Hydrogen storage for fuel cell vehicles
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The concerns over diminishing resources and the environmental impact of burning fossil fuels have focused attention on the development of alternative and sustainable energy sources for transportation applications. In this context, hydrogen is an attractive option to replace current hydrocarbon-based systems. A major obstacle for the development of hydrogen powered fuel cell vehicles is the lack of safe, light weight and energy efficient means for on-board hydrogen storage. During the last fifteen years, significant effort has been made to develop effective hydrogen storage methods, including hydrogen tank, sorbents and metal/chemical hydrides. In the present article, we concisely review the current status of each on-board hydrogen storage technology, along with its advantages and disadvantages, and offer a perspective for future developments.

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Introduction

Hydrogen is a potential clean and environmentally friendly energy carrier because, in proton exchange membrane (PEM) fuel cells, hydrogen protons released at the anode transfer through the electrolyte, to react with oxygen at the cathode to produce water while work is generated in the external circuit via electron transfer from the anode to the cathode. In this context, hydrogen is an important alternative to address some adverse aspects of the current hydrocarbon liquid fuels for transportation applications. It has high energy density on a mass basis as compared to gasoline (120 MJ/kg for hydrogen vs. 44 MJ/kg for gasoline). Unfortunately, it has poor volumetric energy density (0.01 MJ/L for hydrogen at STP vs. 32 MJ/L for gasoline), which presents significant difficulty in storing large quantity of hydrogen for vehicle applications. A critical challenge for the development of fuel cell vehicles is how to store hydrogen on-board for a driving range (>500 km or 300 miles) on single fill with the constraints of safety, weight, volume, efficiency and cost [1–3].

As illustrated in Figure 1, current approaches for on-board hydrogen storage include compressed hydrogen gas, cryogenic and liquid hydrogen, sorbents, metal hydrides, and chemical hydrides which are categorized as either 'reversible on-board' or 'regenerable off-board'. The U.S. Department of Energy (DOE) has set a 2017 requirement of 5.5 wt% H_2 and 40 g H_2/L for gravimetric and volumetric system targets, respectively, as well as cost, while the ultimate targets are more stringent (see Table 1) [4]. The difference between *system* and *material-based* capacities is noteworthy. Evaluation of a hydrogen storage *system* includes all associated components such as tank, valves, piping, insulation, reactants, among others, while *material-based* value accounts for only reactants or materials possessing hydrogen. For example, the material-based capacity of compressed hydrogen tank is 100% because it contains pure hydrogen, while system capacity drops to ∼5 wt% when all associated components mentioned above are accounted for. In the present article, approaches including sorbents, carbon-based materials, metal hydrides and chemical hydrides provide material-based values unless otherwise noted because these technologies have not been adopted in actual vehicles yet. Apart from gravimetric and volumetric targets, DOE has also addressed the challenges associated with various approaches in terms of meeting key system performance targets, including cost, charge and discharge kinetics, and durability. There are advantages and disadvantages for the different approaches and currently no technology meets all the requirements. In the present paper, the current status of each on-board hydrogen storage method is discussed concisely, along with its advantages and disadvantages. For an extensive review of the topic, the reader is referred to the recent article by Durbin and Malardier-Jugroot [5••].

Compressed gas

The most commonly used method for hydrogen storage in fuel cell vehicles is compressed hydrogen tanks. Indeed, several prototype vehicles (e.g. Honda FCX Clarity, Toyota FCV, Mercedes-Benz F-Cell, and GM Equinox) with such tanks are already in test use for sale in the near future and manufacturers have estimated the fuel economy using EPA test procedures.

The most important consideration for compressed gas is the material composing the tank. It must be lightweight,

Figure 1
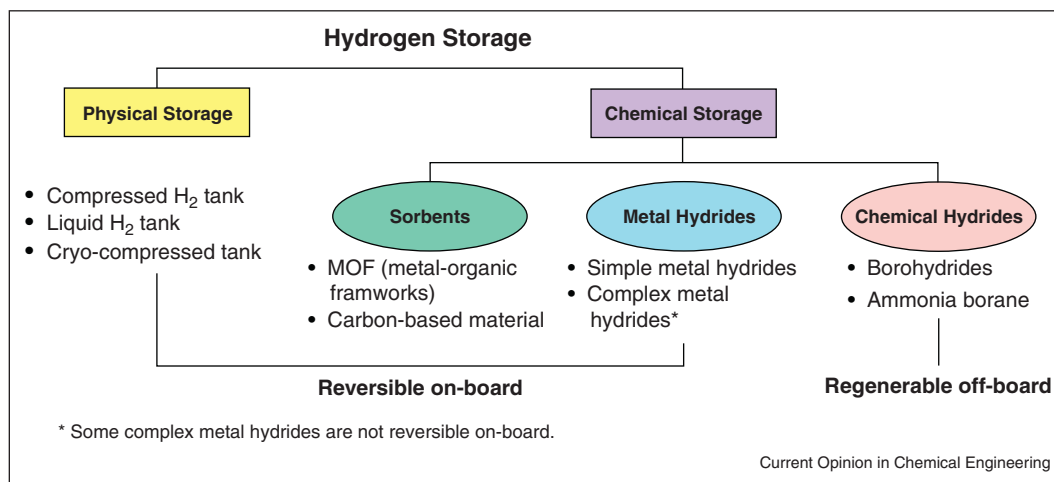
Classification of hydrogen storage methods.

inexpensive and sufficiently strong to meet the required stress, strain and safety specifications [6]. In addition, thermal conductivity of the material must be high enough to manage exothermic heat during filling the tank. Accounting for these requirements, carbon fiber reinforced plastic (CFRP) is promising as material for the compressed gas tank. The CFRP tanks are light-weight and durable, however, they have relatively low thermal conductivity which requires further improvement [7].

For a 300 mile driving range, assuming 50% fuel cell efficiency, 5.6 kg of usable H_2 is required. The CFRP (Type IV, made from carbon fiber with a polymer liner) tanks are estimated to provide 5.2 and 5.5 wt% H_2 for 700 and 350 bar, respectively (Table 2). Compressed gas tanks offer a near-term option for initial commercialization and currently focus on reducing the cost of the carbon fiber composite, which dominates the cost (>65%) of the compressed gas systems. The volumetric capacity (18 and 28 g H_2/L for 350 and 700 bar, respectively) and the cost of tanks, however, are still challenges [4].

Cryogenic storage
The volumetric density of hydrogen can be increased by liquefying it. For example, the theoretical volumetric

capacity of hydrogen increases from 24 or 40 g/L (for compressed H_2 at 350 or 700 bar at 300 K) to 70 g/L (for liquid H_2 at 1 atm and 20 K).

When hydrogen is stored as liquid at 1 atm, it must be maintained below its boiling point (20 K). Therefore, effective thermal insulation is essential to maximize the efficiency of the liquid hydrogen (LH_2) tank. Therefore, typical LH_2 tanks consist of metallic double-walled container, where the inner and outer walls are separated by vacuum for thermal insulation purposes.

Despite improved volumetric density, LH_2 storage is not frequently used for several reasons. One of main issues is hydrogen boil-off. The LH_2 can evaporate even with highly insulated tank, which causes hydrogen loss [8].

Table 1

US DOE hydrogen storage performance and cost targets [3].

	Gravimetric, wt% (kWh/kg sys)	Volumetric, g/L (kWh/L sys)	Costs, $/kWh
2017	5.5 (1.8)	40 (1.3)	12
Ultimate	7.5 (2.5)	70 (2.3)	8

Table 2

Estimated performance and cost for different hydrogen storage approaches [3].

H_2 storage system	Gravimetric, wt% (kWh/kg sys)	Volumetric, g/L (kWh/L sys)	Costs, $/kWh
700 bar compressed (Type IV)	5.2 (1.7)	27.7 (0.9)	19
350 bar compressed (Type IV)	5.5 (1.8)	18.5 (0.6)	16
Cryo-compressed (276 bar)	5.8 (1.9)	43.1 (1.4)	12
Metal hydride ($NaAlH_4$)	1.2 (0.4)	12.3 (0.4)	TBD
Sorbent (AX-21 carbon, 200 bar)	4.0 (1.3)	24.6 (0.8)	TBD
Chemical hydride (NH_3BH_3-liquid)	4.0 (1.3)	33.8 (1.1)	TBD

In addition, the boil-off occurs even when the system is dormant and increases the pressure of the tank which must be vented to prevent rupture. Apart from cost and energy efficiency penalty due to hydrogen loss, the boil-off also presents safety concerns, particularly for vehicles parked in confined space such as containers and parking garages. Second, 30–35% of energy value of hydrogen is required to liquefy it, which is ∼3 times larger than needed for compressed H_2 tank [5••]. For these reasons, even though there is room for further improvements, it is unlikely for cryogenic storage to meet DOE requirements.

Cryo-compressed storage

As noted above, compressed tank requires a relatively large volume while LH_2 can vaporize to cause loss of hydrogen as well as safety concerns. Consequently, studies of physical hydrogen storage have currently shifted to cryo-compressed H_2, which combines compression and cryogenic storage [9•,10]. The volumetric density of hydrogen can be increased by pressurizing LH_2 at 20 K from 70 g/L at 1 bar to 87 g/L at 240 bar, which reduces the requirement for expensive carbon fiber composite. In addition, it can decrease evaporative loss of hydrogen as well as extend the dormancy period in insulated pressure vessels. Researchers at Lawrence Livermore National Laboratory have recently demonstrated that a prototype using cryo-compressed H_2 allows the longest driving distance with a single tank (660 miles) and no evaporative losses were observed during parking for 8 days [10].

Cryo-compressed tanks (276 bar, 20 K) are estimated to provide 5.8 wt% and 43 g H_2/L, which slightly exceed DOE 2017 gravimetric and volumetric targets, respectively (Table 2). Currently, cryo-compressed H_2 tank approach is the only one that meets DOE 2017 system target values.

Metal hydrides

Some metal hydrides have the potential for reversible on-board hydrogen storage and release hydrogen at the relatively low temperatures and pressures required for fuel cells. For example, $LaNi_5H_6$ can release hydrogen under PEM fuel cell operating conditions (1–10 atm and 25–100 °C), but its gravimetric capacity is too low (∼1.4 wt%) and its cost too high for vehicular applications [11,12].

As compared to conventional metal hydrides, complex metal hydrides offer the potential to improve gravimetric hydrogen capacity. By introducing titanium dopants, sodium alanate ($NaAlH_4$) can store and release hydrogen reversibly at modest temperature (∼150 °C) [13,14]. However, complex metal hydrides still provide relatively low hydrogen capacity and slow hydrogen uptake and release kinetics. For example, the maximum theoretical material (not system) gravimetric capacity of sodium

alanate is 7.4 wt% hydrogen, while actual material capacities are currently only 3–4 wt%. In addition, hydrogen release kinetics are too slow for vehicular applications [15,16•].

Recently, amides and imides have attracted interest due to their high hydrogen storage capacity [16•,17]. The overall dehydrogenation of lithium amide ($LiNH_2$) and hydride (LiH) is shown as

$$LiNH_2 + LiH \rightarrow Li_2NH + H_2 \qquad (1)$$
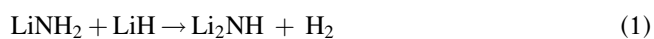
which is composed of the following two steps:

$$2LiNH_2 \rightarrow Li_2NH + NH_3 \qquad (2)$$

$$NH_3 + LiH \rightarrow LiNH_2 + H_2 \qquad (3)$$

In this reaction, 6.5 wt% hydrogen can be theoretically absorbed/desorbed at 285 °C via the two steps given by Eqs. (2) and (3). However, the temperature is outside the operating window to utilize the waste heat of a PEM fuel cell. A possible way to achieve such temperature value on-board vehicles is by sacrificing some hydrogen in a burner, which constitutes penalty in system cost, volume, weight and efficiency. Another issue with this system is that ammonia is formed as by-product, which poisons the PEM fuel cell catalyst [18–20].

Table 3 lists theoretical material-based H_2 capacities for various hydrides including metal, complex metal, and chemical hydrides. Many different types of metal hydrides have been studied as means of hydrogen storage. However, superior hydrogen release properties (yield and kinetics) are obtained at temperatures much higher than PEM fuel cell operation conditions. The kinetics can be improved by adding catalyst as well as by introducing ball-milling which improves surface properties [15,21–23]. In addition, effective heat management in the system is important to improve the system efficiency [24]. Even if these problems are overcome, however, it is unlikely that this approach will meet DOE targets in the foreseeable future. For example, sodium alanate, one of the most

Table 3

Hydrogen capacities of selected hydrides.

Hydride	Compound	Gravimetric H_2 content (wt%)
Metal hydrides	LiH	12.6
	NaH	4.2
	CaH_2	4.8
	MgH_2	7.6
Complex metal hydrides	$LiAlH_4$	10.6
	$NaAlH_4$	7.4
	$Mg(AlH_4)_2$	9.3
	$LaNi_5H_6$	1.4
Chemical hydrides	$LiBH_4$	18.4
	$NaBH_4$	10.6
	NH_3BH_3	19.8

promising metal hydrides, is estimated to provide system yield only 1.2 wt% H_2 and 12 g H_2/L, which are much lower than DOE targets (Table 2).

High surface area sorbents and carbon-based materials

High surface area sorbents based on metal-organic frameworks (MOFs) have been considered as promising materials for hydrogen storage ever since the work of Rosi *et al.* [25], due to their high porosity and controllable structural characteristics [26]. The MOFs are crystalline and microporous solids composed of metal ions or clusters linked with organic molecules and typically have surface area greater than 3000 m²/g. Hydrogen storage of 7.5 wt% in MOF-177 material was reported by Wong-Foy *et al.* [27], who measured the saturation hydrogen uptake in a series of MOFs at 77 K in the pressure range 25–80 bar. Sumida *et al.* [28] obtained a beryllium-based framework, $Be_{12}(OH)_{12}$(1,3,5-benzenetrisbenzoate)$_4$ with high surface area (4020 m²/g), which translates to attractive hydrogen storage properties, 9.1 wt% H_2 adsorbed at 77 K and 95 bar. Li and Yang [29,30] observed that the hydrogen storage capacity of MOFs could be significantly improved by modification with metal supported catalysts through a bridged hydrogen spillover. However, due to the highly porous nature of these materials, volumetric capacity is still a significant issue.

Carbon-based materials such as activated carbon, carbon nanotubes and fullerenes have attracted interest as hydrogen storage materials owing to their high surface areas and thermal stability. The KUA5, one of the most promising activated carbons, adsorbs 3.2 and 8 wt% hydrogen at 298 K, 187 atm and at 77 K, 39 atm, respectively [31]. Assfour *et al.* [32•] reported that the simulated structure of carbon nanotubes is energetically and mechanically stable with high hydrogen uptake up to 5.5 and 19 wt% at 300 and 77 K, respectively, at pressure 100 bar. Modeling of binding energies and theoretical predictions of optimum carbon-based compounds for hydrogen storage are under way. For example, based on theoretical studies, modified fullerenes have recently been proposed as potential adsorbents for the high density, room temperature and ambient pressure storage of hydrogen [28]. Some studies suggest that the fullerenes can store up to 25 hydrogen molecules within a single C_{60} cage, while others claim that only one H_2 will stay. These materials have yet to be synthesized, however, to confirm the theoretical predictions [33].

Despite reversible nature of the hydrogen absorption/desorption process for high surface area sorbents and carbon-based materials, they suffer from lower hydrogen capacity, especially under mild operating conditions. It is hoped that recent research on modified and doped materials to enhance hydrogen uptake could lead to more promising achievements in the future [34].

Chemical hydrides

As compared to metal hydrides, chemical hydrides offer higher energy densities since they contain lighter elements. In addition, they can release hydrogen under relatively mild operating conditions. The dehydrogenation reactions, however, are irreversible, so the resulting products have to be regenerated off-board the vehicle [35,36].
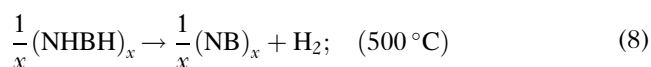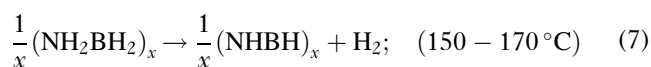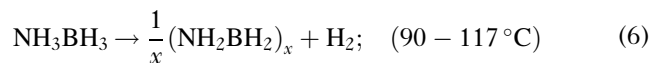
Sodium borohydride ($NaBH_4$) can provide relatively high theoretical hydrogen yield (10.8 wt%) via hydrolysis reaction (Eq. (4)) [16•], which proceeds in an aqueous medium with a catalyst [37]. To achieve higher hydrogen capacity, hydrolysis by steam has been proposed instead of water [38]. While the material capacity can be high and the hydrogen release kinetics are fast, regeneration of borohydride from borate requires multi-step conditions which are not possible on-board a vehicle. A $NaBH_4$-based system has been estimated to possess system gravimetric and volumetric capacities of 4.5 wt% and 36 g/L, respectively [39].

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \qquad (4)$$
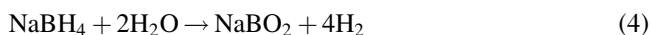
There are a number of boron-hydrogen compounds that have high hydrogen content. Ammonia borane (AB, NH_3BH_3) has high material capacity (19.6 wt% H_2), where the hydrogen can be released by either hydrolysis or thermolysis. Hydrolysis provides low theoretical H_2 yield due to limited AB solubility in water (Eq. (5)) [36,40].

$$NH_3BH_3 + 3H_2O \rightarrow B(OH)_3 + NH_3 + 3H_2 \qquad (5)$$
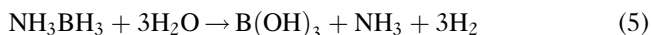
The products of thermolysis can include compounds such as cyclotriborazane, borazine, and polymeric analogues (Eqs. (6) and (7)). Above 500 °C, AB can be completely decomposed to form boron nitride (Eq. (8)). Using hydro-thermolysis, which combines hydrolysis and thermolysis, high H_2 yield (∼14 wt%) has been demonstrated [41,42].

$$NH_3BH_3 \rightarrow \frac{1}{x}(NH_2BH_2)_x + H_2; \quad (90 - 117\,°C) \qquad (6)$$

$$\frac{1}{x}(NH_2BH_2)_x \rightarrow \frac{1}{x}(NHBH)_x + H_2; \quad (150 - 170\,°C) \qquad (7)$$

$$\frac{1}{x}(NHBH)_x \rightarrow \frac{1}{x}(NB)_x + H_2; \quad (500\,°C) \qquad (8)$$

It has been reported that at PEM fuel cell operating temperature in the absence of any additive, H_2-release from solid-state AB exhibits an induction period of up to 3 h. After hydrogen release, only ∼1 equivalent of H_2 (6.5 wt% H_2) is obtained even with prolonged duration (>20 h). For this reason, catalysts or additives have been demonstrated to enhance the amount as well as the

Table 4

Advantages and disadvantages of different hydrogen storage approaches.

H$_2$ storage system	Advantages	Disadvantages	Ongoing efforts
Compressed H$_2$	Commercially available	Low volumetric capacity High compression energy Heat management during charging required	Develop and design cost-effective vessel/container.
Liquid H$_2$	Commercially available	H$_2$ loss Safety issue High liquefaction energy Heat management to reduce boil-off	
Cryo-compressed	High volumetric capacity	High compression/liquefaction energy	
Metal hydride	Reversible on-board	Low gravimetric/volumetric capacity Heat management during charging required High operating temperature for H$_2$ release	Improve kinetics of hydrogen adsorption/desorption along with heat management.
Sorbent and carbon-based materials	Reversible on-board	Low volumetric density Loss of useable H$_2$ Low operating temperature for H$_2$ uptake	Increase dihydrogen binding energies. Optimize material's properties (pore size, pore volume, surface area, among others).
Chemical hydride	Good volumetric capacity Proper operating temperatures	Thermal management required Off-board regeneration	Develop cost effective and energy efficient regeneration methods for the spent material.

kinetics for hydrogen release [43–46]. High material-based H$_2$ yield 11.4 wt% was obtained by Himmelberger et al. from AB with 20 wt% ionic liquid (1-butyl-3-methylimidazolium chloride, bmimCl) at 110 °C [47]. Hwang et al. [48•] reported that in the presence of 10 wt% boric acid as additive, high H$_2$ yield (13 wt%) was obtained at 80 °C.

Recently, AB slurry in silicone oil has been suggested as a possible storage medium to meet DOE targets while remaining in liquid state after dehydrogenation [49]. Similar to NaBH$_4$-based system, however, efficient and cost effective regeneration of the spent fuel is critical for the successful application of ammonia borane as an on-board hydrogen storage material. Although significant progress in this direction has been demonstrated in several laboratories [50,51], the regeneration efficiency needs to be improved further for AB-based systems to be practically viable.

Concluding remarks

With growing energy demand, limited supply of fossil fuels, and their adverse effects on the environment, hydrogen has attracted interest as a clean and sustainable alternative to current hydrocarbon-based fuels. Although hydrogen has high gravimetric energy density, its volumetric energy density is poor, which presents a significant barrier for use of hydrogen on-board fuel cell vehicles. Current approaches for on-board hydrogen storage include compressed hydrogen gas, cryogenic and liquid hydrogen, sorbents, metal hydrides, and chemical hydrides. The advantages and disadvantages for each approach are summarized in Table 4. No current technology meets the ultimate U.S. DOE system targets, however, compressed gas storage offers a near term option

for initial commercialization even though the cost of tanks is still a challenge. For the longer term, solid-state hydrogen storage materials such as high surface area sorbents and hydrides, offer potential. For these materials, however, effort is required to improve gravimetric and volumetric capacities, kinetics within appropriate temperature and pressure ranges, along with overall cost. An understanding of the relationship between cost, energy efficiency and environmental impact for the various approaches is necessary to assess system life-cycle issues. Particularly for chemical hydrides, it is critical to develop cost effective and energy efficient regeneration methods for the spent materials to complete life cycle. In addition, the energy associated with compression, cooling, and liquefaction of hydrogen must be considered for the physical storage approaches. Finally, for hydrogen to be widely used in vehicle applications, along with material discoveries, efforts in optimizing overall system performance are needed to overcome technical barriers relevant to all hydrogen storage approaches.

Acknowledgements

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