basic hydrogen binding mechanism is at the root of this effect. Alloying may partially blend the requirements, however at the expense of weight increase and capacity loss. Magnesium metal, coated with a hydrogen-adsorbing transition metal, is a good possibility for obtaining low temperature hydriding/dehydriding behavior, with small increase in weight and a small loss in capacity.

Key Recommendations

- Develop a lower operating temperature, and a poisoning- and oxidation-resistant magnesium (alloy) hydride material.
- Develop a safe and easy to use refueling capability.
- Design an optimized maximum volume efficiency hydride bed using both powdered hydride and metal matrix hydrides.
- Evaluate safety characteristics of candidate hydride beds.
- Evaluate needed gas purity requirements for extended bed lifetimes, and regeneration methods.

Surface Adsorbed Media Storage

Of the various surface adsorbing media activated carbon is the most common and generally accepted as the best performing for hydrogen storage, though recent advances in carbon aerogel technology appear promising. Activated carbon has a very porous structure, allowing hydrogen molecules to be condensed (adsorbed) onto the surface while gaseous hydrogen fills available void spaces. Adsorption is enhanced by a reduction in temperature and by an increase in pressure. There are, however, inherent limits in the total amount of hydrogen (hydrogen to carbon ratio) which can effectively be adsorbed. Also, with continued increase in pressure the amount of additional hydrogen adsorbed significantly decreases (approaches saturation) and the amount of hydrogen stored in the carbon void spaces surpasses that adsorbed on the surface (at about 5.6 MPa or 810 psi, for AX-31M superactivated carbon) [10]. As temperature decreases active cooling and containment costs increase. Effective insulation can minimize cooling needs. However, this occurs at the expense of system weight and volume storage densities. Studies have shown that moderate storage densities can be achieved at 150 K and 5.6 MPa (810 psi) [12]. Utilizing recent advances in composite pressure vessel technology a proto-typical storage system was developed having weight and volume storage densities of 4.1 wt % H₂ and 14.0 kg H₂/m³ respectively [12].

The most significant need in the use of surface adsorbed media for hydrogen storage is the development of a higher efficiency and/or room temperature adsorbent material. Future storage densities of 8 - 10 wt % and 50 kg/m³ are often cited, but these are currently goals and may or may not prove obtainable. Several activities are currently in progress to investigate various means of improving the density and/or adsorptive capabilities of carbon.

A variety of other design, reliability, and safety issues are also yet to be resolved. The use of carbon, while lowering the required operating pressure, adds net weight reducing efficiency. Extended dormancy requires active cooling and significant insulation to minimize heat influx. Refrigeration equipment must be carried on-board the vehicle, adding weight and complexity, consuming fuel and further reducing efficiency. Activation of the carbon must take place in-situ, or activated carbon must be loaded into vessels, presenting handling and contamination problems. The surface can be readily poisoned by oxygen or other impurities. Relief devices and/or pressure vessel overdesign will be required to guard against warm-up, both of which add complexity to and decrease efficiency of the system.

Cost, while difficult to estimate because of the lack of a storage medium with suitable performance characteristics, will likely exceed that of compressed gas systems, likely be greater than refrigerated liquid systems, and likely be much less than hydride systems.

Technology Assessment

The major disadvantages of utilizing surface media adsorption for hydrogen storage are low demonstrated storage densities (especially volumetric) on a usable scale and the need for active cooling and control. The primary focus of this technology should be the development of higher efficiency and/or room temperature adsorbent materials, including full scale storage density demonstrations.

Key Recommendations

- Develop a higher efficiency and/or a room temperature adsorbent material.
- Develop a safe and easy to use refueling capability.
- Develop an active cooling and control system.
- Address safety concerns.

Glass Microsphere Storage

Hollow glass microspheres have been proposed as a hydrogen storage technique for vehicular applications due to good dormancy characteristics and intrinsic safety against catastrophic hydrogen release. For utilization, microspheres would be loaded off-vehicle by subjecting them to high pressure hydrogen at elevated temperature. Having the capability of being pumped or poured, the charged microspheres could be loaded into a storage vessel of virtually any shape. To release hydrogen for use the spheres would be reheated. The permeation characteristics of the microspheres are such that while not in use, extended periods of dormancy can be achieved. Once the flow of hydrogen out of the spheres is insufficient to power the vehicle the spent spheres must be removed and replaced by fully charged ones. Glass microspheres are resistant to poisoning by atmospheric gases, and are expected to be intrinsically safe against hydrogen fires under accident conditions since only a small quantity of hydrogen can be released at a given time.

A significant amount of research on the use of glass microspheres for hydrogen storage has been completed by Robert J. Teitel Associates (RJTA) under contract by the US. Department of Energy through Brookhaven National Laboratory [13-16]. In their studies RJTA obtained weight and volume bed (not system) densities of 5.3 wt % H₂ and 12 kg H₂/m³, respectively, at fill conditions of 300°C and 3500 psi. Ultimately, Brookhaven National Laboratory Project Management Staff concluded[16] "The use of commercial grade hollow-glass microspheres for high pressure hydrogen storage has been shown to be cost ineffective." This conclusion was based upon costs associated with the initial material, microsphere breakage, low hydrogen storage densities, low fraction of recoverable hydrogen, and fill and release energy requirements. More recently, Ontario Research Foundation has investigated the use of cylindrical glass microcapsules for hydrogen storage [17]. Through process refinements microcapsules with axial tensile strengths of over 100 ksi were produced. Hydrogen storage capacities of over 2 wt % were achieved at moderate charging pressures and temperatures. Lawrence Livermore National Laboratory is working on the development of glass microspheres with a pressurization capability of 62 MPa (9000 psi) at 500°C [18]. If successful, this increased capability could significantly improve storage bed characteristics, with 10% weight and 20 kg H₂/m³ volume densities possible.

The primary disadvantage of glass microsphere storage is poor volumetric efficiency. Even if the development of higher pressurization spheres proves successful, high pressure pumping efficiencies may significantly limit overall system performance improvements. A secondary, but none the less significant, disadvantage is the necessity of processing spent microspheres. It is unlikely that the limitations of glass microsphere hydrogen storage can be overcome sufficiently to make this technology suitable for passenger vehicular application, where volumetric efficiency and refueling ease are critical. However, with volumetric efficiency improvements, this technology may be suitable to fleet applications with low volume sensitivity, where refueling concerns are less important. The microspheres do not present an inhalation hazard, although fragmented debris would be a concern.

Technology Assessment

The technical risks associated with glass microsphere storage utilization are minor. However, uncertainty in the ability to achieve suitable performance characteristics is significant. Development of improved microsphere bed performance is warranted since this is the limiting factor in terms of future utilization. Uncertainty in terms of scaling between laboratory and full scale utilization is minimal, and so full scale demonstration activities are not needed at this time.

Key Recommendations

- Explore new materials and development of processes to manufacture economically attractive microspheres.
- Perform a total system energy balance including recycle, transport, energy costs, etc.

Chemical Reaction and Liquid Chemical Storage

Chemical reaction and liquid chemical storage technologies are most appropriate for applications which are not weight sensitive. Chemical reaction hydrogen generation methods, such as oxidation of sponge iron, offer claimed high volumetric efficiencies of storage ($>41 \text{ kg H}_2/\text{m}^3$) but at a severe weight penalty (2 wt % H_2). In practice, it is difficult to achieve total oxidation of the medium and, therefore, the claimed volumetric and weight efficiencies. Refueling would probably involve exchanging standardized tanks; any remaining unreacted finely divided particulate would be potentially pyrophoric and hazardous. Assertions about industrial scale reduction and recycling of the oxidizable medium have not been substantiated, and the potential mass of recycled iron is of the order of 150 million tons per year. Furthermore, the generation process itself requires energy input, lowering the overall efficiency of the system. Arthur D. Little Corp. estimates that these losses could be well over 10% [4]. The use of improved catalysts may reduce elevated temperature requirements, but these catalysts have not as yet been developed.

Liquid chemical storage methods based upon storage and cracking of naphthenes to aromatics, such as cracking of methylcyclohexane to toluene and hydrogen require large volumes of liquid to be recycled through the fueling system and represent dead weight to be carried on board. Large volumes of toxic chemicals must be stored. Complex, heavy and expensive chemical cracking equipment must be carried onboard to generate hydrogen. Furthermore, the higher the hydrogen density, the greater the cracking temperature requirements. Dramatic improvements are required to equal other storage methods in weight and volume efficiency, and in cost. One possible liquid carrier is methanol, a high hydrogen density liquid at 12.5% by weight and about $100 \text{ kg H}_2/\text{m}^3$. Methanol may be reformed to yield hydrogen, and DOE programs are underway to evaluate candidate technologies. Complex, though not necessarily heavy equipment, is required. System controls and thermal management will require a high degree of engineering development. System efficiencies of about 7.5 wt % H_2 and $42 \text{ kg H}_2/\text{m}^3$ are estimated. Liquefied ammonia is more dense in hydrogen (17%) and could be chemically cracked to yield hydrogen and nitrogen, but it is toxic in low concentrations and does not readily disperse, adding a new and probably unacceptable hazard.

Technology Assessment

The iron reduction/oxidation storage technique has the potential for moderately high volumetric storage densities. To achieve this potential the development of an effective catalyst which operates at near ambient temperatures is required. Upon development, storage performance characteristics should be evaluated using full scale demonstrations. Low weight storage densities and the substantial quantities of iron required will likely limit the application of this technology to niche markets. Most techniques of hydrogen storage as chemical media are unacceptable in weight, volume, or complexity. It is not clear that the extensive development and breakthroughs required to overcome these deficiencies can be realized.

Key Recommendations

- Develop appropriate sensors and microprocessor control to manage catalytic reforming of methanol and methane.
- Develop an economical and effective catalyst for catalytic reforming of methanol and methane.
- Design, manufacture and test a prototype methanol/methane hydrogen generation/storage system.
- Develop an economical and environmentally sound method of sponge iron production.
- Investigation of refueling logistics (fuel replacement, spent fuel disposition).

Conclusions

The current state-of-the-art of hydrogen storage technology has been reviewed, the advantages and disadvantages of each storage technique summarized, and a listing of potential research and development activities has been presented. In defining the preferred research paths, and therefore the supporting or enabling technology development tasks, the discriminating factors were the following:

Is the technology appropriate for near or far term payoff?

What are the prospects of technical success?
(achieving weight and volume density, dormancy)

What are the prospects for economic success?

How does the technology fit with volume and weight sensitive applications?

What must be done to assure both safety, and the perception of safety?

The following discussion summarizes the conformance of these requirements and the enabling technologies, with the intent of identifying the preferred technological and investment path for short- and long-term hydrogen storage development.

We assume that mandated pressures for near-zero, zero emissions, and greenhouse gas free power plants will accelerate a trend towards hydrogen and/or electrically powered vehicles. We have not treated the problems of the primary energy sources for hydrogen or electrical power generation, and the byproducts from those processes. However, it is apparent that the relative importance of minimizing localized pollutant emissions versus distant emissions will need to be considered. Also, technologies which increase greenhouse gas emissions will need to be evaluated for their overall desirability. These considerations should ultimately be added to those above.

Two hydrogen-fueled transportation options need to be considered: the near future (1-10 years) and the distant (greater than 15-20 years) future. In the short term, highly modified internal combustion engines and low technology storage solutions make sense (which does not imply that attempts to apply fuel cell technologies to large vehicles, such as buses, is premature) to develop engineering experience, public familiarity, and to demonstrate hydrogen as a potential solution to transportation problems in impacted air basins. This approach will also emphasize the developing need for a hydrogen infrastructure, and perhaps stimulate alternatives to an extended infrastructure such as distributed generation. The transition to long-term technologies is somewhat approximate, but we consider that in the long term, the introduction of fuel cells, lighter but more robust automobile bodies, and many small innovations will make personal vehicles many-fold more efficient than is currently the case.

Preferred Development Options

In the near-term, hydrogen vehicles fueled by hydrogen from either high pressure gas or transition metal hydride storage may compare favorably with electric vehicles on cost, range, and performance. This is especially so in small, highly efficient (low fuel consumption) vehicles. Advanced high pressure storage in composite vessels is a high-certainty technology, although the ultimate performance limits, especially volumetric efficiency, are sufficiently low that over the long term, other technologies promise better performance. However, since there are uncertainties in developing those technologies, and since there will continue to be a need for some (limited) volume

of compressed hydrogen storage, for start-up and transient demands, some attention to compressed gas storage is appropriate.

The development of high-efficiency vehicles will significantly reduce the quantity of hydrogen needed and the required weight and volume. Even now, subcompact 'town cars' may require less than 1 kg of hydrogen (occupying less than 80 liters 2.8 ft³ and weighing less than 20 kg) to achieve range (greater than 160 km) and performance superior to current electric vehicles. Compressed hydrogen storage is probably unlikely to provide the 500+ km range expected in general purpose vehicles because of the volume requirements. Perceptions of the safety of compressed hydrogen will undoubtedly benefit from the large number of CNG vessels/vehicles on the road. In order to improve weight and volume performance and safety, it is appropriate to pursue developments in the toughening of matrix materials and application of textile technologies to the fiber reinforcing materials.

Hydride storage media using transition metal hydrides have been developed, and vehicle-based hydride beds have been engineered by Mercedes-Benz and Mazda, followed by fleet demonstrations. In the near-future, transition metal hydrides may be useful for small, highly efficient vehicles having short ranges, especially if the vehicle structure does not allow sufficient crush space to protect a compressed gas tank. Improvements in bed volume efficiency would make them attractive for small vehicles. Over the long term, a suitable lightweight hydride must be developed if required dormancy, high density, safe hydrogen storage for personal vehicles is to be obtained. High surface area magnesium, coated with appropriate hydrogen dissociating metals, is the most promising long-term approach to obtaining both high volumetric and mass storage densities. While the development of this technology carries high risk, the payoffs are correspondingly high. The development of more volumetrically efficient hydride beds requires innovative geometries and extensive thermal modeling and testing, and should interact extensively with the materials development. While the goal seems to be technically achievable, the realization of the technology is too distant for economics to be considered.

Liquid storage is appropriate for fleet-type applications, since regular schedules and professional training in liquid handling are required. There have been numerous demonstrations of liquid hydrogen handling and use. Dormancy problems, the necessity of fuel-venting and the losses associated with small vessels contribute to this recommendation. Automation of filling and handling as pioneered by BMW are essential to acceptance of liquid storage in general purpose vehicles. Similarly, a solution to the boil-off and venting requirements is essential. It is difficult to see a role for high pressure liquid storage in these applications.

Cryogenic storage of hydrogen gas has great potential today for fleet-type applications if satisfactory high-efficiency cryogenic cooling devices and superinsulators become economically attractive. As with liquid storage, small containers suitable for personal vehicles will pay a thermal efficiency penalty resulting in economic penalties. These technologies represent moderate risk items.

In the long-term development arena, adsorbate media, represented by superactivated carbon and carbon aerogels, offer moderately high energy densities. Currently these media require a cryogenic system to maintain the adsorbed state (that is, dormancy), and also require an overpressure of 5.6 MPa (810 psi), necessitating a pressure vessel. Analysis therefore shows that the addition of the adsorbate and the cooling requirement reduces the weight efficiency of storage compared to compressed gas storage. Scale-up has not been demonstrated. Efficiency and performance characteristics should be evaluated from full scale demonstrations followed by the determination of system requirements through a conceptual design. The development of a higher efficiency and a room temperature absorbent material is needed. This includes a more complete understanding of the fundamental mechanisms by which the adsorption process occurs. Without room temperature

adsorption, cooling requirements prevent the attainment of significant dormancy, making the technology suitable only for fleet-type operations. The development of room temperature adsorbate media paces the future acceptability of this technology.

Current high-performance glass microspheres are too expensive, and the volumetric efficiency is still too low even with high (62 MPa) fill pressures to be useful in any but volume-insensitive applications. Therefore, glass microsphere performance and production methodology should be addressed if microsphere storage development is to proceed. It is not clear where microsphere storage will be applicable, since other options are available even for volume-insensitive vehicles.

Steam oxidation of iron has the potential for moderately high volumetric efficiency, requiring catalyst development and extensive process engineering to perform at near-ambient temperatures. Even at full potential the technology cannot provide weight efficient performance. It may be suitable for niche market applications which are relatively weight insensitive (such as locomotives), but probably does not have general applicability. Most techniques of hydrogen storage as chemical media (methanol, methylcyclohexane) which are reacted to yield hydrogen are inefficient in weight, volume, or entail complex technologies to recover hydrogen. These technologies need extensive development and breakthrough thinking in catalyst development, sensor development and process controls. However, it is not clear that these inefficiencies can be economically overcome for mobile applications. Ammonia, often cited as a high hydrogen density carrier, is probably unacceptable due to its toxicity in low concentrations. Clearly, a breakthrough in the choice of hydrogen-bearing storage medium is required, making all of these options long-term at best. As a stationary source of hydrogen, natural gas reforming has good potential as a distributed hydrogen source, since the natural gas infrastructure is well developed.

Mode of Storage	Volume Efficiency	Weight Efficiency	Dormancy	Mech. Energy	Pyrophoricity	Toxicity	Cryogenic Hazards	Complexity Ancillary Equipment	Gas purity requirement	Parasitic Energy Requirements
Advanced Pressure Vessel @ Room temperature	-	+	+	-	+	+	+	+	+	+
Pressure Vessel @ 150 K	+	+	-	-	+	+	-	-	+	+
LH2 as liquid hydrogen only	+	+	-	(+)	+	+	-	=	+	-
LH2 in a pressure vessel	+	+	-	-	+	+	-	=	+	-
Light Hydride, modified magnesium	+	+	+	-	-	+	+	-	-	+
Transition metal hydride	-	-	+	+	-	+	+	-	-	+
Activated Carbon, @ cryogenic temperature	+	+	-	(-)	-	+	-	-	-	-
Activated Carbon, @ room temperature	+to-	+to-	+	+	-	+	+	+	-	+
Steam / iron oxidation	+	-	+	+	-	-	-	+	+	-
Micro-spheres (glass)	-	+	+	+	+	-	+	(+)	+	-

+ favorable
- unfavorable (+ or -) normal state, may change due to failure of critical component.
+ very unfavorable

Table I. Advantages/Disadvantages of Hydrogen Storage Methods

Figure 1. Weight and Volume Needs of Various Transportation Modes.

Figure 2A. System Weight and Volume per Kilogram Hydrogen for Various Storage Technologies.

Figure 2B. Comparison of Hydrogen Storage Densities.

Figure 3. Hydrogen Gas Density as a Function of Pressure and Temperature.

APPENDIX

REVIEW OF DEVELOPMENTS IN HYDROGEN STORAGE AND DELIVERY SYSTEM TECHNOLOGY

In the following, we discuss the system requirements, and the state of the art for each particular technology, including advantages and disadvantages. Safety issues, including DOT qualification and other factors, and reliability issues associated with each technology, are also discussed. Finally, a number of potential technological improvements resulting in performance improvements are identified.

High Pressure Gaseous Storage

Pressure vessel development

High pressure gaseous storage is conceptually a relatively simple technology, offering extended dormancy and requiring only tankage and appropriate valving and metering to deliver product. Filling a container is straightforward in theory, although in practice achieving leak-free couplings, freedom from contamination by air, and satisfactory pumping rates at high pressures are important design considerations. In practice, the design and qualification of highly efficient storage containers is not straight forward. Furthermore, the vessel and distribution system must be hydrogen embrittlement-resistant. The materials and techniques for handling high pressure hydrogen are well-known and require somewhat more expensive materials and procedures than compressed natural gas. The purity of the hydrogen has a dominant effect in the manifestation of hydrogen embrittlement.

Storage of acceptable quantities of hydrogen in gaseous form (which we define as 7 kg, the DOE target for a hydrogen-fueled vehicle [9]) requires pressures exceeding that of the current natural gas 3000 psi (20.7 MPa) standard in order to avoid excessively large storage containers. For example, at 3000 psi, 7 kg of hydrogen will occupy 462 liters (16.3 ft³) exclusive of the vessel, while at 8000 psi (55 MPa) the gas occupies 208 liters (7.35 ft³). DeLucchi [1] has stated that storage to 8000 psi is feasible. Safety, pumping costs, and engineering constraints, discussed below, must be considered to determine whether this pressure represents an optimal or a desirable design point.

The safety concerns arising from increased containment pressure stem from the increasing mechanical work (Pressure x Volume = Energy) contained in the gas. As pressure increases, the gas becomes non-ideal, e.g. a given pressure increment results in less gas being stored than the previous identical pressure increment. A useful figure of merit for the mechanical hazard is the stored mechanical energy at different pressures, assuming a constant quantity of gas. Increasing pressure from 3000 to 8000 psi (21-55 MPa), as in the previous example, and using a constant quantity (at Standard Temperature and Pressure) of gas, causes only a few percent increase in contained mechanical energy, since the compressibility deviates only slightly from ideal, e.g. the volume decrease counterbalances the increased energy per unit volume. For 7 kg, the magnitude of the energy is significant, that is, 13.1×10^6 ft-lbs, or the equivalent of 9.24 lbs of TNT. On an equivalent BTU basis, hydrogen tankage would contain approximately three times the mechanical energy as would natural gas. In practice, the extraordinary thermodynamic efficiency with which hydrogen may be used in optimized applications (fuel cells, optimized internal compression engines) means that very little additional mechanical energy is contained compared to compressed natural gas storage. Above 55 MPa (8000 psi), the increasingly non-ideal behavior of compressed hydrogen causes unacceptably large increases in contained mechanical energy.

The engineering constraints which limit compressed gas storage arise primarily from considerations of vessel performance in off-normal operating conditions. DOT requires that fuel storage containers fail in benign ways when subjected to deliberate burst testing, fire, gunfire and impact. In the latter cases, this involves leak-before-burst response. Appropriate factors of safety, which include static fatigue, cyclic fatigue, and environmental considerations, must be selected. These factors interact strongly with vessel design, materials, and duty cycle. Since composite vessel tankage is considered as the only weight-viable option for vehicular applications, we will consider their behavior. Low performance vessels (the volumetric and gravimetric efficiencies are low), such as fiberglass with polyester resin over an aluminum liner, offer a benign burst mode. The use of Kevlar filaments over aluminum improves storage efficiency, and at low stresses the vessels fail benignly. At high stresses, their burst failure modes can shift to fragmentation. High performance (Pressure x Volume / Weight $> 1 \times 10^6$ inches) carbon/epoxy vessels, which offer high volumetric (about 20 kg/m^3) and gravimetric (about 10 wt % H_2) efficiencies, may fail burst and gunfire tests. Burst failures occur because of the very high energies released by the high strength fibers into the matrix material which lacks sufficient toughness to absorb the energy. Gunfire testing for example induces shock waves [19] emanating from the point of penetration that exceed the fracture toughness of the matrix. Mitigation of these vessel response modes while maintaining high storage efficiencies is not straightforward. Pressure down-rating these vessels will alter the failure modes but is not cost-effective, and greatly diminishes storage efficiencies. Simple hybridizing, by layering a tough composite layer such as Kevlar and E-glass inside the carbon/epoxy layers, is effective but also reduces efficiencies significantly. Alternative approaches are needed.

The development of analytical methods can minimize the reliance on expensive testing for technical guidance. Modeling can provide mechanistic insight into failure modes, reduce the scope of required (expensive) testing, and supply an understanding of design alternatives and limitations. Three-dimensional finite element models can be used to analyze (1) the dependence of vessel burst strength on fiber selection and lay-up process, (2) liner thickness-overwrap design tradeoffs, and (3) response of pressure vessels to quasi-static localized penetration. The primary issues are stress distribution and the response to localized cracking. The first goal is to predict the evolution of subcritical damage to failure in a quasi-static loading mode. Dynamic behavior predictions must follow. Fabricators of high performance composite vessels recognize the value in developing this approach, but there is currently no centralized effort to fund and coordinate the many facets of this effort.

In the interim, detailed testing will remain crucial to the development of high performance alternatives. Alternative resin matrices, fibers, and lay-up processes must be explored, often in combination. For example, Spectra® fibers (a linear polyethylene fiber with a low glass transition temperature polyester resin matrix) offer improved toughness and strength at high deformation rates typical of impact or gunfire penetration. These fibers also offer static strengths comparable to many high performance graphite fibers and are currently in use in ballistic body armor. Techniques which should be investigated for use in pressure vessels would include hybridizing lay-ups, hybridized fiber construction, and 3-dimensional fiber weaves. Further experimentation in improved fiber-matrix bonding should be conducted, that is, processes such as plasma treatment and chemical pre-conditioning of carbon or other fiber tows, should be examined in detail. Tougher matrix materials are highly desirable. Work has proceeded in this area for some time, and although it has not brought significant benefits as yet, any initiatives in this arena should be considered for support, since matrix toughness is a primary limiting factor in the response to impact, penetration and fiber failures.

Monolithic liners are commonly used in small composite vessels. However, large vessels may require joined liners. Joints in either metallic or non-metallic liner materials have the potential for defects. Joining techniques for candidate liner materials must be further developed, defects characterized and controlled, and their consequences known. Since permeation of hydrogen will be a major issue, the development of low permeation barrier materials is crucial. Since most testing is done at low pressure, and since candidate barrier materials are likely to be pressure sensitive, testing equipment

will be needed for measuring permeation at full rated vessel pressures. Molecular alignment through processing or welding may become instrumental in controlling permeation. A multiple barrier approach may also be fruitful. Thin layers of metallic materials applied to the inner liner material surface may be adequate for permeation minimization, although such coatings must adhere to the liner over a wide temperature range.

Normal working environments for a high pressure vessel include the potential of hydrogen embrittlement of the vessel wall. Hydrogen is known to severely effect the mechanical behavior of most metals. Its effects on organic composite materials is not known, although it is anticipated that there will be no effect. Accelerated chemical interaction phenomena need to be examined for liner materials and for strength members. Some composite vessels use liners of aluminum alloys, and their response to cyclic pressure fatigue in hydrogen needs to be examined. Aluminum is normally only little affected by hydrogen; its protective oxide layer excludes hydrogen from contact and solution in the metal. Vessel design to avoid plastic strains at corners, flanges, etc. is imperative to avoid rupture of the protective oxide coating.

A related hydrogen storage technique is cryogenic storage of hydrogen gas. Hydrogen density as a function of pressure and temperature approaches or exceeds that of liquid hydrogen over a range of temperatures and pressures (Figure 3, from [20]); utilizing this density to advantage requires a high degree of development of containment vessels and insulation in order to operate in the 50-100 K temperature range. The actual choice of pressure and temperature is somewhat complex. For example, at 34.5 MPa (5000 psi) and 77 K, the density of the gas is equivalent to that of LH₂; at higher pressure and/or lower temperature the density exceeds that of LH₂. This is achieved without paying the full energy cost of liquefaction, and with less heat influx and reduced insulation requirements compared to LH₂. Lowering the temperature while raising pressure would allow increased density, up to approximately 96 kg H₂/m³ (6 lbs/ft³) at 69 MPa (10,000 psi) and 30-40 K; the practicality of these conditions is suspect since the thermally related design problems are like LH₂, and the system energetics become similar to that of LH₂ because of the high compression requirements. In addition, cryogenic pressurization technology appears to be undeveloped. At the somewhat higher liquid nitrogen temperature (77 K), the technology is well developed and much of it could be applied to hydrogen handling. The addition of high pressure, pressure reliefs and active cooling complicate the problem but are not insurmountable.

For gaseous cryogenic hydrogen storage at temperatures below 77 K, a highly capable and heavily insulated pressure vessel is required. The pressure vessel technology problem is similar to that discussed previously, except for the consideration of thermal expansivity and mechanical mismatch between liner and strength member should metallic liners be required. Insulation technologies (multi-layer, perlite and aerogels for example) exist to hold heat leakage to the watt level, however the cost of these insulations must be significantly decreased to be practical. A highly reliable cryogenic pressure relief is required to guard against overpressure caused by warm-up, otherwise the vessel must be capable of containing the room temperature gas. This is probably an unrealistic expectation for the following reason. Warming from 77 K and 34.5 MPa (5000 psi) to 293 K, results in a gas pressure of 190 MPa (27600 psi), and requires a pressure vessel of ca. 276 MPa (40 ksi) proof test capability at an internal volume of 100 liters if it is to meet common code requirements for pressure vessels. The cryogenic relief valve becomes a serious consideration below 90 K, since oxygen can condense, freezing a valve and also providing a highly oxidative medium. Any satisfactory cryogenic device will not expose valving to air, primarily because of heat leakage but also to avoid these possibilities. Finally, active cooling is necessary to achieve significant dormancy times. Typical cryogenic coolers needed to achieve this temperature are expensive, bulky and inefficient. Electrically driven cooling, e.g., currently available Peltier junction devices, are capable of removing only milliwatt quantities of heat leakage and are likely to be inefficient. These devices need development to the watt level. LLNL has conceptualized the "Intellitank", [21] a microprocessor controlled cryotank composed of composite materials, having a thermally conductive lining and using Peltier junction cooling devices.

This design concept responds to the dormancy, active cooling and gas delivery requirements. Most of the vessel design considerations were discussed previously; thermally conductive liners may require detailed development to avoid excessive mass and volume, thereby compromising the performance efficiencies of the tank. Further development of the components of the "Intellitank" is desirable, in part because it would also be applicable to adsorbate media discussed later. The temperatures could be higher, which would have advantages for avoiding "freezeup" and condensation of air, and diminished thermal influx. A preliminary conceptual design, incorporating strength member, insulation, valving, pressure reliefs etc. should be performed to compare to ambient temperature storage as high pressure gas. The figures of merit would be estimated cost and weight and volume efficiencies of storage. To be attractive, significant improvements would be necessary over ambient temperature gas storage.

A few comments are in order on the high pressure storage of hythane, that is, blends of natural gas and hydrogen, such as hythane 5 which is 5% (by BTU's) hydrogen in methane. The blending of hydrogen and methane has the potential to provide an exceptionally clean-burning fuel, albeit a fuel which continues to exhibit greenhouse gas emissions. In the absence of oxygen or carbon monoxide, most of the hydrogen embrittlement effects exhibited by pure hydrogen must be mitigated [22-24] in these blends. Compressibility is anticipated to decrease, and therefore the BTU content of the gas stored at the Natural Gas Vessel standard 3000 psi (20.7 MPa) will decrease. In order to provide vehicular range, there appears to be a need to increase storage pressure and quantity, just as is the case for hydrogen gas.

Balance of Plant

Balance of plant is that part of the system between the storage device and the energy conversion device. The primary engineering issues for balance of plant are,

- reliable and safe containment/delivery of hydrogen gas,
- controlled conversion of gas from storage (cryogenic if applicable) or high pressure containment to moderate pressure compressed gas, from hydride bed, etc.
- efficiency of operation, e.g recovery of compression energy or heating of cryogenic gas, for example.

With all storage devices and energy conversion devices, hydrogen gas must be handled at pressures from roughly 0.3 MPa (fuel cell) to 7 MPa (fuel injection for internal mixture formation in an internal combustion engine). (A discussion of the effects of hydrogen on the materials used in existing qualified (DOT) natural gas containers is found in [21])

A primary issue in reliability and safety is design for hydrogen embrittlement. The choice of appropriate materials is crucial. Hydrogen embrittles most structural materials in the anticipated service environment, which consists of pressure cycles, mechanical fatigue cycles, and temperature cycles. Increasing the hydrogen pressure, as for example in a fuel-injected internal combustion engine, will accelerate hydrogen embrittlement and inevitably conflicts in material requirements will arise. In addition, fittings and seals must be hydrogen-embrittlement and hydrogen-accelerated fatigue resistant. Depending upon the service pressure, shielding or double containment of high pressure fittings may be necessary, yet accessibility and inspectability must be provided. Inertial and electrical shutoffs would be required in order to isolate gas in small volumes. Similarly, mounting of lines, etc., to prevent failure in the event of collision should be addressed. Minimal volumes and venting requirements must be established in order to preclude ignition/deflagration/detonation events in case of leakage; illuminant materials to allow detection of underhood hydrogen flames, normally invisible, should be considered. Finally, hydrogen sensors need further development, to preclude false alarms of leakage.

Mitigation of hydrogen embrittlement by trace oxygen should be explored. Small amounts of oxygen in hydrogen or in hydrogen/natural gas mixtures apparently mitigates most hydrogen effects on susceptible steels [22,24]. Oxygen doped hydrogen could be labeled "safety grade" hydrogen. Although oxygen is incompatible with hydride beds and possibly superactivated carbon beds, the addition of oxygen to compressed gas might be satisfactory. Removal of oxygen, for use in a fuel cell, could be performed by passing the gas over a hot filament. The additional few ppm of water would not pose difficulties in maintaining fuel cell moisture balance.

Other plant development needs include reliable systems for

1. the controlled feed of hydrogen from cryogenic apparatus;
2. development of refueling capabilities with positive and fail-safe interlocks, discussed under each storage option;
3. assessment and design of energy recovery devices such as turbochargers for pressurization of fuel cell air supply using compressed hydrogen gas;
4. development of lower temperature (<150 K) refrigerant systems for cryogenic storage techniques.

Technology Assessment

Some storage of compressed gas may be necessary for all hydrogen technologies. Safe hydrogen gas handling equipment and infrastructure will be mandatory, but from a consumer perspective is not yet developed. The potential for achieving high storage densities by using pressures of 21-69 MPa (3000-10,000 psi) is limited by the compressibility of the gas, fatigue, hydrogen embrittlement, and mechanical energy and safety considerations. However, if highly efficient hydrogen-using vehicles become available, gas storage is viable for at least short- to moderate range applications. Cryogenic storage has the potential of 50-100% increases in storage densities, but must be compared to liquid hydrogen storage.

State of the Art

Advantages

- System is relatively simple and inexpensive.
- Ready availability of gas at almost any flow rate desired.
- Technology is well in hand to field demonstration vehicles.
- Long dormancy without energy input or active control circuitry requirements.

Disadvantages

- Low weight and volume storage efficiency.
- DOT approved storage vessels are too large and heavy for efficient storage.
- Significant pumping losses above 55 MPa (8000 psi).
- Safety concerns associated with high pressure gas storage.

Key Research and Development Activities

1. Development of a demonstration pressure vessel and delivery system.

Utilizing existing technology develop a demonstration pressure vessel and delivery (valve, metering and fill devices) system. Design constraints are to develop a system which can:

- 1) supply hydrogen to a fuel cell to safely operate a lightweight vehicle
 - 2.5 - 7.0 kg hydrogen capacity
 - flow rates to 0.5 g/sec
 - minimum 5 wt % efficiency
 - minimum 15 kg/m³ volume density

- 2) be used to evaluate performance changes caused by modification of hydrogen storage components.

2. Assess methane qualified DOT vessels for hydrogen storage use.

Any pressure vessel selected for high pressure gaseous hydrogen storage will require DOT qualification for road use applications. An assessment of methane qualified DOT vessels for use in hydrogen storage should be completed to identify likely vessel candidates and expected performance characteristics for near term utilization. Specific areas of assessment should include:

- short and long term hydrogen compatibility
- cyclic loading effects
- hydrogen embrittlement

3. Develop a DOT-qualifiable advanced composite high pressure gaseous hydrogen vessel.

To maximize volumetric and weight energy density efficiencies for high pressure gaseous hydrogen storage some form of composite pressure vessels will likely be required. Evaluate composite pressure vessel technology with the goal of identifying potential candidates for high pressure gaseous hydrogen DOT qualification. Vessel performance criteria should include:

- 2.5 - 7.0 kg hydrogen capacity
- flow rates to 0.5 g/sec
- minimum 6 wt efficiency
- up to 34.5-55 MPa (5000 - 8000 psi) fill pressure
- operation at a suitably high safety factor (2.25-3.0) and DOT qualifiable

Activities shall include:

- 1) Assess composite pressure vessel technology for potential suitable candidates
 - armoring efficiency and effectiveness
 - multi-layer crack retardation construction
 - alternative polymer matrix materials
- 2) Select the most promising candidates for further evaluation
- 3) Fabricate prototype vessels
- 4) Conduct safety and DOT burst and projectile tests
- 5) Evaluate performance characteristics
- 6) Document findings including identification of technical activities needed to further vessel design and performance

4. Investigate the effects of hydrogen exposure on composite vessel liner materials.

The use of polymeric liners in composite pressure vessels may provide an opportunity for increasing the performance of high pressure hydrogen containers. However, combined high cycle fatigue and high pressure hydrogen environments may lead to accelerated liner failure, especially at joints. Investigation of these issues and determination of appropriate safety factor ratings should be completed. This investigation should include the identification and testing of low permeability polymeric liner materials.

Liquid Storage

Liquid hydrogen has been extensively studied as a motor vehicle fuel, and vehicles have been operated on LH₂ in Japan, Germany and the USA. It is often considered to be the ideal means of high-pressure injection of hydrogen into engines for internal mixture formation due to the cooling effects and prevention of "hot spot" preignition; hence there is much interest in cryogenic storage systems for liquid hydrogen. Moderately high hydrogen storage densities are attainable, that is 15-

20 wt % and ca. 30 kg H₂/m³; however, on an equal energy basis an LH₂ system is 6-8 times the volume of gasoline. On an equivalent range basis, it is believed to be 5-6 times as voluminous[1]. Kukkonen has observed that this volume presents difficulties in safe containment [25], although BMW has not substantiated this observation for its LH₂-fueled vehicles. Dormancy is poor since the boil-off rate even with superior insulation is equal to or in excess of 1.5-2%/day. Fractional losses are inversely related to the tankage size, and so light vehicles are at a disadvantage. BMW achieved 1.8%/day in a 130 liter tank [26]. Recent advances in thermal design, shielding using boil-off gases, and insulating materials (such as aerogels) may improve the performance of even small tanks. However, boil-off will remain a technical obstacle and an expensive problem for small, infrequently used vehicles. While systems for collecting the boil-off add greatly to the complexity, weight and cost of the system, they will need to be incorporated for long dormancy periods. Finally, cryogenic hazards exist which would require robust systems. BMW's automated filling system apparently solves this problem, although demonstration of high use reliability is required.

An economic trade-off between the costs of hardware to mitigate boil-off losses, and the costs of simply venting gas can be made. At 6-8 \$/Gigajoule, a commonly cited production cost range for hydrogen fuel gas from reformation of natural gas, a capital cost of \$2000-3000 might be born for reducing or eliminating boil-off losses, which is within reason for vehicular sized systems. Attempts to develop reliable catalytic systems to oxidize boil-off gas were reported a decade ago, but no new work seems to have been performed since then. BMW has chosen to flare the gas instead. The poor dormancy of liquid hydrogen may be partially overcome through the placement of a pressure vessel within a liquid hydrogen cryostat. Cryostats vent at about 2.5 bar, but actual failure pressures may be several hundred bar. A pressure capability of 345 bar (5 ksi) will extend dormancy to three to five days[3]. The primary disadvantages are those of liquid hydrogen with the addition of potentially very high stored mechanical energy (due to the volume phase change).

Technology Assessment

Commercial experience in handling and delivering large volumes of liquid hydrogen has been good, although it relies upon careful training and strict procedures. It is doubtful that this level of rigor could be transferred en masse to the driving public. Furthermore, dormancy of the containment is inadequate for infrequently used vehicles, releases are unacceptable, and catalytic burning technology has not been demonstrated. Fleet applications would be most suitable. Adequate ruggedness and resistance to failure of vehicular LH₂ containers have been demonstrated.

State of the Art

Advantages

- Moderately high weight and volume energy densities.
- Storage has been demonstrated.
- Refueling experience exists.

Disadvantages

- Liquefaction of hydrogen is relatively expensive.
- Hydrogen being lost due to evaporation during dormancy and refueling must be captured or used.
- Safety concerns associated with handling cryogenic liquids.
- Hybrid cryogenic/pressure vessel systems have high stored energy.

Key Research and Development Activities

1. Investigate techniques for extending dormancy/develop and demonstrate equipment.

The goal is to achieve 7 days dormancy and to limit losses (not by venting) to less than 1%/day thereafter. This may be achieved through improved insulation and through hybrid systems incorporating moderate pressure storage, coupled with active cooling using the fuel cell to power a refrigeration unit.

2. Develop a safe and easy to use refueling capability.

The refueling system would require recovery of boil-off for economic and safety reasons, as well as secure couplings and interlocks. Much of this technology exists requiring primarily refinements.

3. Investigate techniques for improving weight and volume storage efficiencies.

In a hybrid pressure vessel/liquid hydrogen container, the optimal ullage volume must be reconsidered. However, weight will increase with the additional pressure capacity, necessitating system trade-offs. Insulation requirements must be addressed in an actively cooled system.

4. Address safety concerns associated with cryogenic liquid utilization.

Cryogenic safety, storage vessel and pressure control/relief, reliability and, ultimately, crash safety need to be addressed. This concern should be integrated into the above activities.

Hydride Storage

Hydride storage avoids the concerns of high pressure storage, since candidate hydrides are stable with low gas overpressures. It also avoids the cryogenic related-concerns of activated media storage and LH₂ storage. The theoretical volume density of the materials themselves is high (about 100-115 kg/m³), and they exhibit long dormancy. Hydride storage for fixed site and mobile applications have been demonstrated several times, as summarized most recently and completely by DeLuchi [2]. However, current hydride materials exhibit several shortcomings:

Hydrides are readily poisoned by impure gas [2] but can be regenerated by high temperature vacuum treatment. This treatment may or may not be compatible with the containment vessel.

Hydrides are expected to be pyrophoric in accidental releases due to the high area of very clean (oxide free) metal surface.

Hydrides which readily exchange gas in and out at low temperatures are generally transition metals or their alloys, but these alloys exhibit low (1 to 2 wt %) weight efficiency. High weight efficiency hydrides (magnesium, 7.6 wt %) require high temperatures to discharge at usable rates and are exceedingly slow to charge at low (room) temperatures. Previous attempts to reduce the temperature for charging/discharging hydrogen by alloying magnesium, usually with nickel [25], have been unsatisfactory due to the resulting 50% loss in capacity and increased weight (most alloying elements are heavier than magnesium).

Current hydride bed designs are inefficient, e.g. they obtain 1/3 of the theoretical H₂ storage density. There are a number of sources for these losses. A volume expansion allowance for the formation of the hydride is necessary. Allowances must be made for particle decrepitation and wedging, which may swell vessels upon repeated cycling. Heat exchange manifolding requires 10-20% of the volume. Designing for a specific gas discharge rate requires a balance between thermal requirements (thermal diffusivity of finely divided

hydrides is low) and the need for small hydride particles to obtain significant mass flow. Pour densities of fine particles as perfect spheres seldom exceeds 60 % of theoretical density. The last factor is amenable to improvement and is discussed later. The cost of metal hydrides is high.

Hydride Materials

It is possible to minimize most of the listed technical shortcomings through an ordered approach to hydride design based on understanding the sources of the limitations. First of all, in order to obtain high storage density parameters, a low Z hydride material must be the basis, implying magnesium. Magnesium suffers from slow hydrogen adsorption and release kinetics [28], requiring high sorption and release temperatures, ca. 350-400°C. Two processes decrease the discharging or charging rates: surface dissociation of the hydrogen and hydrogen diffusion through a magnesium hydride shell formed during the hydriding process. A coating which diminishes the activation barrier to hydrogen dissociation will facilitate the charging/discharging process, making the dissociation kinetics that of the coating material. The coating material may be a high permeability material such as palladium [29,31] or a normal metal such as nickel [31]. The coating should withstand volumetric expansion during hydride expansion. The lowering of hydriding temperatures from 350-400°C to near room temperature would be expected to prevent diffusion of the surface layer into the magnesium. Second, hydrogen must diffuse through the hydride layer inhibiting hydride formation at thicknesses ca. 0.6-1.3 μm [29]. Therefore, particle diameters from 10 nm-500 nm should facilitate full hydriding of particles at maximum rates. A complete review of these phenomena has been published by Selvan et al [32]. Since particle cracking during hydriding typically occurs on grain boundaries [33], small single crystal particulate should be tolerant of the hydride volume expansion and not crack readily. Vessel design should not require additional volume to allow for decrepitation if the particulate is resistant to decrepitation. Thus a suitable low Z material, with a very fine particulate size of 10 nm - 500 nm, coated with a normal metal coating selected for compatibility during hydride phase change expansion, would be expected to exhibit high volume efficiency and hydriding/dehydriding kinetics similar to that of the coating material.

Additional benefits of coated magnesium hydride are likely. The presence of a catalytic coating such as palladium over the magnesium would diminish the possibility of fire upon vessel rupture, improving the safety of hydride beds. In addition, it would improve resistance to poisoning by oxygen or by carbon monoxide [34] which we believe would be reversible and would be amenable to easier clean-up and re-activation processes than the typical very high temperature processing and multiple hydriding steps currently required.

Alloying of magnesium can still play a role in the design of the hydride. The equilibrium overpressure can be tailored to meet demands by judicious additions of nickel or aluminum. However, in each case the overall weight efficiency of the hydride will diminish, making it less attractive for weight sensitive applications. Lower weight efficiency hydrides with tailored characteristics may find other applications than the stringent conditions which a vehicular environment imposes.

Innovative new hydride materials may be formed by aqueous chemistry, and this route has been touted to obtain size distributions of particulate like that of multiple-hydride/dehydride cycled materials [35]. In aqueous electrochemical techniques, hydrogen-hydrogen bonds are not broken as is the case in gas-phase hydriding, which removes an activation energy from the initial hydride forming step. Thus hydride forming reactions are available using borohydride compounds which mimic electrochemical reactions [34], reduction of intermetallics by alcohols [36,37] or by hydrazine in KOH [38]. The borohydride techniques have been used successfully to make many hydrides and should be considered for scale-up. Alternative electrochemical schemes should be evaluated as well.

Hydride Bed Designs

Hydride bed efficiencies, stated in terms of energy densities on both a weight and volume basis, represent a loss of 65-75% of the hydrogen density of the host hydride metal. Heat transfer limitations are the primary driver of this aspect of hydride bed design. Convective models [39,40] and one- and two-dimensional conduction models [41-43] have been applied to hydride bed design. Some differences in assigning importance of variables exist between the models. More importantly, convective models have not incorporated detailed knowledge of heat transfer as a function of hydrogen concentration and hydrogen pressure and do not at this time consider hysteresis. Their applicability seems limited to AB₅ (such as lanthanum-nickel) and FeTi hydrides, which due to their weight are of limited value to hydrogen storage for transportation. Of the two approaches, the conduction models most fully account for the specific properties of hydride materials, thermal properties as a function of composition, temperature and hydride composition and appear to offer the most promise as design tools for optimization of conventional bed designs.

The single-most important obstacle to applying conduction models to hydride bed design appears to be the prediction of the effective thermal conductivity for extremely fine particulate sizes in hydride beds and correlation with measurement. Effective thermal conductivity is decreased as particle size is diminished, and since reaction pressures exceed one atmosphere while particle sizes are small, packed bed thermal analysis becomes inadequate. Recently, improvements in the correlation of theoretical and experimental thermal diffusivities have been made [44]. Conduction-based models imply that thermal path length reductions and improved effective thermal diffusivity are required, necessitating some innovative design approaches. The thermal diffusivity problem will magnify should nano-phase palladium or nickel-coated magnesium become a viable material. Adequate models must be developed, otherwise the design of efficient hydride beds for this material, having the needed energy density, will be strictly a hit-or-miss process and optimized designs will be elusive. In addition, innovative material schemes of depositing hydridable material on high conductivity substrates, while achieving low pressure loss gas flow and adequate delivery rates, need to be explored. Analyses [45] of porous metal-matrix hydride beds using high conductivity substrates predict 40-fold thermal conductivity improvements. Such bed designs will be important for hydride systems having high heats of hydride formation such as magnesium [45].

Combining an improved magnesium hydride-based material with new bed designs, high storage densities and high performance, consistent with safety, are attainable with the application of the best design and materials science tools. Hydride storage densities of 50 kg H₂/m³ and 5 wt % H₂, approaching DOE's goals of 70 kg H₂/m³ and 7 wt H₂ should be possible.

Technology Assessment

Low temperature (transition metal) hydrides are too heavy for vehicular uses, and light hydrides generally require unsuitably high temperatures for functioning. The basic hydrogen binding mechanism is at the root of this effect. Alloying may partially blend the requirements, at the expense of weight increase and capacity loss. Magnesium metal, coated with a hydrogen-adsorbing transition metal, is a good possibility for obtaining low temperature hydriding/ dehydriding behavior, with small increase in weight and a small loss in capacity.

State of the Art

Advantages

- The hydride bed can be repeatedly recharged.
- High volumetric energy density compared to some technologies; potentially higher volumetric energy density.
- Long dormancy periods are readily available.
- Low overpressure means no significant mechanical energy to contain.
- No significant pumping/pressurizing costs.

Disadvantages

Thermal management is required during charging and discharging hydrogen.
High system weight and low volumetric energy density (current technologies) compared to potential performance.
Gas impurities can substantially decrease hydride bed life.
A light, high hydrogen density, low temperature hydride currently does not exist.
Finely divided clean metal powders are potentially pyrophoric.
Gas- and coolant-flow requirements prohibit achieving near-theoretical efficiencies.

Key Research and Development Activities

1. Develop a lower operating temperature coated magnesium (alloy) hydride.

Experimental programs to destabilize the hydride by alloying while retaining hydrogen storage should be combined with hydrogen dissociation stimulating coatings on nanophase particulate. This is a medium to long term program. Included is an assessment of the critical gas purity requirements (O₂, CO), re-activation, etc.

2. Design an optimized volume efficient hydride bed for (coated) magnesium powder, and for porous metal matrix hydride using coated magnesium.

There are significant volumetric efficiency gains needed in packaging hydride reactors. This effort would require both metal matrix hydride development, and optimized bed development using computational techniques and experiment.

3. Develop a safe and easy to use refueling capability.

Refueling rates control and thermal management will require integration between refueling stations and storage beds. The avoidance of oxygen contamination will require positive sealing and evacuation of filling lines. These systems will need to be interlocked and reliable. The efficient management and reuse of 'waste' heat from hydride beds and fuel cells or engines will improve the thermodynamic efficiency of the system. A conceptual design is appropriate using parametrically stated hydride properties followed by experimental confirmation.

4. Evaluate safety characteristics of candidate hydride beds.

The consequences of loss and/or dispersion of containment of the finely divided hydride powders should be explored analytically and experimentally. Engineered solutions may then be developed including compartmentalization, etc. Confidence in the tractability of the problem will enable continued development of the technology.

Surface Adsorbed Media Storage

The storage of hydrogen on surface adsorbing media has been proposed as an alternative to the more traditional techniques of compressed gas, liquid, and hydride storage. Of the various surface adsorbing media, activated carbon is the most common and generally accepted as the best performing for hydrogen storage, though recent advances in carbon aerogel technology appear promising.

Activated carbon has a very porous structure, yielding a high surface area and void space fraction. During cryoadsorption hydrogen molecules are condensed (adsorbed) onto the surface of an activated carbon particulate while gaseous hydrogen fills available void spaces. The hydrogen/carbon bond on the carbon surface is relatively weak, and so adsorption is enhanced by a reduction in temperature. Adsorption is also enhanced by an increase in pressure. There are,

however, inherent limits in the total amount of hydrogen which can effectively be adsorbed. The primary factor governing adsorption is the total amount of surface area available on the carbon. Also, with continued increase in pressure the amount of additional hydrogen adsorbed significantly decreases and the amount of hydrogen stored in the carbon void spaces surpasses that adsorbed on the surface (this occurs at about 6.5 MPa (810 psi) for AX-31M superactivated carbon) [11]. As temperature decreases active cooling and containment costs increase. For this reason an operating temperature of at least 150 K, the lower bound of that sustainable with freon based refrigeration systems, is typically desired. Effective insulation can minimize cooling needs; this is done, however, at the expense of system weight and volume storage densities. When hydrogen is required for use, a modest increase in temperature will release it from the carbon surface.

Syracuse University has expended considerable effort in the research of cryoadsorption of hydrogen onto carbon particulate [11,12,46]. Studies showed that 14 kg H₂/m³ C storage densities could be achieved at 150 K and 5.6 MPa (810 psi) [12]. Utilizing recent advances in composite pressure vessel technology a proto-typical storage system was developed [12]. The storage system was constructed of a fiber/epoxy filament wound vessel with a 6061-T6 aluminum liner and had an internal volume of 16.5 liters and a weight of 3 kg. Hydrogen was loaded onto the bed at a pressure of 8.1 MPa (1180 psi) and a temperature of 150 K. Following charging, the vessel pressure was reduced to an operating level of 5.6 MPa. The vessel contained 2400 g of carbon, which was able to adsorb about 230 g of hydrogen. The storage system had weight and volume storage densities of 0.041 kg H₂/kg system (4.1 wt %) and 14.0 kg H₂/m³ system, respectively. The system weight calculation was based upon the weight of the hydrogen, carbon, and storage vessel, but the system volume calculation was based only upon the internal volume of the vessel. Based upon the external vessel volume the calculated storage density decreases to 12.5 kg/m³ system, which still does not include insulation or cooling and temperature regulating and metering equipment. While the densities achieved are well below goals stated in the DOE Hydrogen Plan, the development of a storage system within an order of magnitude of an actual use size gives the most accurate indication to date of what storage densities can reasonably be expected utilizing this technology. Realistic sizing studies can now begun to be made for vehicular applications.

Kuhn [3] estimates that a storage system with the ability to contain 15 lbs of hydrogen at 5.5 MPa (800 psi) could do so with 4.8% weight percentage (usable hydrogen/total system weight) and require 15 cubic feet of volume (includes tankage, insulation, and heat exchangers). Based upon these calculations he concludes that an 800 psi cryoadsorption system is not feasible. By increasing the storage pressure to 34.5 MPa (5000 psi) he estimates the weight percentage could be increased to 6.4 % and the required volume reduced to 7.8 cubic feet. But he notes that at these pressures 73% of the hydrogen is stored as compressed gas, making cryoadsorption systems heavier and only slightly more compact than a 150 K, 34.5 MPa (5000 psi) compressed gas system. He concludes that utilization of carbon in high pressure, low temperature systems is not advantageous due to increased complexity and cost. Young [12] calculates that a graphite composite tank holding 1300 g of compressed gaseous hydrogen at 20.7 MPa (3000 psi) and 25°C would only be about 9% heavier than a carbon adsorption vessel (including fuel) with the same hydrogen storage capacity. This difference is minimal considering weight for insulation, cooling devices, and pressure relief devices are not included in the cryoadsorption calculation.

The most significant need in the use of surface adsorbed media for hydrogen storage is the development of a higher efficiency and/or room temperature adsorbent material. While cryoadsorption of hydrogen onto carbon has the benefit of minimal temperature (compared to LH₂) and pressure (compared to compressed gas storage) requirements, it is still less attractive than other storage techniques on a hydrogen density storage basis, especially volumetrically. Future storage densities of 8-10 wt % and 50 kg/m³ are often cited, but these are current goals and may or may not prove obtainable. Several activities are currently in progress to investigate various means of improving the performance of carbon adsorption materials. In these studies the goal is to improve

the density and/or the adsorptive capabilities of the carbon. Improving carbon density increases the amount of hydrogen stored in a given volume but also results in a weight penalty. Improving adsorptive capability increases both the volume and weight storage density.

Surface area is the primary factor governing the amount of hydrogen a particular type of carbon can adsorb. However, Noh et al. have shown that different carbons having the same surface area can have significantly different adsorption capabilities [46]. This led them to investigate Modification/Metal Assisted Cold Storage (MACS) for improving the storage performance of superactivated carbons [46]. This concept involves modifying the surface of carbon, either by changing its acidity or impregnating it with metal. In either case, the goal is to increase the amount of hydrogen which can be adsorbed on the carbon surface. They found that by increasing the acidity, and therefore the surface oxygen complexes which act as adsorption sites, from 0.1 to 0.4 milliequivalents NaOH/g of Witco carbon hydrogen uptake was increased from about 24 to 29 g H₂/kg C at 25 atm, a 20% increase. They also found that by impregnating the surface of carbon with an active transition metal such as Pd (1%) or Pt/C (5%), an increase in adsorption of 7 - 20% in comparison to the support carbon was achieved. Further work needs to be completed in utilizing these techniques in the development of an activated carbon with performance characteristics suitable for vehicular applications.

Syracuse University has achieved hydrogen storage densities of 12-13% by carbon weight utilizing a new carbon in conjunction with improved activation processes [12]. To achieve these results, however, the storage temperature must be reduced to 77 K. Furthermore, considering that carbon only constitutes about half the weight of a filled storage vessel, the overall improvement in weight density is still unclear. Obviously a reduction in storage temperature increases active cooling requirements, and, therefore, costs. These costs must be weighed against increases in performance.

Allied Signal claims to have achieved moderate adsorption storage densities (2 wt %) at room temperature and elevated pressure (13.8 MPa or 2000 psi) [47]. Further improvements are needed, however, to reach storage density levels practical for vehicular applications.

The National Renewable Energy Laboratory [27] has called for the investigation of the hydrogen storage capabilities of AX-21 carbon. This material has a surface area of ca. 3000 m²/g, a characteristic which could yield favorable hydrogen storage densities.

Increased attention is being given to the use of carbon aerogels for hydrogen storage. The high surface area of this class of material shows promise for obtaining acceptable storage densities. Lawrence Livermore National Laboratory has been investigating the effects of composition, formulation, pyrolysis temperature, and chemical activation on storage capability [48]. Tests on 19 different carbon aerogels at 5.6 MPa (800 psi) and 77 K were completed, with several materials having bed storage densities of greater than 4.3 wt % and 19.8 kg H₂/m³ [48]. While actual system storage densities will be significantly less than those of the bed alone, future work may yield acceptable performance characteristics.

Advocates of cryoadsorption hydrogen storage point out that pressure requirements are well below that for compressed gaseous storage and cooling requirements are much less than that required for liquid hydrogen storage. It remains to be seen, however, if this technique in fact incorporates the advantages or disadvantages of these other techniques. Furthermore, a variety of other design, reliability, and safety issues are yet to be resolved. The use of carbon, while lowering the required operating pressure, adds weight compared to a simple pressure vessel. Extended dormancy requires refrigeration equipment and significant insulation to be carried on-board the vehicle, adding weight, reducing efficiency, and consuming fuel.

Activation of the carbon must take place in-situ, or activated carbon must be loaded into vessels, presenting handling and contamination problems. The surface can be readily poisoned by oxygen

or other impurities. Relief devices and/or pressure vessel overdesign will be required to guard against warm-up, both of which add complexity to and decrease efficiency of the system.

The cost of a practical cryoadsorption storage system is difficult to estimate because development of a storage media with suitable performance characteristics has not been sufficiently developed to allow operating conditions to be adequately defined. The cost of utilizing current materials will exceed that of compressed gas systems due to carbon and active cooling requirements. It will likely also be more costly than liquid cooled systems because the cost of reduced cooling requirements will probably not offset the cost of carbon and material processing for refueling activities. It will likely be much less expensive than hydride systems due to the use of a less expensive fuel carrier. However, before more definitive cost comparisons can be made an adsorbing material with suitable performance characteristics must be developed.

Technology Assessment

The major disadvantages of utilizing surface media adsorption for hydrogen storage are low demonstrated storage densities (especially volumetric) on a usable scale and the need for active cooling and control. The primary focus of this technology should be the development of higher efficiency and/or room temperature adsorbent materials, including full scale storage density demonstrations.

State of the Art

Advantages

- Moderate weight energy densities.
- Moderate operating pressure levels.
- Potential for higher energy densities with further development.

Disadvantages

- Low volumetric energy density.
- System not demonstrated at full size.
- Active cooling is required for operation and extended dormancy.
- Heating is required to release hydrogen supply for use.
- Absorption of gaseous impurities (including oxygen) readily occurs, reducing efficiency.
- Handling and contamination problems exist during the refueling process.

Key Research and Development Activities

1. Development of a higher efficiency and/or room temperature adsorbent material.

The cryogenic requirements for adsorption need to be reduced and the density of storage increased. This includes more fully understanding the fundamental mechanisms by which the hydrogen/carbon adsorption process occurs. The addition of a gas over pressure to improve volumetric efficiency should be explored. Prototype systems using current materials should be built to explore the design requirements for cooling, dormancy, safety, cost and efficiency, etc. Efficiency and performance characteristics should be evaluated from full scale demonstrations.

2. Development of a safe and easy to use refueling capability.

Couplings, gas metering, overflow or heated gas recovery, and the cooling capacity of the storage system, all must be developed prior to fielding demonstration vehicles. The activation of carbon beds may be incompatible with efficient composite vessels. Development of the loading/activation sequence and techniques for mass production of the carbon bed/vessel combination is needed.

3. Development of an active cooling and control system.

A highly efficient system for cryogenic maintenance must be developed for operation and to obtain extended dormancy.

4. Address safety concerns.

Accidental loss of containment and/or dispersion of carbon and hydrogen should be simulated and studied experimentally. Cryogenic apparatus requirements for thermal isolation, and for robust reliability, must be developed.

5. Evaluate needed gas purity requirements for extended bed lifetimes.

The rate at which impure gas causes loss of capacity should be characterized in order to set purity requirements. Regeneration techniques should be developed and characterized.

Glass Microsphere Storage

Hollow glass microspheres have been proposed as a hydrogen storage technique for vehicular applications due to good dormancy characteristics and intrinsic safety against catastrophic hydrogen release. For utilization microspheres would be loaded off vehicle by subjecting them to high pressure hydrogen at elevated temperature. Having the capability of being pumped or poured, the charged microspheres could be loaded into a storage vessel of virtually any shape. To release hydrogen for use the spheres would be reheated. The permeation characteristics of the microspheres are such that while not in use extended periods of dormancy can be achieved. Once the flow of hydrogen out of the spheres is insufficient to power the vehicle the spent spheres must be removed and replaced by fully charged ones. Glass microspheres are resistant to poisoning by atmospheric gases, and are expected to be intrinsically safe against hydrogen fires under accident conditions since only a small quantity of hydrogen can be released at a given time.

A significant amount of research on the use of glass microspheres for hydrogen storage has been completed by Robert J. Teitel Associates (RJTA) under contract by the US. Department of Energy through Brookhaven National Laboratory [13-16]. In 1979 RJTA evaluated several commercial grades of glass microsphere, including Fillite 200/7 and 300/7 and 3M D32/4500. Evaluations completed included pressurization, filling and dispersion, cyclic, and storage tests. Based upon this work 3M grade D32/4500 displayed the best overall performance, and was therefore selected for more detailed characterization studies. Following are some of the key findings of the evaluation for bed characteristics of as received 3M D32/4500 microspheres [14].

Bed characteristics for fill conditions of 300°C for < 1 hr at a fill pressure of 24.1 MPa (3500 psi.)

- 55% of the stored hydrogen was available at 200°C, while 70% was available at 250°C.
- A weight density of 5.3 wt % H₂ (bed) was achieved.
- A volume density of 12 kg H₂/m³ (bed) was achieved.
- A storage half-life of 110 days was achieved.
- Microsphere sizes ranged from 5 to 60 microns, with an average of 27.7 microns.
- Bulk density was 0.2 g/cc or 200 kg/m³.
- Packing fraction was 0.63.

Other findings

- During crush tests 96% of the microspheres survived under a 24.1 MPa (3500 psi) nitrogen over pressure, while only 50% survived at 41.4 MPa (6000 psi).
- Cyclic pressurization at a given amplitude did not generate further microsphere failures.
- Debris from a failing microsphere can cause other microspheres in the vicinity to fail.
- Pressure gradients of 34.5 MPa (5000 psi) across microsphere walls caused failure.

From the bed characteristics listed above, we estimate that a weight density of 4 - 4.5 wt % H₂ and a volume density of 8 - 9 kg/m³ could be obtained in an engineered system including heating, manifolding, and container with low pressure capability.

Following the initial studies described above, additional commercial sources of glass microsphere were evaluated with the goal of gaining an understanding of how microsphere bed designs could be optimized to maximize high pressure hydrogen storage and delivery performance [15,16]. Eight different sources of glass microspheres were evaluated, including 3M grades D32/4500 (two lots), A38/4000, and B38/4000, Emerson & Cuming grades EC-202, EC-SI, EC-HAS, and EC-HASY, and Fillite grade 200/7. The various microsphere grades were screened based upon storage, breakage, and cost considerations. The screening procedure included chemical, surface and microscopic analyses, density, pressure, and hydrogen flow measurements, crush tests, and fill-dispersion tests. From this screening process two grades, 3M D32/4500 and Emerson & Cuming EC-HAS, were chosen for performance optimization studies. During these studies the effects on performance by particle size separation, surface treatment, stress relief heat treatment, and over pressurization treatment processes were evaluated. This phase of the study was not completed due to a redirection of the program. However, from the work which was completed the following conclusions were made [16]:

- For commercial microspheres fill pressure is limited by strength.
- Glass composition must be modified to improve microsphere dispensation characteristics for suitable vehicular application.
- Unacceptable breakage of off-the-shelf microspheres occurs for 400 atm room temperature hydrogen storage fill-dispense cycles.
- Preliminary studies indicate that particle densities (0.35 - 0.42 g/cc, aspect ratios of 34 - 40) suitable for operation up to 40.5 MPa (5900 psi) can be extracted from off-the-shelf microspheres.

Ultimately, Brookhaven National Laboratory Project Management Staff concluded that [16] "The use of commercial grade hollow-glass microspheres for high pressure hydrogen storage has been shown to be cost ineffective." This conclusion was based upon costs associated with the initial material, microsphere breakage, low hydrogen storage densities, low fraction of recoverable hydrogen, and fill and release energy requirements.

More recently, Ontario Research Foundation has investigated the use of cylindrical glass microcapsules for hydrogen storage [17]. The focus of this work was the development of hollow fiber fabrication processes and the measurement of ensuing microcapsule properties. Since storage pressure is primarily controlled by microcapsule dimensions and material tensile strength these attributes were the primary focus of the development program. The ability to increase storage pressure would allow an increase in storage volume and weight densities. The microcapsule material chosen was fused silica due to its favorable hydrogen permeability, strength, and hydrofluoric (HF) acid etching characteristics. Processes examined included shellac coating for retardation of aging effects, fiber end-sealing for strengthening, and HF etching for dimensional control and strengthening. Through process refinements microcapsules with axial tensile strengths of over 100 ksi were produced. Hydrogen storage capacities of over 2 wt % were achieved in laboratory tests at moderate charging pressures and temperatures [17].

Lawrence Livermore National Laboratory is working on the development of glass microspheres with a pressurization capability of 62.1 MPa (9000 psi) at 500°C [18]. If successful, this increased capability could significantly improve storage characteristics of the bed, with 10% weight and 20 kg H₂/m³ volume densities possible. System densities of 7 wt % H₂ and 13 kg H₂/m³ would be obtainable.

The primary disadvantage of glass microsphere storage is poor volumetric efficiency. Even if the development of higher pressurization spheres proves successful, high pressure pumping efficiencies may significantly limit overall system performance improvements. A secondary, but none the less significant, disadvantage is the necessity of processing spent fuel. Increased refueling time will definitely be inconvenient for customers, but increased cost resulting from supplier processing may be prohibitive.

It is unlikely that the limitations of glass microsphere hydrogen storage can be overcome sufficiently to make this technology suitable for passenger vehicular applications where volumetric efficiency and refueling ease are critical. However, with volumetric efficiency improvements, this technology may be suitable to bulk fleet applications where refueling concerns are less important.

Technology Assessment

The technical risks associated with glass microsphere storage utilization are minor. However, uncertainty in the ability to achieve suitable bed performance characteristics are significant. Development of improved microsphere performance characteristics are warranted since this is the limiting factor in terms of future utilization. Uncertainty in terms of scaling between laboratory and full scale utilization is minimal, and so full scale demonstration activities are not needed at this time.

State of the Art

Advantages

- Intrinsically safe against catastrophic hydrogen release.
- A weight density of 5.3% is currently achievable (bed density).
- Good dormancy characteristics.
- Microspheres may be poured to fit nearly any shape.
- Resistant to poisoning by atmospheric gases.

Disadvantages

- Low volumetric storage efficiencies.
- Spent fuel requires processing.
- Heat is required to charge the spheres, as well as to release hydrogen for use.
- Level of glass particulate inhalation hazard undetermined.
- The maximum practical fill pressure is about 41 MPa (6000 psi) due to pumping costs.

Key Research and Development Activities

1. Development of improved glass microsphere performance characteristics.

Development of microsphere beds with characteristics suitable for vehicular applications is needed. The key element in this activity is the development of higher strength microspheres.

Chemical Reaction and Liquid Chemical Storage

Iron Reduction/Oxidation Storage

A patented hydrogen generation/storage method based upon the oxidation of sponge iron has been proposed as an environmentally safe, cost effective alternative to typical hydrogen storage techniques [49]. An overview of the technique is given below, summarized from the detailed descriptions of [2,49, 50]. Feed stock (sponge iron) and steam (H_2O) are produced by reducing iron oxide (Fe_3O_4) with either hydrogen (H_2) or carbon monoxide (CO) gas as follows:

If carbon monoxide is used as the reducing gas the reaction becomes exothermic, requiring no heat input. However, if hydrogen gas is used as the reducing agent the reaction becomes endothermic, requiring the addition of heat for completion. Both reactions occur at about the same temperature (800-1100°C) and are nearly thermally balanced once initiated.

After production, the iron feed stock is loaded as a powder into either steel or reinforced plastic cylinders and placed onto the vehicle. To generate hydrogen for vehicular use the reduction process is reversed. Sponge iron is oxidized with steam at a temperature typically between 600 and 900°C. Hydrogen and iron oxide are produced as follows:

If a catalyst is used the required reaction temperature can be reduced to 100-200°C. A further reduction in reaction temperature to about 25°C may be possible with the use of a very efficient but likely costly catalyst [2]. DeLuchi [2] notes that for practical implementation a balance must be struck between the extremes of using a costly catalyst requiring negligible heat input and using no catalyst, requiring significant heat input and adding to system complexity. For fuel cell applications the catalyst would be necessary since tail gas temperatures (80-110°C) are inadequate for production of high temperature steam.

Once the iron charge has been effectively used up iron oxide is removed from the vehicle allowing the reduction process to be repeated.

Performance figures for hydrogen generation and storage are provided by Maceda and Wills [49]. The stated generation performance figures of the iron storage media based upon thermally available hydrogen energy (LHV) are:

Hydrogen Generation Performance

English units	SI units
700 watt-hours/pound	39 g H ₂ /kg
51 watt-hours/cubic inch or	78.7 kg H ₂ /M ³
\$0.08/kW-Hr	same
3.9 % H ₂ equivalent [#]	same

Corrected from original paper which cited 4.5 wt %.

The stated hydrogen storage performance figures (based upon a 53% system storage efficiency are:

Hydrogen Storage

English units	SI units
370 watt-hours/pound	20.7 g H ₂ /kg
27 watt-hours/cubic inch	41.6 kg H ₂ /M ³
\$0.18/kW-Hr	same
2.06 wt % H ₂ equivalent	same

The proposed reduction/oxidation process clearly has several advantages over other, more traditional, hydrogen storage techniques. The production of hydrogen on demand reduces the inherent safety concerns associated with long term storage of significant quantities of hydrogen. The oxidation reaction occurs at ambient pressure, eliminating high pressure safety concerns. (In exchange for the reduction of one hazard, however, the presence of finely divided, oxidizable iron powder presents two safety concerns in the event of cell rupture and dispersal, that is pyrotechnic oxidation and dispersal/inhalation of fine particulate.) The hydrogen produced will be of high purity provided the

iron and water are sufficiently pure, making it suitable for fuel cell use. Finally, Maceda and Wills [50] claim that this technique represents a significant opportunity for the development of a very economical system.

There remain, however, a variety of technical and practical issues which must be resolved by ongoing research and development activities. The initial reduction process used to generate the sponge iron feed stock requires very high temperature (800-1100°C), resulting in a variety of high temperature design issues and expenses. To a lesser degree the elevated temperature generation of hydrogen on board also requires additional mechanical design considerations. Furthermore, the generation process itself requires energy input, lowering the overall efficiency of the system. Arthur D. Little Corp. estimates that these losses could be well over 10% [4]. The use of improved catalysts may reduce elevated temperature requirements, but these catalysts have not as of yet been developed.

Also, concern has been raised that during the oxidation process only surface iron is reacted, thereby greatly reducing reaction efficiencies[4]. Additional processing steps may be necessary to obtain near-theoretical reaction efficiency. Furthermore, it is possible that iron powder, necessarily fine to improve surface area exposure to maintain efficiency, may tend to pack together upon repeated use [4]. Finally, the response to vibration and shock in the vehicular environment are uncharacterized, and may result in compaction.

Further difficulties may arise during the engineering of a prototype system. For instance, it is not clear how efficient the oxidation process will be on the scale necessary for vehicular applications. The iron powder must be easily loaded in a configuration which allows effective oxidation. After use the iron oxide must be easily removed and processed.

It is unclear whether the reduction of spent iron oxide fuel would occur at local refueling sites (service stations) or at centrally located reprocessing facilities where chemicals such as carbon monoxide could be more safely handled. While local processing would eliminate shipping and transportation costs, economies of scale may preclude the feasibility of local processing sites. Issues of refueling(who does it, how long it takes), tank exchange, couplings, purging, etc. have not been addressed. Multiple tankage will probably be necessary to avoid "running out", increasing the number of exchanges required. A major obstacle to full-scale implementation of the technology is the mass of recycle material. R. Williams [51] has calculated the amount of recycled sponge iron to sustain the US. light vehicle fleet to be 700 million tons per year, assuming high efficiency vehicles. New production quantity is about 50 million tons per year. The transportation and infrastructure costs would be exorbitant. If this problem is not solved, sponge iron oxidation may forever be a niche market commodity.

It is difficult to estimate what the cost of an iron based system would be. The quoted hydrogen storage cost of \$0.18/kilowatt-hour is definitely superior to many storage techniques. This value does not cover auxiliary system costs such as plumbing, catalysts, and spent fuel removal or the cost of incomplete reaction. From a system perspective, it does not include the fuel economy cost of the low weight efficiency. For example, the DOE target 7 kg of hydrogen would require a storage system weight of ca. 350 kg, roughly equivalent to a 2 mpg decrease in gasoline equivalent in today's vehicles. Consideration of all additional costs would appreciably raise the projected energy costs.

Work on the iron reduction/oxidation process is in the early developmental stage. Further developmental effort will help resolve remaining unknowns, many of which are related to system implementation on a scale suitable to vehicular use. These unknowns include actual system performance and cost, the most effective means of sponge iron production, logistics of adequate refueling operations, the overall system complexity, and the mass of material which must be handled.

Technology Assessment

The iron reduction/oxidation storage technique has the potential for moderately high volumetric storage densities. To achieve this potential the development of an effective catalyst which operates at near ambient temperatures is required. Upon development, storage performance characteristics should be evaluated using full scale demonstrations. Low weight storage densities and the substantial quantities of iron required will likely limit the application of this technology to niche markets.

State of the Art

Advantages

- On-demand hydrogen generation rather than storage.
- Avoids storage of significant quantities of hydrogen.
- Operates at ambient pressure.
- Potentially volume efficient compared to other hydrogen storage techniques.

Disadvantages

- Elevated temperature operation requires additional design considerations.
- Replacement of solid material required for refueling.
- A catalyst may be required to achieve acceptable reaction temperatures and efficiencies.
- An onboard energy supply is required.
- Necessity for processing spent fuel(iron oxide) implies infrastructure with unquantified concerns.
- Low weight efficiency as a hydrogen storage medium implies vehicular efficiency loss.
- Unproven oxidation efficiency on a scale necessary for vehicular applications.
- Potential safety concerns stem from oxidizable fine particulate.

Key Research and Development Activities:

1. Development of an economical and effective catalyst.

Development of a more effective, lower temperature catalyst is required to yield necessary improvements in the overall efficiency of the system. Studies should be completed to assess the degree of reaction of the oxidation process and to establish a suitable means of processing unreacted particulate. The catalyst material must be relatively inexpensive to make the system economically viable.

2. Development of an economical and environmentally sound method of sponge iron production.

Development of an economical and environmentally sound method of sponge iron production is needed. Processing temperature and user distribution requirements of the fuel may make the technique too costly.

3. Investigation of refueling logistics (fuel replacement, spent fuel disposition).

Logistics for refueling should be investigated, followed by a demonstration. Requirements for assuring availability of fuel and handling of unreacted particulate must be established.

4. Design, manufacture and testing of a prototype hydrogen generation/storage system.

To date only laboratory reduced scale experiments have been completed utilizing this hydrogen storage/delivery technique. Performance characteristics should be evaluated on a full scale system to allow a more comprehensive assessment of the technology to be completed.

Liquid Chemical Storage

There are currently several candidate liquid chemical systems under consideration. Methylcyclohexane can be stored onboard a vehicle, and can then be catalytically cracked to yield hydrogen and toluene. The toluene is returned to a storage tank for later rehydrogenation. As with the iron oxidation concept, this material represents an inert mass to be carried with the vehicle, diminishing the overall system efficiency. Toluene is toxic and heavier than air, and so represents a significant accidental release hazard. The hydrogen density of the medium is 1 kg H₂/18 kg of methylcyclohexane, that is, 5.55 wt %, and about 43 kg/m³ volumetric density. Taube [52,53] cites a 700 kg dehydrogenation system. Thus the system weight efficiency is very low, and only locomotives or other heavy vehicles could utilize this technology. Breakthrough improvements in cost and weight are needed, with the probable result that efficiencies would only equal that of systems using other more benign components.

Methanol can also be reformed to produce hydrogen. The methanol reformer (which must be carried onboard to generate the hydrogen) is under development. Bentley [4] estimates that an advanced methanol reformer system, assuming 80% efficiency and no onboard water storage, would achieve about 7.5 wt % and 42 kg/m³ volumetric hydrogen density. Methanol is also toxic, but is probably only marginally different from gasoline in its hazards. Ammonia is an excellent example of a high hydrogen-density chemical medium. The technology to crack ammonia has not been applied to vehicular concerns; indeed its toxicity would argue against its extensive use.

Technology Assessment

Most techniques of hydrogen storage as chemical media are unacceptable in weight, volume, or complexity. It is not clear that the extensive development and breakthroughs required to overcome these deficiencies can be realized.

State of the Art

Advantages

Potentially high volumetric efficiencies.

Disadvantages

Low weight energy density.
Incomplete reaction.
Significant on-board heat requirements.
Potentially pyrophoric powders.
Complex reformer technologies.

Key Research and Development Activities

1. Analyze proposed storage systems.

Alternative media such as chemical hydrides should continue to be analyzed, and the total energy balance of these systems studied from the practical perspective of design and development. Otherwise, a significant technology could be overlooked. These efforts are very long-term, in excess of ten years.

2. Develop appropriate catalysts, sensors and microprocessor control to manage reforming of methanol and methane.

Satisfactory stationary reforming equipment could provide the means to sidestep hydrogen infrastructure questions; that is, reforming of methane could be distributed, avoiding long-range transport of hydrogen. Methanol reforming to hydrogen has relevance to biomass schemes, although it would be probably less distributed than methane reforming. Microprocessor control

is available, provided affordable catalysts can be developed, and sensor development and process control can be established.

References

1. M.A. DeLuchi, "Hydrogen Vehicles: An Evaluation of Fuel Storage, Performance, Safety, Environmental Impacts, and Cost," *Int. J. Hydrogen Energy* **14**: 81-130 (1989).
2. DeLuchi, M.A., Hydrogen Fuel-Cell Vehicles, Institute of Transportation Studies, University of California, Davis, Sept. 1, 1992, Report UCD-ITS-RR-92-14.
3. Kuhn, I.F., *Comparative Performance of Onboard Hydrogen Storage Techniques For Vehicles*, Jr., (Directed Technologies Inc., December 9 1992).
4. J.M. Bentley, *Multifuel Reformer and On-Board Hydrogen Storage Program Update*, 1992 DOE Contractors Coordination Mtg. Dearborn Michigan, (Arthur D. Little, November 4, 1992). also, Multifuel Reformer and Hydrogen Storage Review Meeting #2, Section 2-Hydrogen Storage, (A.D. Little, October 26, 1992).
5. D. Gregory, *A Hydrogen Economy*, (Institute for Gas Technology 1974).
6. J.J. Iannucci, S.L. Robinson, *Fixed Site Hydrogen Storage:I. Applications Impact*, in Proceedings of the 2nd Miami International Conference on Alternative Energy Sources, edited by T.N. Veziroglu, (U. of Miami, 1979)p. 3595
7. S.L. Robinson, J.J. Iannucci, *Fixed Site Hydrogen Storage:II Comparison of Technologies and Economics* in Proceedings of the 2nd Miami International Conference on Alternative Energy Sources, edited by T.N. Veziroglu,(U. of Miami, 1979)pg. 3607.
8. Lovins, A.B., J.W. Barnett, L H Lovins, "Supercars: The Next Industrial Revolution", presentation, 11 August 1993, LLNL Livermore CA.
9. US. D.O.E., Hydrogen Multi-Year Program Plan FY1993-1997, May 1992.
10. J.T. Ringland, *Safety Issues for Hydrogen-Powered Vehicles*, Sandia National Laboratories/CA, draft ms in preparation for SNL/CA Transportation Program Office..
11. K.A.G. Amankwah, J. S. Noh, and J. A. Schwarz, "Hydrogen Storage on Superactivated Carbon at Refrigeration Temperatures", *Int. J. Hydrogen Energy* **14**:437(1989).
12. K.S. Young "Advanced Composites Storage Containment for Hydrogen", *Int. J. Hydrogen Energy* **17**:505(1992).
13. R.J. Teitel, *Development Status of Microcavity Hydrogen Storage Systems for Automotive Applications*, RJTA Report, USDOE Program Review, (Upton NY, 1979).
14. Teitel, R.J. and J. Powers, *Microcavity Systems for Automotive Applications*, Final Progress Report Prepared for US. Department of Energy, RJTA Report No. 79-7, December 31, 1979.
15. R.J. Teitel, *Microcavity Storage Update*, prepared for USDOE Program Review, (Upton NY, 1980)
16. Teitel, R.J., *Microcavity Hydrogen Storage Final Progress Report*, Prepared for US. Department of Energy and Environment, Contract No. DE-AC02-76CH00016, Report BNL 51439, May 1981.
17. K.L. Yan, B.G. Sellars, J. Lo, S. Johar and M.K. Murthy, Storage of Hydrogen by High Pressure Microencapsulation in Glass, *Int. J. Hydrogen Energy* **10**:517(1985).
18. Berry, G., A Smooth Transition to a Hydrogen Energy Economy, Draft Report, University of Illinois/Lawrence Livermore National Laboratory, September 22, 1993.
19. D.C. Prevorsek, H.B. Chin and Y.D. Kwon, *Strain Rate Effects in Spectra Armor*, in High Performance Composites For The '90's, edited by (Minerals Metals and Materials Society, 1991).
20. D. Murphy, *Hydrogen Properties*, in Hydrogen: Its Technology and Implications, Volume III: Edited by. K.E. Cox and K.D. Williamson, (CRC Press, Cleveland OH 1975) p. 59.
21. G. Rambach, LLNL, private communication (November 1993)
22. H.J. Cialone, J.H. Holbrook, *Sensitivity of Steels to Degradation in Gaseous Hydrogen*, p. 134 in ASTM STP 962, Hydrogen Embrittlement:Prevention and Control, edited by L. Raymond ASTM, 1984.

23. C.T. Oien, J.R. Spingarn, S.L. Robinson, J.J. Bartel, and D.R. Adolphson, *Hydrogen Storage in Natural Gas Pressure Vessels*, Sandia National Laboratories/CA, draft ms in preparation for SNL/CA Transportation Program Office, December 1993.
24. Nelson, H.G., *Hydrogen-induced Slow Crack Growth of a Plain Carbon Pipeline Steel under Conditions of Cyclic Loading* in, *Effect of Hydrogen on Behavior of Materials*, edited by A.W. Thompson and I.M. Bernstein (A.I.M.E., 1976) p. 602.
25. Kukkonen, C.A., *Hydrogen As An Alternative Automotive Fuel*, in *Alternative Power Source Technology*, 1992 P. 127.
26. W. Strobl and W. Peschka, *Liquid hydrogen as a fuel of the future for individual transport*, in *Hydrogen Energy Progress VI. Proc. 6th World Hydrogen Energy Conf*, ed. T.N. Veziroglu (Pergamon press, New York, 1986)p. 1171.
27. National Renewable Energy Laboratory, Hydrogen Program Annual Operating Plan for FY93, February 1993.
28. B. Vigeholm, J. Kjoller and B. Larsen, *J. of the Less-Common Metals* **74**:341(1980).
29. J. Ryden, B. Hjorvarsson, T. Ericsson, E. Karlsson, A. Krozer and B. Kasemo, *J. Less-Common Metals*, **152**:295(1989).
30. A. Krozer, B. Kasemo, *J. Less-Common Metals* **160**: 323(1990).
31. B. Bogdanovic, T.H. Hartwig, B. Spliethoff, *Int. J. Hydrogen Energy* **18**:575-589 (1993).
32. P. Selvam, B. Viswanathan, C.S. Swamy, and V. Srinivasan, "Magnesium and Magnesium Alloy Hydrides", *Int. J. Hydrogen Energy* **11**,169(1986)
33. S. Guthrie, N.Y.C. Yang, unpublished research, Sandia National Laboratories/CA, May 1993.
34. A.S. Pederson, B. Larsen, *Int. J. Hydrogen Energy* **18**:297(1993)].
35. Murphy, D.W., S.M. Zahurak, B. Vyas, M. Thomas, M.E. Badding, W.-C. Fang, "A New Route to Metal Hydrides, *Chem. Mater.* **5**:767(1993).
36. H. Imamura, K. Yamada, K. Nukui, S. Tsuchiia, *J. Less Common Met.* **123**:L1 (1986).
37. H. Imamura, , T. Takada, S. Tsuchiya, *Int. J. Hydrogen Energy* **13**:11 (1988).
38. S. Wakao, H. Nakano, S. Chubachi, *J. Less Common Metals* **104**:3085(1984).
39. M.A. El-Osairy, I.A. El-Osery, A.M. Metwally and M.M. Kesh, *Int. J. Hydrogen Energy* **17**:125- (1992).
40. M.A. El-Osairy, I.A. El-Osery, A.M. Metwally and M.M. Kesh, *Int. J. Hydrogen Energy* **17**:961(1992).
41. M.A. El-Osairy, I.A. El-Osery, A.M. Metwally and M.A. Hassan, *Int. J. Hydrogen Energy*, **18**:517(1993) .
42. D.Sun and S. Deng, *Int. J. Hydrogen Energy* **15**:807(1990).
43. D. Sun, *Int. J. Hydrogen Energy* **17**:945(1992).
44. D. Sun and S. Deng, *Int. J. Hydrogen Energy* **15**:331(1990) and *J. Less-Common Metals* **160**:387(1990).
45. M. Ron, and M. Elemelach, *Heat Transfer Characteristics of Porous Metallic Matrix Metal-Hydrides*,. in *Hydrides for Energy Storage. Proceedings of an International Symposium*, August 1977, edited by . A.F. Andreson, A.J. Maeland, Pergamon Press p. 417.
46. J.S. Noh, R K. Agarwal, and J. A. Schwarz, "Hydrogen Storage Systems Using Activated Carbon," *Int. J. Hydrogen Energy*, **12**:693(1987).
47. S. Hynek, J. Bentley, B. Barnett, E. Shanley, and G. Melham, "Hydrogen Storage Technologies: Present and Future", presented at technical seminar on *Storage Technologies: Status and Challenges*, Hydrogen Industry Council, Montreal, Quebec, December 9, 1992(unpublished report).
48. R.W. Pekala, P. R. Coronado, "Carbon Aerogels for Hydrogen Adsorption", FY93 Progress Report, Lawrence Livermore National Laboratory, 1993 (unpublished report).
49. J. Werth, US. Patent Application of John Werth for Hydrogen Generating System, docket HPOW-102, April 21, 1992.
50. M.P. Maceda and J. Will, *Advanced Hydrogen Generation and Storage Systems for Fuel Cell Vehicle Support*, presentation at Windsor Workshop on Alternative Fuels, June 16, 1992 (unpublished report).
51. R.H. Williams, Princeton University Center for Energy and Environmental Studies, private communication (November 1993)

52. M. Taube, et al "A Prototype Truck Powered by Hydrogen from Organic Liquid Hydrides", *Int. J. Hydrogen Energy* 10,595(1985)
53. M. Taube et al "A system of hydrogen-powered vehicles with liquid organic hydrides", *Int. J. Hydrogen Energy* 8,213(1983)

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