A Review of Heat Transfer Issues in Hydrogen Storage Technologies

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Significant heat transfer issues associated with four alternative hydrogen storage methods are identified and discussed, with particular emphasis on technologies for vehicle applications. For compressed hydrogen storage, efficient heat transfer during compression and intercooling decreases compression work. In addition, enhanced heat transfer inside the tank during the fueling process can minimize additional compression work. For liquid hydrogen storage, improved thermal insulation of cryogenic tanks can significantly reduce energy loss caused by liquid boil-off. For storage systems using metal hydrides, enhanced heat transfer is essential because of the low effective thermal conductivity of particle beds. Enhanced heat transfer is also necessary to ensure that both hydriding and dehydriding processes achieve completion and to prevent hydride bed meltdown. For hydrogen storage in the form of chemical hydrides, innovative vehicle cooling design will be needed to enable their acceptance. [DOI: 10.1115/1.2098875]

Introduction

Hydrogen has been recognized as the likely energy carrier for future energy systems because it may enable the use of a diverse array of primary energy sources, including fossil fuels as well as sustainable long-term energy sources, such as hydropower, biomass, wind, and solar. As an energy carrier, hydrogen offers the advantage of clean and complete conversion to water, which has generally benign environmental impacts. The development of a hydrogen-based energy economy with the use of sustainable energy sources promises to alleviate numerous current problems facing our nation and the world—such as air pollution, greenhouse gas production, and global security. Recent reports [1–4] have identified many critical technical challenges that remain to be addressed before a hydrogen-based energy economy can become viable. While much contemporary research has focused on the conversion of hydrogen-carried energy to electrical form using fuel cells, upstream issues involving production, distribution, and storage of hydrogen are also critically important. Of these, on-board hydrogen storage for vehicle applications involves many technical challenges and opportunities. This review summarizes the technical characteristics and requirements of the most promising hydrogen storage approaches, particularly for fuel-cell-powered vehicles, while identifying significant heat transfer issues associated with each.

To realize the full potential of the hydrogen economy, the challenges of storage and distribution must be addressed, particularly for the transportation sector. Vehicle-based hydrogen storage systems must meet stringent requirements of gravimetric and volumetric energy densities. According to the U.S. Department of Energy's Freedom Car Program targets, the gravimetric density should be at least 6 wt.% (i.e., 6 kg H_2 in a 100 kg tank), and the volumetric density should be at least 45 g H_2/L by 2010 [3], while even more aggressive targets have been set for future years. In addition, fast hydrogen fueling processes are needed to meet the ingrained expectations of consumers, with a targeted fueling rate of 1.5–2.0 kg H_2/min [3].

Hydrogen storage and distribution systems must be energy efficient in order to retain the inherent efficiency advantages of fuel cells. The energy efficiency of hydrogen storage is typically measured by comparing the lower heating value (LHV) of hydrogen (approximately 120,000 kJ/kg or 240 kJ/mol) to the total energy input during a complete use cycle. Current hydrogen storage methods include compression, liquefaction, absorption, and chemical binding as the four potential processes for increasing energy density. Each of these processes involves exothermic and endothermic operations and requires thermal management for controlling process temperatures and enhancing process efficiencies. For the entire system to be practical, on-board thermal management devices for hydrogen storage must be designed to be as compact and lightweight as possible while minimizing parasitic losses. In this respect, passive cooling systems, such as thermosyphons [5,6], which do not require pumping power, may be highly attractive. Nevertheless, thermal management will surely involve a trade-off between energy efficiency gains from improved thermal management and efficiency losses from additional weight and the energy consumption of the thermal management system itself.

Recently, several review articles have addressed various aspects of hydrogen storage technologies [7–12], but none has specifically considered heat transfer and related energy-efficiency issues, which are the focus of this review. The storage methods considered here include compressed hydrogen, liquid hydrogen, metal hydrides (including complex hydrides), and chemical hydrides. (Nanostructured carbon for hydrogen storage is not discussed because of inconsistent experimental results [13].) This review describes each of these technologies with an emphasis on thermal management and heat transfer issues. Throughout the text, opportunities for heat transfer research are highlighted.

Compressed Hydrogen

Compressed hydrogen storage is one of the few commercially available hydrogen storage technologies. Because of hydrogen's relatively low energy density, it must be compressed to high pressure to store a sufficient amount of hydrogen for vehicle use. At room temperature, the density of compressed hydrogen at 350 bar (~5000 psi) is approximately 22.9 g/L, and at 700 bar (~10,000 psi) it is approximately 39.6 g/L. Industry standards

for compressed hydrogen storage have been set at 350 bar, with a future target of 700 bar [7,14–16]. High-strength, carbon-fiber composite pressure vessels rated to 700 bar may achieve a gravimetric storage density of 6 wt.% and a volumetric storage density of 30 g/L [14], which falls short of the Freedom Car Program's goal for volumetric density.

One of the main advantages of compressed hydrogen storage is that it is relatively simple and filling of a vehicle tank can be completed in a short time. Because of these advantages, compressed hydrogen has been adopted in many prototype fuel-cell vehicles. The main disadvantages are its low volumetric and gravimetric densities compared to other storage methods. Another shortcoming of compressed hydrogen is the public's perception of safety concerns associated with extremely high-pressure hydrogen tanks. However, recent test results have indicated that 700 bar composite vessels may actually be safer than their low pressure counterparts widely used in industry, primarily because of thicker tank walls [17].

The process of compressing hydrogen from atmospheric pressure to 700 bar consumes a large amount of energy. Thermodynamically, isothermal reversible compression consumes the least work [18], which can be calculated as (assuming ideal gas behavior)

$$w = RT_1 \ln\left(\frac{P_2}{P_1}\right) = 4.157 \cdot 300 \cdot \ln\left(\frac{700}{1}\right) = 8170 \text{ kJ/kg} \quad (1)$$

In reality, the temperature rise of hydrogen during compression is substantial even with multi-stage intercooling technology. Therefore, the compression process is better described by a polytropic process [18]. The energy consumption for such a process can be calculated as

$$w = \frac{n}{n-1} RT_1 \left[\left(\frac{P_2}{P_1}\right)^{(n-1)/n} - 1 \right] \quad (2)$$

Because the pressure ratio for each stage is limited to approximately 7.0 for diaphragm compressors and much less for other types [19], at least four compression stages would be necessary to obtain a pressure of 700 bar. Assuming perfect intercooling (i.e., gas cooled to the initial temperature before the next stage begins), the minimum compression work is 10,161 kJ/kg ($n=1.36$ [19]), which is still 24% greater than that of the isothermal process. Consequently, significant potential and interest exist in achieving energy savings by means of enhanced heat transfer during the compression process [20].

Two types of compressors are widely used in industry to boost hydrogen pressure to at least 150 bar: reciprocating piston compressors and diaphragm compressors. Reciprocating piston compressors can be used for both large-scale applications (e.g., pipelines [21]) and small-scale applications (e.g., fueling stations), while diaphragm compressors are mainly used for small-scale applications due to their limited flow rates imposed by the size of the diaphragm [20]. Improvements in energy efficiency for both compressor types are still possible by enhancing heat transfer.

In general, diaphragm compressors remove heat more effectively than piston compressors because of the relatively large surface area of the compression chamber, the presence of the cooled compression oil near the diaphragm, and the ability to include a cooling system in the cover of the compressor [19]. Nevertheless, the compression ratio for diaphragm compressors remains limited by the gas temperature increase during compression. Most existing diaphragm compressors employ a simple one-loop cooling system in the cover of the compressor, which can be improved significantly by increasing the number of cooling loops, implementing micro- or mini-channels, and/or coupling to a refrigeration loop.

For piston compressors, the high speed and cyclic nature of the compression process make heat transfer modeling and design quite challenging [22–24]. Traditionally, such compressors are cooled by lubricant oil, but this approach may not be feasible for hydrogen because high-purity hydrogen is required by the fuel cell. Yong [25] developed a cooling approach that employed a water spray inside a compressed-gas cylinder to reduce gas temperature via evaporation. Because PEM fuel cells require a humidified hydrogen stream, this method may be used to boost hydrogen from pipeline pressure to final charging pressure. A new approach in the design of piston compressors involves the use of a long, slow stroke in conjunction with a water-cooled gas cylinder to improve cooling performance [26]. However, the flow rates for this type of compressor are small because of the slow motion of the piston.

Equations (1) and (2) indicated that reducing the inlet hydrogen temperature decreases compression work proportionally [27]. Intercooling techniques have been designed to compensate for insufficient cooling during the compression process, and water sprays have been proposed for intercooling of air compressors [28] and may be useful for hydrogen compressors as well.

Another important heat-transfer issue for compressed hydrogen storage is the temperature increase during fast tank-filling processes [4,15]. Hydrogen exhibits a reverse Joule-Thomson effect at room temperature, i.e., throttling processes from a high-pressure stationary tank to a tank being filled cause heating of the gas instead of cooling [29,30]. During rapid filling (>1 kg H$_2$/min), the temperature rise inside the tank can be as high as 50°C [29], and overheating can adversely affect the integrity of the composite tank [31]. Further, with increasing temperature, the tank carries less hydrogen at a given pressure. If this temperature rise is compensated by transient overpressurization, the extra compression work, typically more than 10% of the nominal work, is wasted. Another possible remedy to overheating is precooling of the filling gas [31], but such an approach would require additional energy for refrigeration. An energy-efficient solution may be to enhance both internal and external heat transfer during the filling process and to optimize the pressure throttling process. The former approach would likely require cylinder frames made of materials with high thermal conductivities or installing heat pipes to transfer heat from inside the vehicle tank to an external heat sink, such as the vehicle frame. We note that hydrogen has a much higher thermal conductivity than most industrial gases [32], and this property may enable innovative heat transfer design.

To minimize throttling losses and resulting overheating during filling processes, multi-bank cascade systems can be employed. For example, to fill a vehicle tank to 350 bar, three banks at 450, 300, and 160 bar could be employed. The 160 bar bank would fill the vehicle tank to 130 bar, and then the 300 bar bank would fill the tank to 270 bar. Ultimately, the 450 bar bank would fill the tank to 350 bar (or higher to account for overheating). The overall temperature rise and the total fueling time in such a process can be optimized by using thermodynamic and heat transfer principles [33].

Liquid Hydrogen

Liquid hydrogen (LH$_2$) storage is another commercially available technology [34]. LH$_2$ is stored at atmospheric pressure in cryogenic tanks (20.3 K) with a density of 70.8 g/L—almost twice that of compressed hydrogen at 700 bar (39.6 g/L). An 18 gal (68 L inner vessel) cryogenic tank can carry approximately 5 kg LH$_2$, which is sufficient to power a fuel-cell passenger vehicle approximately 300 miles (480 km). LH$_2$ tanks can be filled in a relatively short time and are perceptually much safer at appropriate cryogenic temperatures than high-pressure hydrogen tanks. The main disadvantages with LH$_2$ are the high energy consumption associated with liquefaction processes and continuous boil-off during storage [7,35].

The simplest liquefaction cycle is the Joule-Thomson cycle [36] in which hydrogen gas is first compressed to a high pressure

(e.g., $P = 100$ bar) and then cooled in a heat exchanger before passing through a throttling valve, where it undergoes isenthalpic Joule-Thomson expansion and produces some liquid. The cooled gas is separated from the liquid and returned to the compressor through a heat exchanger. Because the inversion temperature (i.e., the temperature below which throttling produces a cooling effect) of hydrogen is only approximately 200 K, expansion at room temperature will not induce a cooling effect, and liquid nitrogen ($T = 77$ K) is often used to precool hydrogen before expansion [37,38].

Thermodynamically, liquefying hydrogen involves three heat transfer stages. The first stage extracts sensible heat (4000 kJ/kg) to reduce the temperature from 300 K to 20.3 K [32]. In the second stage, latent heat (450 kJ/kg) is extracted to condense hydrogen at 20.3 K [32]. The third stage is called ortho-para conversion, which requires heat extraction of 703 kJ/kg [39]. The entire liquefaction process requires heat removal of 5153 kJ/kg that must be provided by a liquefaction cycle. The minimum theoretical work to liquefy normal hydrogen to 99.79% para form is 14,280 kJ/kg (~12% H_2 LHV) [39]. In comparison, the minimum theoretical work to liquefy nitrogen is only 6% that of liquid hydrogen. The actual energy consumption for hydrogen liquefaction is usually at least 2.5 times the theoretical minimum, depending on the capacity of the liquefaction plant [40].

The storage of LH_2 requires highly insulated cryogenic tanks. To minimize heat ingress, the three basic mechanisms of heat transfer should be considered. The rate of radiation heat transfer is proportional to the emissivity of the shields between the warm and cold surfaces and inversely proportional to the number of these shields. To minimize radiation heat transfer, multilayer insulation (MLI), also called superinsulation, is often used. The apparent thermal conductivity of MLI is $1-8 \times 10^{-5}$ W/m-K, which is approximately three orders of magnitude lower than the thermal conductivity of fiberglass building insulation [41]. MLI consists of 30–80 layers of low-emissivity radiation shields, e.g., aluminum foil ($\varepsilon = 0.05$), separated by low-conductivity spacers, e.g., fiberglass paper. When placed against each other, the shields touch at only a few discrete points to minimize heat conduction. For MLI, the apparent thermal conductivity parallel to the radiation shields is typically three to six orders of magnitude higher than that normal to the layers [36]. Such a large disparity in directional thermal conductivity presents considerable challenges in thermal insulation design for systems where structural supports and feedlines penetrate the insulation. An alternative to MLI is to use microsphere insulation, which exhibits isotropic thermal conductivity and can tolerate significantly higher compression; nevertheless, the apparent thermal conductivity of microsphere insulation is one order of magnitude higher than that of MLI [42].

A critical design variable for MLI-insulated vessels is the optimal number of insulation layers per unit thickness. If the layer density is too high, the increase in conductive heat loss through the spacers can outweigh the decrease in radiative heat flux provided by more insulation layers. A typical dependence of the apparent thermal conductivity on layer density for MLI is shown in Fig. 1 [42]. To minimize convection, the volume between the inner vessel and the outer vessel is typically evacuated to high vacuum, e.g., 1.3×10^{-8} bar [41]. The vacuum is maintained by gas-adsorbing getter materials such as activated carbon [36]. Under such high vacuum conditions, free molecular conduction can occur because the molecular mean free path is large relative to the distance between the boundaries, and, typically, heat flux by free-molecular conduction varies linearly with pressure, as shown in Fig. 2 [42].

To accelerate the time required for cooling and to reduce evaporation losses during the cool-down process of the vessel, the thickness of the inner shell is usually designed to be as thin as needed to withstand the maximum internal pressure and bending forces. The outer shell is designed to keep the vessel wall from collapsing due to the difference between atmospheric pressure on the outside
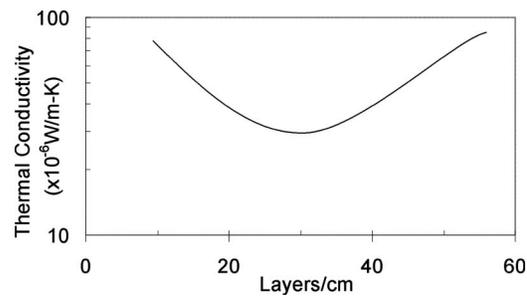
Fig. 1 Typical variation of thermal conductivity with layer density for a typical MLI with boundary temperatures of 294 and 78 K, adapted from Ref. [42]

and vacuum pressure on the inside [43]. Support members are installed within the outer shell to buttress the inner shell and must balance the competing needs for adequate mechanical support and minimal heat conduction. Further research on materials with appropriate combinations of mechanical and thermal properties is warranted.

Heat flow from the ambient to the tank's cryogenic interior will inevitably cause evaporation, or "boil-off," and the vessel's pressure will increase. When the pressure increases to a prescribed level, hydrogen vapor must be vented through a pressure relief valve. Cryogenic storage vessels are generally designed for a vapor volume of 10% to extend the dormancy time—the time that the inner vessel can be sealed before the pressure level reaches a critical value [36]. Because of heat ingress, LH_2 can stratify inside the vessel, and this phenomenon increases the boil-off rate because the segregated warmer fluid vaporizes more readily, thus raising the tank pressure to the saturation pressure of the warm layer. This pressure rise shortens the storage period between successive ventings and is especially severe with large vessels. For small-sized vehicle tanks, metal conducting rods can be used to redistribute heat from the top to the bottom portions of the inner vessel [36].

To reduce boil-off rates, liquid or vapor shields can be employed. Vapor shields take advantage of the cold vent gas from the liquid hydrogen vessel. The escaping vent gas is routed through a vapor shield and sensibly absorbs some of the heat that would otherwise warm the LH_2 [42]. A patented recooling system using a similar principle can extend the dormancy time of a 68 L vehicle vessel to more than 12 days before evaporation losses occur [44,45]. Liquid shields use a similar process to absorb latent heat in an inexpensive cryogenic liquid such as nitrogen. Nevertheless, the addition of liquid or vapor shielding adds extra volume and weight to the storage system.

Another source of boil-off is sloshing—the motion of liquid inside a vessel caused by acceleration and deceleration—which
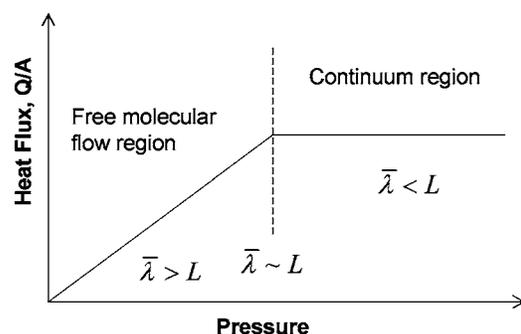
Fig. 2 Heat transfer as a function of pressure for vacuum insulation, adapted from Ref. [42]
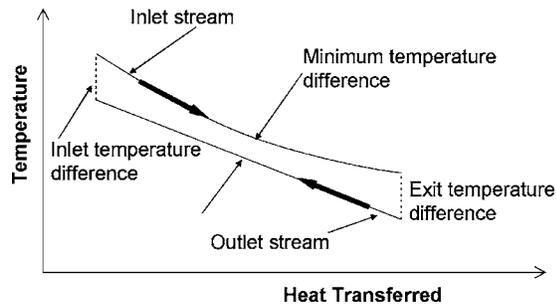
Fig. 3 Temperature profile in a countercurrent hydrogen heat exchanger, adapted from Ref. [36]

Fig. 4 Schematic of a patented metal-hydride hydrogen storage bed, adapted from Ref. [52]

transforms some of the liquid's kinetic energy and impact energy to thermal energy [46]. Sloshing can be significant for vehicles in a city driving environment. A potential solution is to insert traverse or antislosh baffles to restrain the motion of the liquid [46], but this approach will reduce the system's gravimetric storage density.

To appreciate the challenges in designing LH_2 tanks for vehicle applications, a sample design is given here. Assuming a 68 L inner vessel design volume, 300 K ambient temperature, and 4% daily boil-off rate, the allowable heat ingress rate is 1 W for a full tank. A vessel wall thickness of 10 cm would require an apparent thermal conductivity of 3.2×10^{-5} W/m-K with a resulting exterior volume of 185 L (assuming a spherical vessel structure). A wall thickness of 5 cm would require an apparent thermal conductivity of 1.9×10^{-5} W/m-K with an exterior volume of 117 L, and the resulting volumetric density would be approximately 37 g H_2/L, which is slightly below the DOE target of 45 g H_2/L.

The design of liquid hydrogen transfer lines also involves many heat transfer issues. Two-phase flow is common in the transfer of liquid hydrogen as a result of heat transfer to the fluid, particularly during the start-up transient of the filling process. The existence of vapor in a transfer line can critically reduce its carrying capacity; therefore, evaporation must be minimized by insulation. The insulation strategies for the transfer line are similar to those for the storage vessel. Additional issues, such as severe contractions and expansions of the transfer piping in station filling cycles, need to be addressed through the analysis and design of expansion joints, bellows, and U-bends [36].

Heat exchangers are used extensively in LH_2 production. Because of the low operating temperature, cryogenic liquefiers cannot produce liquid if the heat exchanger effectiveness is less than approximately 85% [41]. Several measures can be utilized to improve heat exchanger effectiveness, including small temperature differences between inlet and outlet streams, large surface area-to-volume ratios, and high heat transfer coefficients [36,41]. Because of the variation of the specific heat of hydrogen during heat transfer processes, an unusual situation can occur in which the minimum temperature difference between the heat exchanging streams occurs in the middle of the flow path, as shown in Fig. 3 [36]. This phenomenon should be considered when attempting to improve heat exchanger efficiency by minimizing temperature differences between inlet and outlet streams.

A new method of storage involves cryo-compressed hydrogen [47,48]. In this process, medium-pressure hydrogen (e.g., 150 bar) is adsorbed by activated carbon inside a tank that is maintained at 77 K by a liquid nitrogen jacket, which must be replenished approximately once per week [47]. The advantage of this method is that it does not require the direct input energy associated with hydrogen liquefaction, yet its storage capacity is similar to that of a high-pressure hydrogen tank at 700 bar [47]. Nevertheless, the overall energy consumption may not be favorable because of the work involved with compression and nitrogen liquefaction.
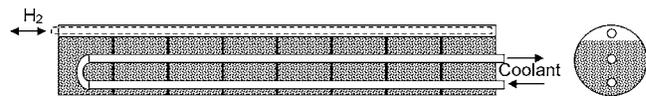
Metal Hydrides

The broad family of metal hydrides comprises an alternative to the previously discussed storage approaches, which do not involve chemical reactions. Thousands of metals and alloys can react reversibly with hydrogen to form hydrides [10]. Such a reversible process from a metal M and hydrogen to a metal hydride can be expressed as

$$M + 0.5x H_2 \rightleftharpoons MH_x + \text{heat} \qquad (3)$$

The charging, or hydriding, process releases heat, while the discharging, or dehydriding, process requires heat input. Most prior research has focused on conventional metal hydrides—hydrides of alloys and intermetallic compounds in which a strong hydride forming metal element (A) combines with a weak hydriding metal element (B) to achieve desired intermediate thermodynamic affinities for hydrogen [49]. The intermetallic compounds used in conventional metal-hydride systems can be generally classified into four categories: AB_5, AB_2, AB, and A_2B [49]. Some typical intermetallic compounds are $LaNi_5$, ZrV_2, $ZrMn_2$, $TiFe$, $ZrNi$, Mg_2Ni, and Ti_2Ni [7]. To promote better information exchange and to encourage discovery, a public hydride database has been established by the U.S. Department of Energy [50].

Conventional metal hydrides are commercially available [51,52] and are perceptually much safer than compressed hydrogen, as evidenced by their application in fuel-cell-powered mining locomotives [53]. Their material volumetric densities are comparable to that of liquid hydrogen [7], but the main disadvantage of metal hydrides is low gravimetric density, which is currently less than 2.0 wt.% [51]. Another serious drawback is associated with low hydriding and dehydriding rates, which are limited in part by thermal properties. Hydriding processes release large amounts of heat, as dictated by the heat of reaction, while the hydride expands in volume. If the heat is not removed efficiently, the temperature rise can be so large that the process will stall. Furthermore, metal hydrides may sinter at high internal temperatures [54] and lose hydrogen storage capacity. The dehydriding process requires heating at a specific temperature, dictated by chemical thermodynamics, to proceed. Without sufficient heat supply, the release of hydrogen will cease because of the reduced temperature in the hydride bed. Therefore, enhanced internal heat transfer is essential to improve system performance and to maintain system reliability [55]. Utilizing the waste heat from a fuel cell to dehydrogenate the metal-hydride bed could improve overall energy efficiency and, consequently, metal-hydride research [7] has focused on materials that can release hydrogen near 80°C, the normal operating temperature of a PEM fuel cell. The coupling of fuel cells with metal-hydride beds would not only enable higher energy efficiencies but also save scarce on-board space [56].

Metal-hydride powder has a typical grain size of 50–100 μm. After approximately 10 to 100 hydriding/dehydriding cycles, the powder decomposes to an equilibrium grain size approximately 1 μm [57]. Such fine metal-hydride powders typically have low effective thermal conductivities of the order of 0.1 W/m-K [58]. Heat and mass transfer enhancement methods suggested for metal-hydride beds can be broadly classified into two categories: extended areas in the forms of fins, foams, or meshes, and binding metal hydrides into a solid matrix formed by high-conductivity materials such as copper, aluminum, or nickel [59].

Figure 4 illustrates the design of a developmental metal-hydride hydrogen storage vessel using metal foams [60]. The vessel is

divided into compartments by metal plates, and each compartment is filled with a metal foam and fitted with a porous metal filter and U-shape coolant tube. The foam material, normally aluminum, provides support for the metal-hydride powders and enhances internal heat transfer [60]. The foam generally occupies approximately 6% of the volume. Metal-hydride powders occupy approximately 80% of the open space, while the remainder is left for expansion [60].

Expanded natural graphite/metal-hydride compacts have recently been proposed to enhance heat transfer and have exhibited promising results [57,58,61]. To make such compacts, commercially available expandable graphite is heated in order to expand in volume, and the expanded graphite is then homogeneously mixed with metal-hydride particles. The mixture is then pressed into small cylindrical blocks to make compacts [57]. Compacts with 2.1% mass fraction of expanded graphite can increase the effective thermal conductivity of metal-hydride powders from 0.1 W/m-K to above 3 W/m-K [57].

The effective thermal conductivity of a powder bed depends strongly on the thermal contact resistance among particles. When particles are pressed against each other, the contact area and effective thermal conductivity increase. Consequently, particle beds under high internal stress have much higher thermal conductivities than those that are loosely packed [62,63]. However, particles that are pressed too tightly against each other suffer from significantly reduced hydrogen storage capacity. For example, highly compacted alanates (discussed in detail below) exhibit 67% lower reversible hydrogen storage capacities than unconstrained samples [64]. In addition, the containing vessel may rupture at high internal stresses [51]. A potential design that can take advantage of this phenomenon would involve a piston-type structure for the containing vessel. The piston would be preset to a certain pressure by springs or other mechanisms. Once the internal stress of metal-hydride bed exceeds the preset pressure, the piston would move outward to allow for expansion of the metal-hydride bed and maintain an appropriate stress level to achieve adequate internal heat transfer.

To illustrate more quantitatively the issues involved with metal hydrides, we consider sodium alanate (sodium aluminum hydride), which can reversibly absorb and desorb hydrogen in the presence of titanium catalyst, as reported by Bogdanovic [65,66] in 1997. This discovery has stimulated much recent research in complex hydrides, such as sodium aluminum hydride (sodium alanate), lithium aluminum hydride (lithium alanate), ammonia borane, and magnesium-modified lithium-amide compound [11,64,67–72]. The absorption (desorption) of hydrogen to (from) sodium alanate proceeds in two stages as follows:

$$NaAlH_4 \rightleftarrows \tfrac{1}{3}Na_3AlH_6 + \tfrac{2}{3}Al + H_2 \rightleftarrows NaH + Al + \tfrac{3}{2}H_2 \quad (4)$$
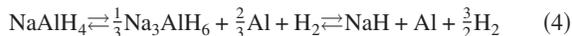
The first step releases 3.7 wt.% H_2, while the second step releases additional 1.9 wt.% H_2 for a total theoretical gravimetric storage capacity of 5.6 wt.% H_2. The heats of formation for the two steps are 37 kJ/mol (15% of the H_2 LHV) and 47 kJ/mol (20% of the H_2 LHV), respectively [66]. Though research on $NaAlH_4$ may not provide an ultimate solution to hydrogen storage because of its limited gravimetric density, developments in catalysis could produce true reversibility with related borohydride and transition metal complexes [73]. The weighted average heat of formation of sodium alanate is 40.3 kJ/mol H_2. For a hydride bed with a capacity of 5 kg H_2 and a fueling rate of 1.5 kg/min (750 mol/min), the average heat dissipation rate is an astounding 0.50 MW during the fueling process.

Because of the extremely high required heat transfer rates and stringent space and weight requirements, on-board regeneration of metal-hydride beds may not be practical. One alternative is to develop cartridge-type metal-hydride beds that can be inserted and removed at fueling stations. Then, in an off-board process at the station, the heat transfer rate for the charging process could be significantly reduced by extending the charging time. However,

this solution presents other practical challenges because the cartridge's mass will be of the order of 100 kg, and active heat transfer measures will likely be required even for off-board regeneration. Another possibility is to transfer charged metal-hydride powder from the fueling station to the vehicle tank and to transfer the discharged metal-hydride powder from the vehicle tank back to the fueling station for recharging. The viability of this powder-based method will depend largely on thermal hardware required for on-board heat exchange processes. Plate-fin heat exchangers with wide plate spacing could allow relatively simple powder injection and removal processes. However, if compact heat-exchangers are needed, then powder transfer processes could become excessively unreliable and time consuming. One benefit of any off-board charging process would be the possibility of using waste heat for domestic or commercial processes, such as water and space heating.

Another issue with the sodium alanate system is that the final discharged products consist of sodium hydride and aluminum. For the hydriding process to reach completion, all reactants (sodium hydride, aluminum, and hydrogen) must exist in close proximity to each other. This requirement applies to other promising complex hydrides as well and suggests that partial chemical immobilization could be used to enhance system performance. To this end, glass microspheres have been proposed to confine the metal-hydride particles [74] in a shell that is gas-permeable at higher temperatures and gas-tight at room temperature [75]. The advantage of this method is that the shell dramatically reduces diffusion of the metal hydride, thus inhibiting separation of the dehydrogenation products inside the bed. The disadvantage of this method is a decrease in volumetric storage density (weight is not a serious issue because glass microspheres are extremely light-weight). Another challenge lies in reduced heat conduction caused by the shells. Because of the low thermal conductivity of glass and the large number of material interfaces, improved heat exchange processes as well as fundamental studies of thermal conductivity and heat capacity are needed, such as those that employ the transient hot-wire method [76].

With ongoing research on potential complex hydrides [7,67], characterization of their thermal properties will be an essential step in developing well engineered systems [1]. Most of the potential complex hydrides are extremely moisture sensitive and readily react with air-borne water vapor, generating highly flammable and explosive hydrogen gas [55]. Therefore, experiments must be conducted under inert environments. To make matters more difficult, critical thermal properties vary significantly from the hydrogenated and dehydrogenated states and also can depend strongly on particle diameter and density. Therefore, the thermal properties of partially and fully dehydrogenated tanks will differ significantly, and the heat transfer systems must be flexible enough to accommodate all such conditions [64].

Most prior modeling work has involved conventional metal hydrides. Metal-hydride beds are usually modeled as porous media, and Darcy's law is used to calculate the gas velocity [77]. The chemical kinetics of the hydriding and dehydriding processes may be described by an Arrhenius equation [78]. The shrinking core model, which describes a chemical reaction progressing from outside a spherical reactant to the inside, has been used to model hydriding and dehydriding processes [79]. The pressure inside the hydride bed can be related to temperature by van't Hoff's equation [77]:

$$\ln(P_{eq}) = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (5)$$

Klein et al. [61] calculated effective thermal conductivity based on a model assuming two half-spherical particles in contact and using a deformation factor to account for the change in shape under stress. A homogenization method that is capable of considering microscopic behaviors, such as pulverization, changes of void fraction, and contact area, has been proposed to calculate the

effective thermal conductivities of metal-hydride beds [63,79,80]. Gadre et al. [60] explored the possibility of using a simple numerical model to predict the discharging behavior of a practical metal hydride bed and obtained relatively good agreement with experimental data. Askri et al. [78] examined the validity of ignoring radiation heat transfer for LaNi$_5$ and magnesium hydride systems and also examined hydrogen flow and heat transfer in the expansion section of the metal-hydride bed. Guo et al. [81] examined the importance of considering conjugate heat transfer between gas-phase convection and solid-phase conduction. Given the early state of the field and the limited amount of prior work, a significant need exists for combined modeling and experimental studies [82] of metal-hydride systems to include conjugate heat and mass transfer, stress analysis, and thermo-mechanical effects on thermal conductivities and mass transfer coefficients.

Chemical Hydrides

Chemical compounds that release hydrogen when they react with water or other substances are classified as chemical hydrides. Unlike metal hydrides, chemical hydrides generally do not hydrogenate and dehydrogenate reversibly. The dehydrogenated products are not easily converted back to chemical hydrides, and central recycling facilities would likely be needed to provide such conversion. The recycling process usually involves a significant number of chemical reactions; therefore, the overall energy efficiency of chemical-hydride systems must account for the following factors: energy consumption to transport chemical hydrides from recycling facilities to fueling stations, energy consumption to transfer reaction products from fueling stations to recycling facilities, energy efficiency of the hydrogen release reaction, and energy efficiencies of all the physical treatments and chemical reactions involved in a complete recycling process.

Many chemical hydrides such as sodium hydride (NaH), magnesium hydride (MgH$_2$), and sodium borohydride (NaBH$_4$) are under investigation [83–86]. Sodium borohydride is the most developed among chemical hydrides for hydrogen storage applications, as evidenced by its use in Daimler-Chrysler's fuel-cell-powered Natrium™ minivan [87]. Because sodium borohydride reacts very slowly with water at room temperature except in the presence of catalysts such as RuCl$_3$ and CoCl$_3$ [88], it can be stored stably in aqueous solution containing a few percent NaOH as a stabilizer [89]. The solution can be pumped through a chamber to interact with a catalyst bed to produce hydrogen [90,91] according to the following reaction [89–92]:

$$\text{NaBH}_4 + 2\text{H}_2\text{O} \xrightarrow{\text{Catalyst}} \text{NaBO}_2 + 4\text{H}_2 + \text{Heat} \qquad (6)$$

The exothermic reaction releases approximately 55 kJ of heat per mole of H$_2$ [92] (23% of the H$_2$ LHV). Assuming a PEM fuel-cell efficiency of 50%, heat generation from a sodium borohydride storage system represents an additional 46% increase above the heat rejection from the fuel cell alone. Given that thermal management of PEM fuel cells is already a serious issue [93], this extra heat load will only intensify the need for innovative, vehicle-scale heat transfer systems, as discussed below.

One of the main advantages of sodium borohydride is its intrinsic safety. Accidental spillage of the solution will not cause severe problems because the uncatalyzed reaction rate is very low. Sodium borohydride systems exhibit fast response to fuel demand and potentially high gravimetric (up to 21 wt.%) and volumetric densities, and the use of aqueous solution is generally compatible with current gasoline-based fueling facilities. Therefore, commercial conversion could be relatively straightforward. Furthermore, hydrogen produced from the catalyst chamber is inherently humidified and, with appropriate system design [94], can be fed directly to PEM fuel cells without extra humidification processing.

A major challenge of sodium borohydride involves the cost and energetics of recycling. The current price of sodium borohydride

is approximately 50 times higher than the energy-equivalent price of gasoline. The high cost is inherent to the current industrial process, called the Schlesinger-Brown process [95], in which one mole of NaBH$_4$ requires four moles of metallic sodium produced by sodium chloride (NaCl) electrolysis, which a very energy-intensive process. Several ongoing projects are addressing these recycling issues [92,96–98]. Even if the overall cost cannot match that of gasoline, sodium borohydride systems may be useful in less cost-sensitive applications, such as powering portable electronics [92].

Another impediment to the adoption of sodium borohydride or other chemical hydrides, which typically have similar heats of reaction, involves the cooling requirements. Though fuel-cell vehicles need to dissipate approximately the same amount of the waste heat as internal-combustion (IC) engines [99], the low operational temperature of the PEM fuel cell, approximately 80°C, makes vehicle cooling design particularly challenging. The coolant temperature for an IC engine can reach as high as 120°C, while that for a PEM fuel cell can be only 60–65°C. Given a maximum design ambient temperature of 38°C [100], the temperature difference from the radiator to ambient in IC engine vehicles is two to four times that of fuel-cell vehicles. Furthermore, because of the extremely low electrical conductivity required of the fuel-cell coolant, the fuel cell is normally cooled directly by deionized water, which then transfers heat to an antifreeze loop through a heat exchanger, reducing the operating temperature of the radiator even further [101]. To satisfy all heat rejection requirements, larger radiator surface areas and much higher coolant and air flow rates are needed. These requirements will contribute to significant increases in parasitic power consumption and vehicle volume for the cooling systems in fuel-cell vehicles.

Because most on-board waste heat is eventually dissipated to the ambient through the radiator, innovative radiator designs must be adopted to address the cooling challenges faced by chemical-hydride storage systems. Because of the inefficiency of air as a heat transfer medium, the air-side heat transfer coefficient is considerably smaller than that of the coolant side [99]. In most existing vehicle designs, the flow field around the radiator is generally not optimized for heat transfer. With such a high on-board cooling load, a great need exists to integrate cooling system design with aerodynamic vehicle design. A prior study on the interaction of cooling air flow and aerodynamic performance suggests that aerodynamic improvements need not necessarily interfere with cooling requirements [102], and recent back-end radiator designs have demonstrated simultaneous improvements in cooling performance and aerodynamic performance [101]. In addition to air-side improvements, adoption of multiple-pass crossflow heat exchangers may also improve radiator performance [103]. Other heat transfer enhancement techniques (e.g., variable-roughness exchanger tube inserts, interrupted and wavy fins) could also provide significant performance improvements [104].

Summary and Conclusions

The foregoing review indicates that each potential hydrogen storage method for vehicle applications involves substantial heat transfer challenges. In some cases, heat transfer issues could become the determining factor in the feasibility of a given storage method, and heat transfer research is needed for each of the four identified hydrogen storage methods. Enhanced cooling during compression processes is not only important for compressed hydrogen systems, but also essential for hydrogen storage approaches involving liquid hydrogen and metal hydrides. Many opportunities for improved thermal insulation exist for liquid hydrogen systems because of the need to maintain extremely low temperatures over long time periods. Enhanced heat transfer for metal-hydride systems is essential in allowing rapid hydrogen uptake (i.e., tank filling) and sufficiently fast kinetics for hydrogen

release. Innovative vehicle radiator designs will be needed for chemical-hydride systems, which require very high rates of heat dissipation during vehicle operation.

In the near term, compressed hydrogen systems will likely remain dominant for fuel-cell demonstration vehicles. Liquid hydrogen systems may soon gain in popularity because most existing hydrogen fueling stations are already supplied by liquid hydrogen tankers. Metal- and chemical-hydride systems are currently less developed, but each offers both significant advantages and disadvantages relative to the alternatives. Much of the uncertainty surrounding their feasibility involves technical issues that require the attention of the heat transfer research community, particularly in the areas of thermophysical properties and on-board vehicle thermal management systems.

Acknowledgment

Nomenclature

ΔH = enthalpy change, kJ/kg
L = distance between two surfaces, m
LH_2 = liquid hydrogen
LHV = lower heating value, kJ/kg
n = polytropic constant, 1.41 for isentropic process for hydrogen
P = pressure, bar
P_1 = initial pressure, bar
P_2 = final pressure, bar
P_{eq} = equilibrium pressure, Pa
R = gas constant for hydrogen, 4.157 kJ/kg-K
ΔS = entropy change, kJ/kg-K
T = temperature, K
T_1 = initial temperature, K
w = specific compression work, kJ/kg
ε = emissivity
λ = mean free path, m

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