

Materials-based hydrogen storage: Attributes for near-term, early market PEM fuel cells

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ABSTRACT

Although hydrogen is widely recognized as a promising energy carrier for the transportation sector, widespread adoption of hydrogen and fuel cell technologies depends critically on the ability to store hydrogen at adequate densities, as well as release hydrogen at sufficient rates (among other requirements) to meet PEM fuel cell power plant requirements. At present, no known material or storage means exists that satisfies all requirements to enable high-volume automotive application, however materials do exist that would satisfy requirements for near-term non-vehicular PEM fuel cell applications. The US DOE recognizes that non-vehicular early market applications are the most likely paths for the successful demonstration and application of material-based hydrogen storage technology. In this review, we provide a practical overview of the most probable near-term PEM fuel cell markets as identified through market reviews with an emphasis on the attributes of the relevant materials-based hydrogen storage for those near-term markets.

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1. Introduction

The US Department of Energy (DOE) Fuel Cell Technologies Program maintains a comprehensive effort to overcome barriers for the widespread commercialization of hydrogen and fuel cells technologies including hydrogen production, delivery and storage [1]. The fuel cell industry is an emerging renewable, clean energy industry with the potential for significant growth in the stationary, portable and transportation sectors. Several reports have identified numerous near-term, non-automotive markets for the successful application of hydrogen and fuel cells including portable power, back-up power, auxiliary power units and specialty vehicles (e.g., forklifts, mining vehicles and airport ground support) [2–5]. The DOE recognizes that a likely route for commercialization of direct hydrogen fuel cells in vehicles might include the introduction of fuel cells in near-term markets that may have fewer technical challenges than automobiles and therefore are expected to be more readily deployed.

Hydrogen can be a safe, convenient energy carrier which holds tremendous promise as an energy efficient and clean energy alternative. As a fuel, hydrogen is near ideal as it can be generated from a diverse number of feedstocks and be converted to a desired form

of energy without releasing harmful emissions at the point source, thus reducing greenhouse gas emissions, criteria pollutants and dependence on fossil fuels. The chemical energy per mass (on a gravimetric basis) of H₂ (120 MJ kg⁻¹) is approximately three times greater than that of other chemical fuels (e.g., on average the equivalent value for liquid hydrocarbons is 43 MJ kg⁻¹). However, the energy density of hydrogen (on a volumetric basis) is very low compared to gasoline or other hydrocarbons. For example, one liter of gasoline (31.7 MJ/L, 8.8 kW h/L) contains approximately six times as much energy as a liter of hydrogen compressed to 70 MPa (4.7 MJ/L, 1.3 kW h/L). In light of this fact, research exploring material-based hydrogen storage has grown significantly over the past decade, since materials have the potential to have a greater volumetric energy content compared to compressed hydrogen gas [6–12].

Research into materials-based hydrogen storage has demonstrated the ability to increase the density of hydrogen by a factor of more than twice that of liquid hydrogen, resulting in hydrogen densities of up to 148 g H₂/L (21.1 MJ/L) [13]. Table 1 provides a summary of the properties of some of the most promising hydrogen storage materials. These materials are typically categorized by the way hydrogen is bound which generally ranges from weak van der Waals interactions (i.e., physisorptive binding of molecular H₂) to the stronger chemisorptive binding of formal chemical bonds between atomic H and other atoms. According to this

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Table 1
Summary of capacity and thermodynamic data for hydrogen storage materials of recent interest. All data for T_{des} (units of °C) and ΔH_{des} (units of kJ/mol H₂) are taken from experimental measurements unless otherwise noted.

Rxn. no.	Hydrogen release reaction	wt% H ₂	g H ₂ /L	Reversible	T_{des}	ΔH_{des}	Ref.
1	$V_{0.85}Ti_{0.1}Fe_{0.05}H_2 \leftrightarrow V_{0.85}Ti_{0.1}Fe_{0.05} + H_2$	3.7	~170 ^c	Y	100	43.2	[39]
2	$MgH_2 \leftrightarrow Mg + H_2$	7.7	109	Y	300	65.8–75.2	[52]
3a	$NaAlH_4 \leftrightarrow 1/3Na_3AlH_6 + 2/3Al + H_2^a$	3.7	52	Y	120	37	[24,89]
3b	$Na_3AlH_6 \leftrightarrow 3NaH + Al + 1.5H_2^a$	1.9	43	Y	180	47	
4	$2AlH_3 \leftrightarrow 2Al + 3H_2$	10	147	N	125–175	7.6	[61]
5	$2LiBH_4 + MgH_2 \leftrightarrow MgB_2 + 2LiH + 4H_2$	11.6	96	Y ^e	300–350	41	[69]
6	$Mg(BH_4)_2 \rightarrow MgH_2 + 2B + 3H_2$	11	113	Partial	230	47	
7	$3Ca(BH_4)_2 \rightarrow CaB_6 + 2CaH_2 + 10H_2$	9.6	108	N	300–350	41.4 ^f	[90]
8	$Li_3AlH_6 + 3LiNH_2 \rightarrow 3Li_2NH + Al + 4.5H_2$	7.3		N	200–300	38.4	[91]
9	$LiNH_2 + MgH_2 \rightarrow LiMgN + 2H_2 \leftrightarrow LiH + 0.5MgH_2 + 0.5Mg(NH_2)_2$	8.1		Y	220–270	32 (step 1) 51 (step 2)	[53,92]
10a	$xNH_3BH_3 \leftrightarrow [NH_2BH_2]_x + (x-1)H_2$	6.5	96 ^d	N	100	–21.7	[93–95]
10b	$[NH_2BH_2]_x \leftrightarrow [NHBH]_x + H_2$	6.9		N	150	–(23.9–15.4)	
11	$MOF-5 : H_2 \leftrightarrow MOF-5 + H_2^b$	7.1 (excess) 10 (absolute)	66 (absolute)	Y	–196	3.8	[30]
12	$MOF-177 : H_2 \leftrightarrow MOF-177 + H_2^b$	7.5 (excess) 11 (absolute)	49 (absolute)	Y	–196	4.4	[32]

^a Includes Ti dopant.

^b $P = 7$ MPa.

^c Based on single-crystal density of VH₂.

^d Cumulative, based on NH₃BH₃.

^e 15.5 MPa, 600 °C.

^f Calculated.

convention, hydrogen storage media can be subdivided into four distinct categories (in order of increasing binding energy ranging from <10 kJ/mol H₂ to >60 kJ/mol H₂): (1) adsorbents or sorbents, (2) conventional or interstitial metal hydrides, (3) complex metal hydrides and (4) chemical hydrogen storage materials. Since the properties of these media have been the subject of several review articles [6–8,10,14,15], we have limited the scope of our discussion to the properties of storage media which appear to be relevant for near-term, non-automotive fuel cell markets.

Furthermore, we stress the importance of reliable material property measurement techniques to facilitate the development of hydrogen storage materials. It is imperative to understand that the hydrogen storage properties of a material can be significantly influenced by not only individual sample characteristics including chemical composition and distribution, micro- and macro-scopic material structure, etc., but also pressure, temperature and sample size. A “best practices” manual [16] was commissioned by the DOE Fuel Cell Technologies Program which gives a detailed overview of the recommended best practices in making measurements of the hydrogen storage properties of materials and we recommend consulting it prior to initiating hydrogen storage materials development activities.

2. Overview of near-term early market applications of PEM fuel cells

As mentioned in Section 1, three main near-term growth markets for PEM fuel cell technology include: portable power, stationary power and transportation. Portable power applications, as the name implies, relates to the use of fuel cells not permanently installed at a site or fuel cells in a portable device with typical power outputs ranging from 1 W to 5 kW. Those applications less than 500 W are usually considered “man-portable” devices and will not be discussed here. This paper will review, however, the typical requirements for applications up to 5 kW for other portable power applications. For stationary power, the discussion is limited to only those fuel cells that are operated at a fixed location for back-up power applications where the typical power output ranges from 500 W to 10 kW. Transportation power usually encompasses any

application that supplies motive power to cars, buses or other fuel cell vehicles, although for this paper the scope will be limited to specialty vehicle (SV) applications (e.g., forklifts, pallet jacks and baggage and pushback tractors) that require output power ranging from 3 kW to 15 kW. In the following section we review some common applications of each growth market with a focus on the salient operational features of the fuel cell as it relates to hydrogen supply.

2.1. Portable and stationary back-up power

Recent events ranging from natural disasters such as Hurricane Katrina to power blackouts in the Northeastern United States have exposed the vulnerability of our electric grid. These power outages are often times no more than a temporary inconvenience for most businesses or individuals. However, for facilities in the public and private sector that provide critical services, such as telecommunications towers, hospitals, emergency services, banks and data centers, and even basic infrastructure such as water and sewage pumps, brief outages can represent a significant risk to public safety and impact our economic stability.

These types of critical facilities have relied on back-up power from two main sources: lead acid batteries and generators operating on diesel, propane or gasoline. Most systems actually include a combination of generators and batteries to provide redundancy to avoid service disruptions. These systems are usually designed to deliver nominally 48–480 kW h of energy throughout a 48-h period or for “critical operations power systems” 72–720 kW h (3 days) is required between refueling or recharging. Although these systems are well established, each technology has its drawbacks, particularly when planning for power outages measured in hours and days, not minutes.

Lead acid batteries are continually charged from the power grid and are usually designed to provide power for short term (i.e., 15 min) durations and provide the facility time to properly shut-down equipment. Batteries can also serve to maintain constant power during temporary power transients to protect sensitive equipment. However, batteries are sensitive to temperature extremes that may make them an unsuitable choice for outdoor

applications in many locations, in addition to their limited lifetime due to the declining performance of the electrode materials during power cycling.

Generators are the primary source of back-up power, especially in instances when connection to the power grid is not an option. Generators operate by turning mechanical energy into electrical energy through the use of a motor wherein the source of the mechanical energy is an internal combustion engine. However, depending on the fuel, they can be inefficient (e.g., thermal efficiency of a gasoline engine 15–30% [17]), produce emissions from fuel combustion and require periodic maintenance because of the moving parts of the engine. Oftentimes, the use of generators for back-up power is limited due to regulations over concerns about air and noise pollution and fuel storage. In addition, during prolonged power outages such as after an extreme natural disaster, generators are reliant upon the delivery of fuel to remote locations or where travel is limited.

Compared to batteries and generators, fuel cells can offer longer continuous run times, fewer moving parts to maintain (i.e., lower maintenance costs), and greater durability in harsh environments over a wider range of temperatures, all at a significant cost savings. In a study by Battelle Memorial Institute comparing the lifecycle costs of PEM fuel cells to a 2 kW battery-only backup of 8-h and a 5 kW battery-generator backup of 52-h, 72-h and 176-h, the PEM fuel cell demonstrated substantially lower costs as shown in Table 2 [5], although the hydrogen storage tank rental cost proved to be a significant portion of the overall system cost.

Fig. 1 depicts a standard layout of a fuel cell power plant that provides back-up power for a telecommunications site. The three main components of the power plant are: (1) hydrogen storage, (2) PEM fuel cell stack and (3) battery/capacitor. These installations have traditionally been fueled by a six-pack of compressed hydrogen steel cylinders, each holding approximately 260 standard cubic feet (scf) (0.617-kg each or 3.7-kg total) of H₂ pressurized to 16.5 MPa (2400 psi gauge), approximately 1% by weight. In addition, a battery is used to provide temporary “bridge” power until the fuel cell reaches peak power production and takes over the load. Since a typical 1 kW PEM fuel cell stack consumes approximately 30 scf of H₂ at a flow rate of 0.5 scfm (15 standard liters per minute) to produce 1 kW h of electricity, we can estimate that each six-pack of H₂ has the capacity to provide approximately 1 kW continuously for 52-h or 52 kW h. With steel cylinders, this will amount to approximately a 400-kg storage system which is prohibitive for roof-top or tower mounted applications. Also, to exceed the performance of the equivalent diesel-fueled combustion system, the hydrogen system should have in excess of 50-h of operating time including peak transients between refueling. In this case, a higher energy density storage method such as that based on materials could be advantageous.

2.2. Specialty vehicle applications

Specialty vehicles (SVs) such as forklifts, mining locomotives or pushback tractors, are used in a variety of commercial and industrial applications that involves movement of materials and equipment from one work station to another. The operational time of these types of vehicles can vary significantly over a shift, ranging from a few hours to 24-h per day. The power load during operation is generally somewhat transient where the load varies over each operational shift. The application and power load requirements usually dictate the type of powertrain used in these vehicles. For example, a battery powered electric forklift is typically used indoors in a warehouse facility where there are concerns of mobility, noise and air emissions that make internal combustion engine (ICE) powered forklifts impractical. In fact, emissions and noise regulations implemented over the last decade have increased the capital and operating costs and lowered productivity for these types of vehicles so that fuel cell powered SVs can have a significant advantage compared to battery and ICE powered SVs [18,19].

Battery powered SVs typically use a bay of lead acid batteries to provide enough power for one 8-h shift, or 5–6-h of constant use. However, one of the main disadvantages of these types of vehicles is the time required for battery change-out and charging. On average using an automatic battery change-out system, it takes 5–15 min for battery change-out and up to 45 min or more if it is done manually. The battery then must go through a sequence of events which includes 8-h of charging then 8-h of cool down since there is significant heating during battery charging. Therefore, an around-the-clock operation requires at least three batteries per SV. This scenario drastically limits productivity and significantly increases costs for practical operation. Also, battery powered SVs suffer from declining power during discharge, which is estimated to cause a 7.5% decline in productivity compared to ICE or fuel cell powered SVs [2].

In order to replace a battery powered SV, a fuel cell powered SV must perform at least as well and not require changes in functionality, such as achieving a minimum weight for counterbalancing, maintaining same performance (i.e., speed, braking and lifting), productivity, and at least match the life and refueling frequency. The fuel cell power plant for a SV is very similar to that described in Section 2.1, although there are differences in the operational requirements that are application specific. The power plant will encompass hydrogen storage, the PEM fuel cell, balance of plant (BOP) components, along with a battery/ultracapacitor to provide additional power for start-up, heavy lifting and pushing transients. For forklift applications, the fuel cell power system should weigh a minimum of 200 kg to act as a counterbalance during lifting. Also, for initial designs, the total FC power plant should be no larger than the battery or ICE power plant that

Table 2
Lifecycle cost analysis results for PEM fuel cell vs. battery and battery-generator back-up power sources [5].

	Outdoor installations			Indoor installations		
	Battery/Generator	PEM fuel cell w/no tax incentive	PEM fuel cell w/\$1 K/kW incentive	Battery only	PEM fuel cell w/no tax incentive	PEM fuel cell w/\$1 K/kW incentive
8-h run time				\$19,037	\$14,023	\$12,136
52-h run time	\$61,082	\$61,326	\$56,609			
72-h run time	\$47,318	\$33,901	\$32,014			
176-h run time	\$75,575	\$100,209	\$95,491			

Notes:

- (1) Total costs include capital costs plus operational and maintenance costs.
- (2) Fuel cell tax credit of \$1000/kW assumed.
- (3) Calculations assume a 5-year replacement schedule.

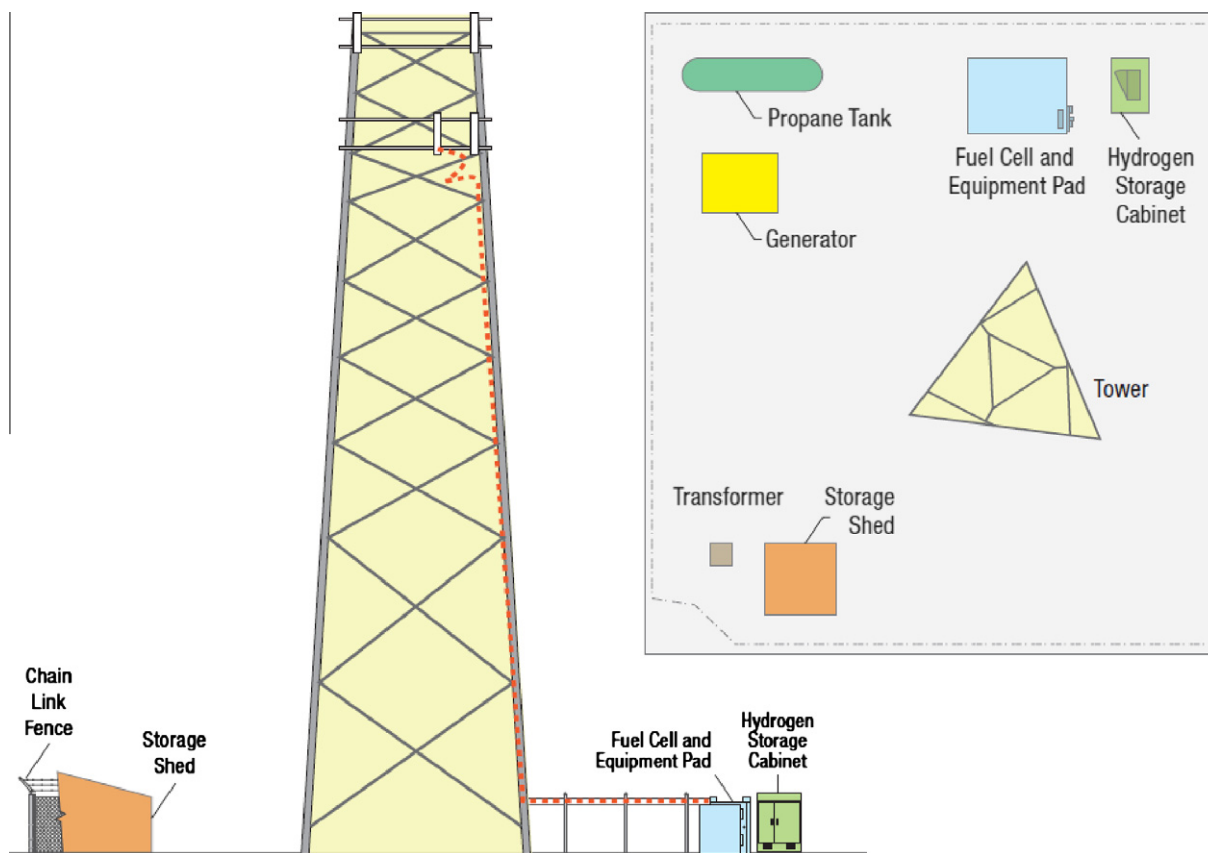


Fig. 1. Standard layout of a PEM fuel cell power plant for telecommunications back-up power. Taken with permission from [86].

it is replacing, although this could change as the fuel cell powered SV market grows¹.

3. Properties of materials-based H₂ storage media for near-term applications

For each of the types of fuel cell applications outlined in Section 2, there exists a general set of bounding constraints on the H₂ storage materials to provide an adequate amount of H₂ fuel to enable efficient operation of the fuel cell system. These constraints are closely related to the properties of the material, such as capacity, refill and discharge kinetics and thermodynamics. Generally speaking, in contrast to H₂ storage for automotive applications, the H₂ storage system for near-term applications can occupy a larger foot print, employ multi-step chemical charging/recharging cycles that operate at higher temperatures and pressures and compensate for slower kinetics with extra capacity. In the following sections, we provide a general description of the materials properties along with several examples of recent advancements in H₂ storage materials that will clearly impact system design for near-term fuel cell markets.

3.1. Capacity

For H₂ storage materials, capacity is defined as the amount of H₂ stored per unit weight (gravimetric capacity) or volume (volumetric capacity) which is often expressed in terms of the chemical energy of stored H₂. Capacity is commonly represented as a

materials- or system-based value where it is characterized as the ratio of H₂ mass stored to the mass or volume of total material or material plus the BOP (system) components. The main difference in the two values lies in the fact that the system-based capacity is an upper limit to the amount of useable H₂ and the materials-based value is a measure of the absolute capacity, not accounting for any ancillary fuel system components such as the material containment vessel, piping and pressure regulators.

Up to now, capacity has been characterized in terms of automotive applications where there are stringent requirements to reduce the overall mass and volume of the storage materials in order to increase the overall fuel efficiency of the automobile. When considering near-term, early market fuel cell applications, those requirements may become more flexible, thus there exists several materials-based H₂ storage media that could satisfy the capacity requirements for the applications discussed in Section 2, even when factoring in a system-based capacity. For example, Ti-catalyzed NaAlH₄, one of the most thoroughly studied complex metal hydride materials [15,20–24], has a measured materials-based gravimetric capacity of approximately 3.7 wt.% H₂ for the first desorption step and its system-based gravimetric capacity is projected to be approximately 2.0 wt.% H₂ (i.e., only considering the first step) [25]. However, even at 2.0 wt.% H₂, the gravimetric capacity of a Ti-catalyzed NaAlH₄ system is approximately double that of traditional steel hydrogen cylinders (i.e., 1 wt.% H₂) that are currently used to supply H₂ for portable applications. Furthermore, for back-up power applications, capacity is thought to be the most crucial material property as extra capacity can overcome slow kinetics, especially for low-cost materials. Consequently, research into materials-based H₂ storage media continues in order to advance their exceptional volumetric and gravimetric capacities.

¹ Information gathered through a Request for Information for Fuel Storage Subsystems for Early Market Fuel Cell Applications, January 2010.

Research efforts in adsorbent or sorbent systems have demonstrated high surface area materials capable of achieving reasonable storage capacities [26,27], although only at cryogenic temperatures due to the low binding energies of the H₂ molecules on the substrate at room temperature. For carbon-based sorbent materials, there is an empirical relation, the Chahine rule, that relates the gravimetric capacity to the specific surface area of the material so that at –196 °C (77 K) one achieves ~1 wt.% H₂ excess gravimetric capacity for every 500 m²/g of surface area, although deviations exist due to differences in the framework density of the sorbent structures [28–31]. For example, a metal–organic framework material (MOF) such as MOF-5 with a reported Langmuir surface area of 4400 m²/g has exhibited an excess H₂ uptake of 0.071 kg/kg (7.1 wt.%) and 0.056 kg/L [30] at 77 K and 4 MPa, which is much higher than that of sorbents with larger surface areas such as MIL-101 (0.061 kg/kg, 0.026 kg/L, 5900 m²/g [31] and UMCM-2 (0.069 kg/kg, 0.027 kg/L, 6060 m²/g) [28]. Additionally, the low framework density (i.e., single-crystal densities) of most porous MOFs usually leads to lower volumetric capacity [32]. Current research involving MOFs is focused on increasing the H₂ binding energy (with coverage) to ca. 10–20 kJ/mol by incorporating a high concentration of unsaturated metal centers into the framework [27,33–36]. Another avenue being investigated towards storing hydrogen at near room temperature and at moderate pressure is utilizing the mechanism of weak chemisorption or spillover [37,38]. These results are encouraging and show promise for development of practical storage systems in the future, however there are fundamental questions that must be addressed including validation of enhanced sorption at room temperature. Thus, there is still considerable research needed for these materials to compete with current commercially available H₂ storage technologies for use in near-term markets.

Hydrogen storage in metal hydrides, including both conventional low-temperature metal hydrides and complex hydrides, has been the focus of intensive research. These materials are known to show ambient temperature–pressure operation while delivering very reasonable gravimetric and volumetric materials-based capacities. Conventional metal hydrides typically have single-crystal densities 2–3 times that of complex hydrides which can lead to exceptional volumetric capacities up to ~170 g H₂/L [39]. However, current alloy compositions which operate under practical lower temperature conditions largely consist of high-Z metals (e.g., La, Ni, Fe, Mn, Cr, V, etc.) which lead to poor gravimetric capacities and in some cases higher costs. These hydrides could make a suitable choice in terms of capacity for applications such as forklifts, which routinely require extra weight for counterbalancing. Additionally, these materials may only require very simple control systems, such as a passive heat transfer systems, that could reduce the overall system mass and cost. For example, most forklift manufacturers require a *minimum* weight of 200 kg for their sub-system components with a H₂ fuel capacity of 2.5 kg in a volume less than 230 L to support a 10 kW forklift vehicle. LaNi₅H_{6.7}, which carries approximately 1.4 wt.% H₂ on a materials basis, would supply nominally 3 kg of H₂ from 200 kg of hydride material in 50–60 L after accounting for material deprecipitation and expansion. More over, after accounting for the BOP materials, these requirements could be met with approximately 250 kg of hydride material plus system components.

On the other hand, many complex hydrides are made up of low-Z elements (e.g., Al, Mg, Na, N, B and Li) and consequently exhibit exceptional gravimetric and volumetric capacities [13,24,40–43]. Current R&D efforts in metal hydrides have focused mainly on these compounds to support the need for lighter materials in automotive applications. Thus, these materials would naturally fit for portable and stationary back-up power applications where the H₂ supply should last for 48–72-h and it must be lightweight in order

to be delivered to remote or rooftop locations. For example, the six-pack of compressed H₂ steel cylinders from Fig. 1 supplied approximately 1 kW continuously for 52 h with 3.7-kg s of H₂ and 400-kg s of system storage weight. AlH₃, which contains 10 wt.% H₂ and 148 g H₂/L (material only) [13], could exceed the capacity of a six-pack of compressed steel cylinders and provide 72-h of 1 kW continuous power operation with less than 1/4 the system weight, assuming 4.3 wt.% useable system capacity [44]. Furthermore, several other complex hydrides contain over 10 wt.% H₂ (e.g., LiBH₄, Mg(BH₄) and NaBH₄) and have the potential to far surpass the gravimetric and volumetric capacities of compressed gas technologies. Research in this area is looking at improving capacities along with increasing hydrogen refill and discharge rates at lower operating temperatures and pressures.

Similar to complex hydrides, chemical hydrogen storage materials are made-up of lighter elements and have demonstrated high gravimetric and volumetric capacities at near ambient temperatures. However, chemical hydrogen storage materials are thought of as single-use fuels, as their reaction enthalpies are too endothermic or exothermic to allow for “reversible” operation within the application site [45] and thus must be regenerated with hydrogen off-board or off-line. Nevertheless, the positive attributes of this class of materials make them compelling candidates for near-term PEM fuel cell applications. One material, in particular, that has attracted much attention due to its very high gravimetric and volumetric capacities of 19.6 wt.% H₂ and 150 g H₂/L (material only), respectively, is ammonia-borane (NH₃BH₃) and its derivatives [46]. Catalyzed release of hydrogen from ammonia borane (AB) in solution has been demonstrated to evolve 6 wt.% H₂ within minutes at temperatures as low as room temperature. Ionic liquid (IL) solvents also promote the hydrogen release reactions, and AB/IL mixtures exhibit high release rates and capacities approaching 10 wt.% at temperatures just above 100 °C, while the addition of catalysts to these AB/IL solutions increases the release rates further. Reasonable hydrogen capacities and release rates have been demonstrated at temperatures ranging from 70 °C to 85 °C for 6–10 wt.% for AB liquid and AB/IL catalytic release materials, and above 100 °C for solid AB to 13–16 wt.% via the thermolytic pathway [46]. Other chemical hydrogen storage materials have demonstrated similar results through the hydrolysis of borohydride or aluminum hydride anions (e.g., NaBH₄, LiAlH₄, undoped-NaAlH₄, etc.) [15,47]. As a result, these materials hold considerable promise to provide storage solutions for near-term PEM fuel cell applications, especially when considering portable and stationary back-up power applications where high capacity could outweigh reversibility as a key operational parameter. However, careful consideration should be given to the operational parameters of the application and materials selection as some exothermic release materials could experience substantial reduction in the useable system capacity during long dormancy periods of some back-up power applications.

3.2. Thermodynamics

Hydrogen can be stored in materials dominated by several different bonding mechanisms that require a fundamental understanding of the thermodynamic properties of the H₂ – material interaction. The thermodynamic properties determine the equilibrium relationship between the operating temperature and pressure, and therefore influence several practical operational parameters of the H₂ storage system such as charge/discharge heat transfer requirements and available pressure of desorbed/discharged H₂. For example, one of the major issues with many complex hydrides is thermal management (e.g., heat removal) during refueling. For instance, a hydrogen storage reaction exhibiting a ΔH of 50 kJ/mol would require ~550 kW of heat to be rejected

while recharging 5 kg of H_2 in less than 4-min, therefore requiring significant cooling systems [11,48]. The thermodynamic requirements for rechargeable hydrogen storage systems for near-term PEM fuel cell applications are expected to be similar to those compiled for automotive applications, while differences in mass and volume requirements may allow for a wider range of acceptable storage materials. With this in mind, we will overview some of the most promising materials with respect to thermodynamics along with recent advancements in the thermodynamic material properties which could allow these materials to be effective for near-term markets.

From a thermodynamics perspective, an optimum material would be reversible and desorb hydrogen near room temperature at a sufficient rate to power the fuel cell system while maintaining an equilibrium H_2 pressure of at least 0.1 MPa. Also, the material would have rehydrogenation/refill kinetics to allow system recharge in a reasonable amount of time with manageable heat dissipation (i.e., thermodynamically neutral). Some metal hydrides have demonstrated the potential to operate within this optimum operating envelope. The van't Hoff plot in Fig. 2 shows the correlation between temperature and pressure for several metal hydrides including the optimum P–T operational window for a PEM fuel cell. Sodium alanate ($NaAlH_4$) can store and release hydrogen reversibly via a multistep reaction, shown in Table 1, in this optimum range when catalyzed with titanium dopants as discovered by Bogdanovic and Schwickardi [24]. At 0.1 MPa pressure, the first reaction becomes thermodynamically favorable at temperatures above 33 °C and can release 3.7 wt.% H_2 , while the second reaction takes place above 110 °C and releases an additional 1.8 wt.% H_2 . In practice, the system gravimetric capacities demonstrated are typically only 2–3 wt.% H_2 [25], although, as mentioned above, this is still approximately double that of steel cylinders currently used for portable hydrogen storage.

More recently, work involving “destabilized” mixtures of hydrides has received significant attention as a means to alter the material's thermodynamic properties [49,50]. Vajo et al. reported the formation of a “destabilized” $LiBH_4/Mg_2NiH_4$ which demonstrated the lowest thermodynamic properties of any reversible complex hydride at $\Delta H = 15$ kJ/mol- H_2 and $\Delta S = 62$ J/K-mol- H_2 with over 8 wt.% H_2 material capacity [49]. $MgNi_{2.5}B_2$ mixed with

LiH and MgH_2 is hydrogenated reversibly to form $LiBH_4$ and Mg_2NiH_4 at temperatures below 300 °C. The formation of the dehydrogenated alloy $MgNi_{2.5}B_2$ can reduce the temperature for hydrogen release (T_{1bar}) by approximately 260 °C as compared to pure $LiBH_4$. While this is a major improvement, the hydrogen release temperatures for these compounds are still too high for practical consideration. Many other potential destabilized reactions have been proposed by theory [51–54] and further thermodynamic improvements will be pursued through dopant/additive screening.

Another potential method for altering thermodynamics is through particle size reduction. While reducing particle size is normally associated with an increase in kinetics via diffusion limited processes, recent theoretical studies have predicted decreases in desorption temperatures for nanometer-sized (<10 nm) particles [55,56]. Experimental results using 7 nm MgH_2 nanoparticles did show a slight reduction in decomposition enthalpy, however, the temperature drop was not as large as expected due to a corresponding decrease in reaction entropy [57]. However, if this approach is able to be effectively realized experimentally, it has the potential to impact both thermodynamics and kinetics of hydrogen storage materials.

A number of chemical hydrogen storage materials, both with exothermic and endothermic hydrogen release, are under investigation; however, most of these reactions are irreversible with direct rehydrogenation. In order to accomplish reversibility, near neutral thermodynamics for the hydrogen release process at the operating temperature are critical. Recent work combining the attributes of the endothermic nature of the carbon–carbon bond with the exothermic nature of the B–N bond, has demonstrated near neutral theoretical free energies of hydrogen release (ΔG) [49,58] for chemical hydrogen storage materials. Liu et al. synthesized a suite of novel liquid carbon–boron–nitrogen (CBN) hydrogen storage materials that can be potentially recharged with molecular H_2 . Theoretical calculations predict that these compounds should have ΔG values ranging from –25 kJ/mol to 12 kJ/mol and have potential to be reversible. With regard to those chemical hydrogen storage materials that are not readily reversible via direct hydrogenation, the material can be regenerated with other chemical reactions and processes. However, it is important for these regeneration processes to be cost and energy efficient.

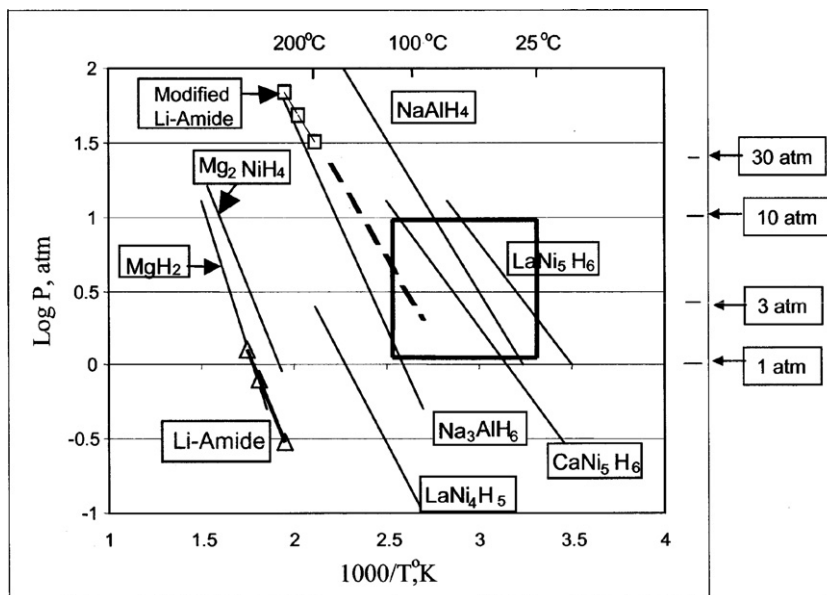


Fig. 2. van't Hoff plot of various metal hydrides with the P–T operating window for a PEM fuel cell indicated by the highlighted box. This operating window indicates conditions of operation that may use the waste heat available from a PEM fuel cell power plant for storage system thermal management. Taken with permission from [87].

As the heat of adsorption is reduced to less than 10–15 kJ/mol, cryogenic temperature and nominal pressure will be required to store sufficient quantities of hydrogen although the heat rejection rates during refill will not be as strenuous. Balancing of thermodynamic properties and temperature/pressure operating window will be required on a system basis.

Recently, several approaches have been demonstrated to enhance hydrogen binding (i.e., raise the heat of adsorption) in sorbent materials including synthesis of coordinately unsaturated metal sites, design of pore aspect ratio and size/diameter, and use of charged frameworks to increase van der Waals-type forces [26,30,33,35,37,59,60]. Of these approaches, one of the most effective means of increasing the hydrogen adsorption enthalpy in sorption materials is through introduction of open metal coordination sites on the surfaces. For example, Long et al. synthesized coordinately-unsaturated Mn^{2+} sites in a MOF $Mn_3[(Mn_4Cl)_3(BTT)_8(CH_3OH)_{10}]_2$ (BTT^{3-} = 1,3,5-benzotriazolate) which exhibited a maximum isosteric heat of adsorption of 10.1 kJ/mol [59]. Improvements in synthetic chemistry along with incorporation of light main group metal ions (i.e., Li^+ , Mg^{2+} , or Al^{3+}) should allow for further advancements in sorbents.

3.3. Kinetics

Understanding the kinetics of hydrogen storage materials involves measuring and understanding the rate and mechanism(s) involved in hydrogen uptake and release. The mechanisms are comprised of various dynamic processes, such as surface interactions, mass transport phenomena, and nucleation, any of which could act as the rate limiting step(s) or kinetic barrier(s). From a practical standpoint, the fuel system kinetics determine the rate at which a material can supply hydrogen to a fuel cell to maintain a desired power load or conversely, the rate at which a material can be refueled. Each class of hydrogen storage material has its own set of unique kinetic barriers which can be a significant factor when selecting these materials for near-term applications. However, the requirements for near-term applications in terms of kinetics can be considerably different than those posed by automotive applications. For instance, refueling of an automobile must typically be less than 5-min for a 5-kg hydrogen charge; however, for back-up power, refueling may likely be accomplished off-board where the H_2 fuel can simply be exchanged and the time to refuel

the supply is not as critical an issue. Hydrogen release rates and conditions, on the other hand, may be very similar to that of an automobile where the storage material should supply a hydrogen pressure of at least 0.5 MPa with some transients during higher current draw for back-up power or loading/unloading for specialty vehicle applications. Although kinetic barriers exist among all storage materials, there are some materials that could meet the kinetic requirements for operation of a PEM fuel cell. Furthermore, recent discoveries in nanoconfinement of hydride materials could prove effective in reducing kinetic barriers for several other classes of materials.

The kinetically stable metal hydrides, such as AlH_3 , have an equilibrium hydrogen pressure much greater than 0.1 MPa at room temperature, but do not decompose due to kinetic limitations. Additionally, these materials exhibit rapid low temperature hydrogen evolution rates due to the low reaction enthalpies observed for

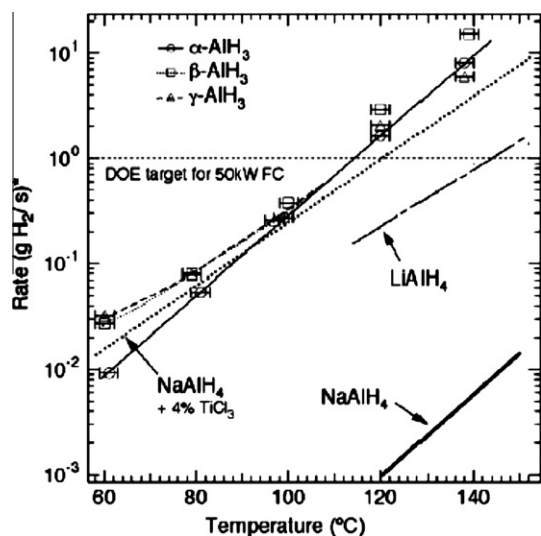


Fig. 3. H_2 evolution rates for various undoped kinetically stabilized metal hydrides and $NaAlH_4$. Taken with permission from [61].

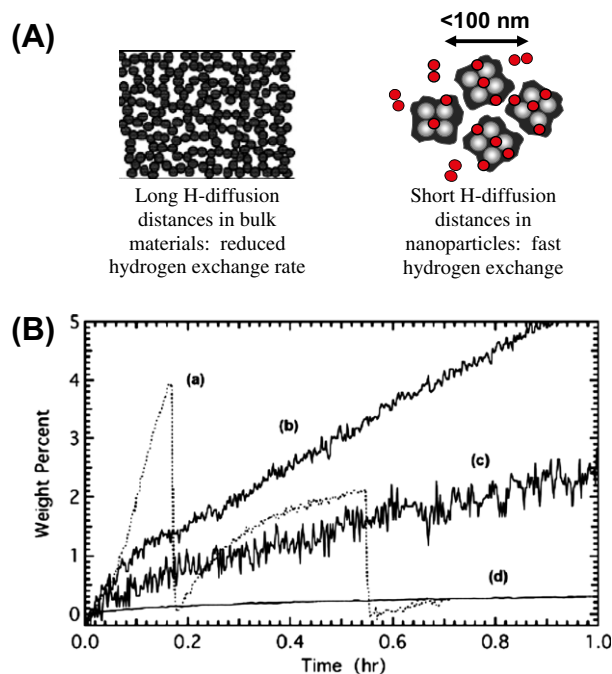


Fig. 4. (A) Schematic of the nanoconfinement method and (B) isothermal dehydrogenation curves for MgH_2 at 250 °C. Curve (a) MgH_2 nanoparticle filled Ni decorated carbon aerogel; curve (b) MgH_2 nanoparticle filled Cu decorated carbon aerogel; curve (c) MgH_2 nanoparticle filled carbon aerogel (no catalyst); (d) 7 wt.% MgH_2 milled with 1–2 μm graphite. Taken with permission from [88].

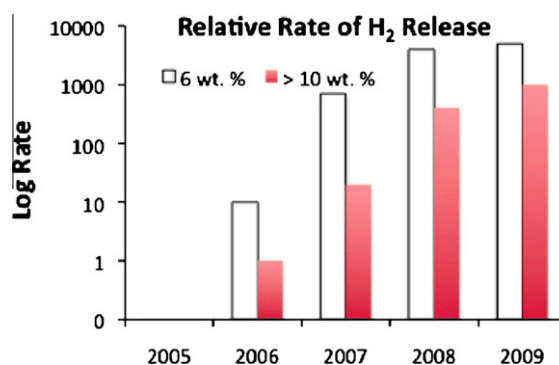


Fig. 5. Hydrogen release rates from ammonia borane have been improved 100–1000 fold from the first formulations in 2006 with the addition of catalysts. Taken with permission from [75].

these materials. Fig. 3 compares the isothermal hydrogen evolution rates for a number of kinetically stabilized metal hydrides to that of NaAlH_4 (doped and undoped) [61]. Above 100°C the hydrogen evolution rates for all three undoped AlH_3 polymorphs and LiAlH_4 are 2–3 orders of magnitude greater than that of undoped NaAlH_4 , while the hydrogen evolution rate for doped NaAlH_4 is very comparable to undoped AlH_3 . In fact, at 112°C the H_2 evolution rates of the AlH_3 polymorphs exceed $0.01\text{ g-H}_2\text{ s}^{-1}\text{ kg}^{-1}$ of material. While these materials have not been shown to be reversible and the traditional organometallic synthesis routes are costly, recent research has demonstrated much more cost and energy efficient synthesis processes [62–65] which could allow these materials to be cost effectively utilized in near-term markets.

Incorporation of storage materials into nanoporous matrices has shown significant improvements in kinetics [49,66–68]. The idea is shown schematically in Fig. 4A. Using this method, the diameter of the pores determine the maximum crystallite size of the hydride, thus, reducing the hydrogen diffusion distance which can result in faster rates of hydrogenation/dehydrogenation. In addition, the pore walls prevent nanoparticle agglomeration. Vajo et al. incorporated 9–16 wt.% MgH_2 into Ni wetted aerogels. The aerogels contained pores ranging in size from <2 to ~ 30 nm in diameter with a mean pore size of 13 nm. Fig. 4B shows that the Ni catalyzed MgH_2 aerogels released hydrogen at over 11 times faster than uncatalyzed MgH_2 aerogels and 200 times the rate of bulk MgH_2 ball milled with synthetic graphite. The benefit from nanoconfinement has been observed for many other hydride materials including LiBH_4 [50,69], NaAlH_4 [68,70] and NH_3BH_3 [71].

Catalysis has been shown to be an effective method to increase hydrogen release rates of chemical hydrogen storage materials at temperatures within the operating range of PEM fuel cells [45,46,72–75]. In particular, heterogeneous catalysis has delivered significant results that have increased the relative hydrogen release kinetics of AB as shown in Fig. 5. The addition of Pt catalyst to AB demonstrated 10 wt.% hydrogen release in 30-min (i.e., $>0.08\text{ g-H}_2\text{ s}^{-1}\text{ kg}^{-1}$) at 70°C [75]. Similar rapid release rates were also measured using much less expensive transition metal catalysts including Ti, Fe, Ni, and Zn. Further reduction in spent material (i.e., spent fuel) regeneration costs and synthetic routes could allow chemical hydrogen storage materials to be a very competitive hydrogen source for near-term markets.

Sorbents, with their inherently low hydrogen binding energy for physisorption, are materials which can provide high hydrogen delivery rates albeit typically at cryogenic temperatures. A recent approach to improving adsorption/desorption kinetics at room temperature is based on the “spillover” mechanism. Hydrogen spillover is a well-established phenomenon in surface science that involves the dissociation of molecular hydrogen (H_2) into atomic hydrogen (H^*) on a metal surface and subsequent migration onto support materials as shown in Fig. 6A [76–80]. Yang and co-workers have investigated this phenomenon in porous sorbent materials where they used mechanically-formed mixtures of Pt/C catalysts combined with various sorbent materials to improve the room temperature kinetics of the materials (Fig. 6B). Experimental results demonstrated that hydrogen uptake capacities at 24°C (298 K) and 10 MPa (100 bar) increased by at least twofold relative to an unmodified MOF. These materials have shown reversibility through 2–3 cycles, however, long-term recyclability at high capacity has not yet been demonstrated. While research in the spillover phenomenon has generated encouraging results, there are still fundamental questions that remain to be addressed including validation of enhanced sorption at room temperature. However, “spillover” could be the key to improving room temperature adsorption/desorption kinetics in sorbent materials allowing these materials to be even more cost efficient for near-term markets.

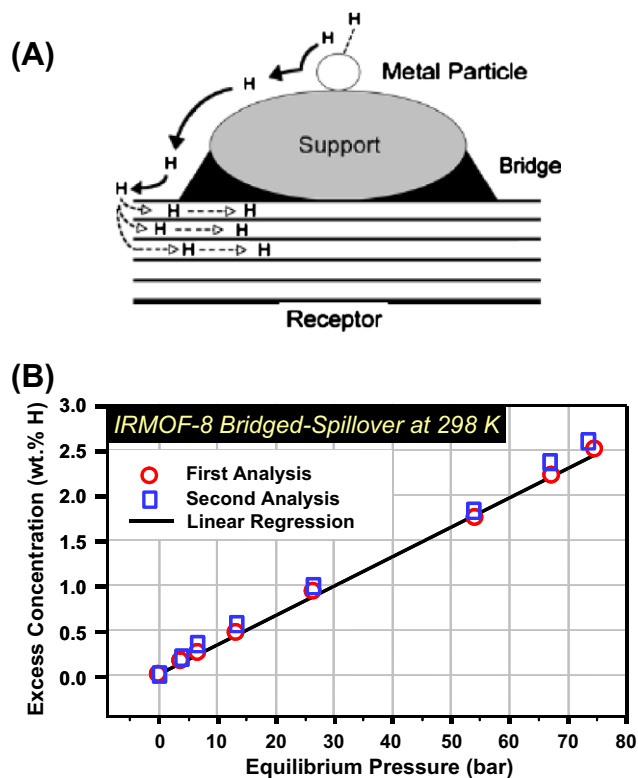


Fig. 6. (A) Simplified schematic of bridged “spillover” mechanism where H_2 is dissociated at a supported metal catalyst, then diffuses to the receptor which is facilitated by a carbon bridge and (B) High-pressure hydrogen uptake (wt.%) at 298 K for IRMOF-8 bridged spillover. The first analysis (red circles), synthesized and tested at University of Michigan (Ann Arbor, MI), then corroborated via a second analysis (blue squares) synthesized and tested by the Institute of Nuclear Energy Research (Taiwan) and Southwest Research Institute (San Antonio, TX). Taken with permission from [78]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.4. Other contributing factors

Many other factors will play a critical role in determining the viability of materials-based storage in near-term markets including cost, cycle life/durability, reactivity and effluent purity. Cost is an issue among all technologies. For materials-based hydrogen storage to be a practical alternative for near-term markets, the cost of the materials must be competitive with that of storage in high pressure cylinders. In addition, the H_2 -FC system must be competitive with other forms of energy such as petroleum and diesel gensets or batteries. Considering the differences in cost and abundance of the light metals, the materials costs may be determined to a large extent by the content of the less abundant elements such as Li or B. Consequently, future systems using more abundant elements such as $\text{Ca}(\text{BH}_4)_2/\text{MgH}_2$ may have an advantage over $\text{LiBH}_4/\text{MgH}_2$ for higher volume markets, despite the slightly lower storage capacity.

Compared to high pressure cylinders, materials-based hydrogen storage technologies have an inherent advantage since these materials can store hydrogen under moderate temperature and pressure. Although some of these materials do demonstrate a high reactivity with water. These hazards can be controlled or eliminated through system engineering or chemical modification of the hydride material.

Hydrogen effluent quality refers to the hydrogen released from the storage material and delivered to the fuel cell where impurity limits for automotive PEM fuel cells have been established to support a fuel index of $\geq 99.99\%$ H_2 [81]. Specified impurities have

been identified to cause significant reduction in fuel cell performance such as catalyst deactivation [82–84] and degradation in membrane ionomer conductivity [82,83,85], ultimately reducing the lifetime of the fuel cell.

4. Conclusions

The focus of the DOE Fuel Cell Technologies Program Storage Activity is on materials and physical systems that meet application derived performance targets. It is important to recognize that the most likely route for successful commercialization of direct hydrogen fuel cells in vehicles will almost certainly include introduction of fuel cells in near-term markets. The three main near-term markets that have been identified for PEM fuel cell technologies include: portable and stationary back-up power and specialty vehicle power. The demands on hydrogen storage systems in these near-term applications can be very different from light-duty automotive, thus potentially allowing for materials with a wider range of properties to potentially meet the hydrogen storage demands of near-term PEM fuel cell markets. However, it is recognized that continued basic and applied research and development of new concepts for materials as well as systems are still required to realistically develop near-term materials-based hydrogen storage options.

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