The U.S. Department of Energy's National Hydrogen Storage Project: Progress towards meeting hydrogen-powered vehicle requirements

Sunita Satyapal [a,*], John Petrovic [b,1], Carole Read [a], George Thomas [c,1], Grace Ordaz [a]

[a] *U.S. Department of Energy, DOE Hydrogen Program, 1000 Independence Avenue SW, Washington, DC 20585, USA*
[b] *Los Alamos National Laboratory, United States*
[c] *Sandia National Laboratory, United States*

Available online 13 November 2006

Abstract

Hydrogen storage is widely recognized as a critical enabling technology for the successful commercialization and market acceptance of hydrogen powered vehicles. Storing sufficient hydrogen on-board a wide range of vehicle platforms, while meeting all consumer requirements (driving range, cost, safety, performance, etc.), without compromising passenger or cargo space, is a tremendous technical challenge. The U.S. Department of Energy (DOE), in collaboration with automotive industry partners, established specific technical targets for on-board hydrogen storage systems to focus R&D and to stimulate research on hydrogen storage. In order to achieve these long-term targets, DOE launched a "Grand Challenge" to the scientific community in 2003. Based on a competitively selected portfolio, DOE established a "National Hydrogen Storage Project" in the U.S. for R&D in the areas of advanced metal hydrides, chemical hydrogen storage, carbon-based and high surface area sorbent materials, as well as new materials and concepts. The current status of vehicular hydrogen storage is reviewed and research associated with the National Hydrogen Storage Project is discussed. Future DOE plans through the International Partnership for the Hydrogen Economy (IPHE) are also presented.
Published by Elsevier B.V.

Keywords: Hydrogen storage; Hydrogen storage review; Hydrogen storage targets; Compressed hydrogen tanks; Conformable high-pressure tanks; Metal hydrides; Chemical hydrides; Chemical hydrogen carriers; Carbon; Nanostructured materials; High surface area adsorbents; Sorbents

1. Introduction

Petroleum dependence in the United States is driven by the transportation sector, which accounts for roughly two-thirds of the 20 million barrels of oil used in the U.S. per day. Currently, the U.S. imports 55% of its oil, and this is expected to grow to 68% by the year 2025 under a status quo scenario [1]. To reduce dependence on imported oil, a number of strategies are under consideration including the increased use of gasoline hybrid vehicles in the near term. For the long term, however, petroleum *substitution* is required and that necessitates the development of alternative energy carriers. Hydrogen has the potential to be an attractive alternative energy carrier, particularly for the transportation sector [2]. It can be clean, efficient, and derived from diverse domestic resources, such as renewables (biomass, hydro, wind, solar, geothermal) as well as fossil fuels and nuclear energy. In the case of fossil fuels, natural gas is likely to be used for the distributed production of hydrogen in the near term, before the infrastructure required for centralized production and hydrogen delivery is developed. In the long term, centralized hydrogen production, using coal with carbon sequestration or nuclear energy (through high temperature water splitting or thermochemical cycles), could be employed to produce hydrogen using a number of delivery options. Hydrogen can then be employed in high-efficiency power generation systems, including internal combustion engines or fuel cells for both vehicular transportation and distributed electricity generation.

The potential energy security and decreased emissions benefits of hydrogen are the basis of the Hydrogen Fuel Initiative launched by President Bush in January 2003. The Hydrogen Fuel Initiative commits government funding for accelerated research, development, and demonstration programs that will enable technology readiness. Should industry decide to proceed, a full

---

transition to a U.S. hydrogen economy would require decades, but hydrogen powered vehicles and limited hydrogen fueling infrastructure could start becoming commercial in the 2020 timeframe. Although the implementation of a hydrogen economy would clearly take time, the key point is that research and development to address the viability of hydrogen technologies needs to occur now, before decisions are made on the best options for a commercially viable and sustainable hydrogen economy.

There are three primary barriers that must be overcome to enable industry commercialization of hydrogen fuel cell vehicles: (1) on-board hydrogen storage systems are needed that allow a vehicle driving range of greater than 300 miles [500 km] while meeting vehicle packaging, cost and performance requirements; (2) fuel cell system cost must be lowered to $30 per kilowatt by 2015 while meeting performance and durability requirements; (3) the cost of safe and efficient hydrogen production and delivery must be lowered to be competitive with gasoline (a target of $2.00 to $3.00 per gallon gasoline equivalent, delivered, untaxed, by 2015) independent of production pathway and without adverse environmental impact.

The barriers associated with hydrogen production, delivery and fuel cells are essentially cost-driven. However, in the case of on-board vehicular hydrogen storage, *no approach currently exists* that can meet the technical requirements for greater than 300-mile range while meeting all performance metrics, *regardless of cost*. Thus, new materials and approaches form the basis for the Department of Energy's (DOE) research priorities for the National Hydrogen Storage Project [3,4].

2. The National Hydrogen Storage Project

The National Hydrogen Storage Project is comprised of three centers of excellence as well as independent projects in applied and basic research and development as shown in Fig. 1. These activities support the President's Hydrogen Fuel Initiative, announced in 2003, which pledged $1.2 billion over 5 years (fiscal year 2004–2008) to accelerate hydrogen research. Planned funding for the National Hydrogen Storage Project is approximately $150 million over a 5-year period (subject to congressional appropriations and direction). The result of this R&D effort will be the development of hydrogen storage systems capable of meeting the 2010 DOE performance targets.

The centers of excellence involve multidisciplinary teams of multiple academic, industrial and federal laboratory partners. The Metal Hydride Center focuses on the development of advanced metal hydrides including lightweight advanced complex hydrides, destabilized binary hydrides, intermetallic hydrides, modified lithium amides and other on-board reversible hydrides. The Center on Chemical Hydrogen Storage focuses on storing hydrogen in covalent chemical bonds where hydrogen can be released via on-board chemical reactions of molecular system such as borohydride-water, dehydrogenation of boron hydrides such as amine boranes and polyhedral boranes, and investigations of non-boron-based materials including organics and nanoparticles. The Carbon Center focuses on breakthrough concepts for storing hydrogen in high surface area sorbents such as hybrid carbon nanotubes, aerogels, and nanofibers, as well as metal-organic frameworks and conducting polymers.

The National Hydrogen Storage Project also involves independent projects on new hydrogen storage materials and concepts, materials testing, and system and life cycle analyses. Examples being studied include nanostructured metal hydride and adsorbent materials, amine borane complexes, clathrates, lithium nitrides, and activation processes for enhanced storage. Independent analysis is also critical, to evaluate the approaches comparatively and to make down-select decisions. Current

1. Coordinated by DOE Energy Efficiency and Renewable Energy, Office of Hydrogen, Fuel Cells and Infrastructure Technologies
2. Basic science for hydrogen storage conducted through DOE Office of Science, Basic Energy Sciences
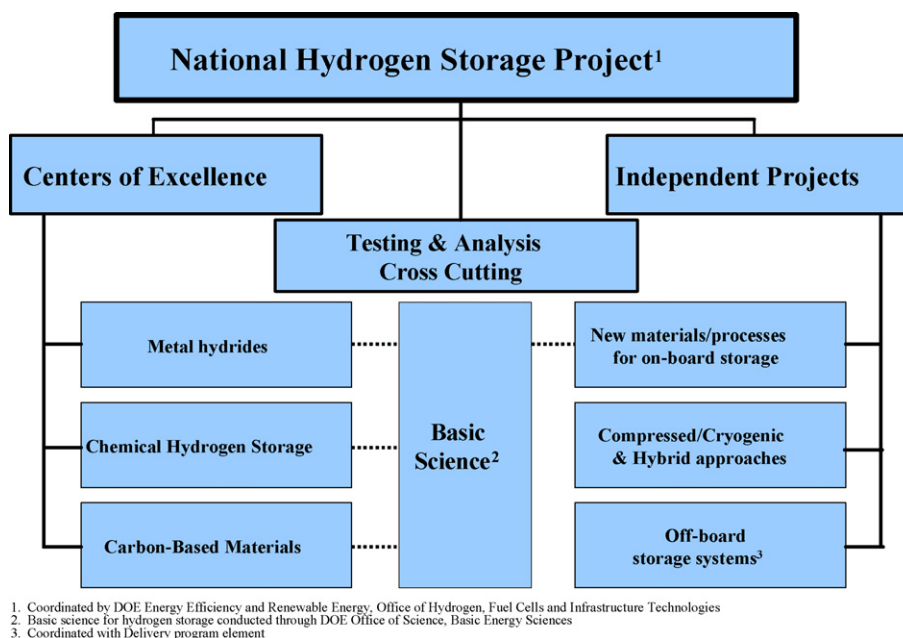3. Coordinated with Delivery program element

Fig. 1. Structure of the U.S. National Hydrogen Storage Project [3].

analysis activities include storage systems analyses to optimize the trade-offs among weight, volume and cost, as well as life-cycle cost, energy efficiency, and environmental impact analyses.

3. U.S. performance targets for hydrogen-powered vehicles

On a weight basis, hydrogen has nearly three times the energy content of gasoline (120 MJ/kg for hydrogen versus 44 MJ/kg for gasoline). However, on a volume basis the situation is reversed and hydrogen has only about a quarter of the energy content of gasoline (8 MJ/L for liquid hydrogen versus 32 MJ/L for gasoline). On-board storage in the range of 5–13 kg [1 kg hydrogen = gallon of gasoline energy equivalent, or gge] of hydrogen is required to encompass the full platform of light-duty automotive fuel cell vehicles. Engine power plants with efficiencies less than PEM fuel cells would require a larger payload of hydrogen to achieve a comparable driving range.

The DOE on-board hydrogen storage system performance targets were developed through FreedomCAR, a partnership between DOE and the U.S. Council for Automotive Research [5]. The FreedomCAR partnership was expanded in 2003 to include major energy companies (BP America, Chevron Corporation, ConocoPhillips, Exxon Mobil Corporation and Shell Hydrogen (U.S.)) and is now known as the FreedomCAR and Fuel Partnership [5]. The performance targets developed are *system* and *application* driven, based on achieving similar performance and cost levels as current gasoline fuel storage systems for light-duty vehicles. The storage system includes the tank, valves, regulators, piping, mounting brackets, insulation, added cooling capacity, thermal management and any other balance-of-plant components in addition to the first charge of hydrogen and any storage media such as solid adsorbent or liquid used to store the hydrogen.

The primary DOE targets for the years 2010 and 2015 are shown in Table 1 [3,4]. The 2015 targets represent what is required based on achieving similar performance to today's gasoline vehicles (greater than 300 mile driving range) and complete market penetration across all light-duty vehicle platforms. These targets include a 20% penalty for the assumption that hydrogen storage systems (unlike conventional gasoline tanks) are not conformable and have limitations on how they may be packaged within a vehicle. The targets also assume a factor of 2.5–3 in terms of efficiency improvement in using a fuel cell power plant as compared to a conventional

Table 1
U.S. DOE hydrogen storage system performance targets [3,4]

Storage parameter	Units	2007	2010	2015
U.S. DOE technical targets for on-board hydrogen storage systems				
System gravimetric capacity: usable, specific-energy from H_2 (net useful energy/max system mass)	kWh/kg (kg H_2/kg system)	1.5 (0.045)	2 (0.06)	3 (0.09)
System volumetric capacity: usable energy density from H_2 (net useful energy/max system volume)	kWh/L (kg H_2/L system)	1.2 (0.036)	1.5 (0.045)	2.7 (0.081)
Storage system cost (and fuel cost)	$/kWh net ($/kg H_2)	6 (200)	4 (133)	2 (67)
	$/gge at pump	–	2–3	2–3
Durability/operability				
Operating ambient temperature	°C	−20/50 (sun)	−30/50 (sun)	−40/60 (sun)
Minimum/maximum delivery temperature	°C	−30/85	−40/85	−40/85
Cycle life variation	% of mean (min) at % confidence	N/A	90/90	99/90
Cycle life (1/4 tank to full)	Cycles	500	1000	1500
Minimum delivery pressure from tank: FC = fuel cell, I = ICE	atm (abs)	8 FC/10 ICE	4 FC/35 ICE	3 FC/35 ICE
Maximum delivery pressure	atm (abs)	100	100	100
Charging/discharging rates				
System fill time (for 5 kg)	min	10	3	2.5
Minimum full flow rate	(g/s)/kW	0.02	0.02	0.02
Start time to full flow (20 °C)	s	15	5	5
Start time to full flow (-20 °C)	s	30	15	15
Transient response 10–90% and 90–0%	s	1.75	0.75	0.75
Fuel purity (H_2 from storage)	% H_2	99.99 (dry basis)		
Environmental health and safety				
Permeation and leakage	scc/h	Meets or exceeds applicable standards		
Toxicity	–			
Safety	–			
Loss of useable H_2	(g/h)/kg H_2 stored	1	0.1	0.05

gasoline internal combustion engine. If efficiency improvements are not as high as projected, this would clearly dictate even more challenging requirements for on-board hydrogen storage to achieve comparable driving range.
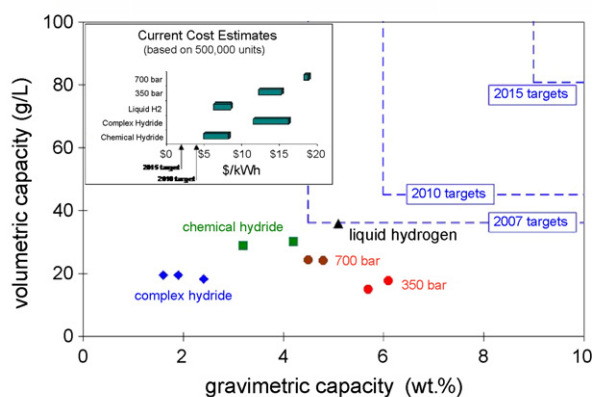
The 2010 targets represent what is required for an early market penetration scenario across various light-duty vehicle platforms. Also shown in Table 1 are interim targets for the year 2007 which can help guide near term R&D and offer lessons learned as new concepts are developed. Note in Fig. 2 that current high pressure hydrogen tanks and liquid hydrogen meet some, though clearly not all, of the near term (2007) targets. These 2007 targets are therefore primarily for materials-based systems, such as solid-state (e.g. metal hydride) or liquid (e.g. chemical hydride) systems. The focus of the DOE National Hydrogen Storage Project is on materials-based technologies to meet 2010 targets and with potential to eventually meet 2015 targets. Currently, research priorities are on achieving the volumetric and gravimetric capacity targets in Table 1, while also paying attention to energy and temperature requirements for hydrogen release as well as kinetics of hydrogen charging and discharging. It is important to note that to achieve *system-level* capacities of 2 kWh/kg (6 wt.% hydrogen) and 1.5 kWh/L (0.045 kg hydrogen/L) in 2010, the gravimetric and volumetric capacities of the material/media alone must clearly be higher than the system-level targets. To restate, development of a hydrogen storage material/media (e.g. metal hydride, carbon nanostructured material) that meets 6 wt.% or 45 g/L is *not* sufficient to meet the system targets. Depending on the material and on the system design, material capacities may need to be a factor of 1.2–2 times higher than system capacity targets. Given the wide number of options for specific materials and system designs, only system level targets are specified.

4. Vehicular hydrogen storage approaches: Reversible on-board versus regenerable off-board

Current on-board hydrogen storage approaches include compressed hydrogen gas, cryogenic and liquid hydrogen, metal hydrides, high surface area sorbents (such as carbon-based nanostructured materials), and chemical hydrogen storage [3,4]. Compressed and cryogenic hydrogen, metal hydrides, high surface area sorbents, and carbon-based materials are categorized as "reversible" on-board, because these approaches may be recharged with hydrogen on-board the vehicle, similar to refueling with gasoline today. Systems that bind hydrogen with low binding energy (less than 20–25 kJ/mol H_2) can undergo relatively easy charging and discharging of hydrogen under conditions that may be applicable at refueling stations. For chemical hydrogen storage approaches as well as selected metal hydrides, the hydrogen is incorporated in much stronger bonds (e.g. with bond energies typically in excess of 60–100 kJ/mol H_2). Once the hydrogen is released, for use during vehicle operation, recharging with hydrogen under operating conditions convenient at a refueling station is problematic. Such systems are referred to as "regenerable off-board", which requires the spent media to be recovered from the vehicle and then regenerated with hydrogen either at the fueling station or at a centralized processing facility. Materials with binding energies between 25 and 60 kJ/mol H_2 may require substantial thermal management during recharging on-board the vehicle.

Both reversible on-board storage and regenerable off-board storage approaches have advantages and disadvantages. DOE is currently supporting research in both areas with a schedule for down-select decisions planned as materials are designed, developed and tested. Referring to Fig. 2 again, the current status of vehicular hydrogen storage systems is shown in comparison to DOE 2010 and 2015 performance targets. These values are system estimates provided by developers and the R&D community, and are updated by DOE as progress is reported. One can see that none of the current systems meet the combined gravimetric, volumetric, and cost targets for either 2010 or 2015. DOE has also assessed the challenges associated with various approaches in terms of meeting key targets, as shown in Fig. 3. It is clear that there are advantages and disadvantages for the different options and no one approach meets all the requirements. Each of

Fig. 2. Current status of hydrogen storage system capacity and cost [4].

Fig. 3. Assessment of challenges for on-board hydrogen storage options showing advantages and disadvantages of various approaches [4].

the current approaches will now be discussed in more detail.

5. Reversible on-board approaches

5.1. Compressed hydrogen gas

Carbon fiber-reinforced composite tanks for 350 bar (5000-psi) and 700 bar (10,000-psi) compressed hydrogen are under development and are already in use in prototype hydrogen-powered vehicles [6]. The driving range of fuel cell vehicles with compressed hydrogen tanks depends on the vehicle type, design and the amount of stored hydrogen. For example, the General Motors HydroGen3 fuel cell vehicle (Opel Zafira minivan with a target curb weight of 1590 kg) is specified for a 270 km (168 mile) driving range with 3.1 kg of hydrogen at 700 bar [7]. By increasing the amount of compressed hydrogen gas beyond 3 kg, a longer driving range can be achieved, but at more cost, weight and reduced passenger and cargo space on the vehicle. Volumetric capacity, limits of high pressure and cost are thus key challenges for compressed hydrogen tanks. Refueling or filling time, compression energy penalty (e.g. 15–20% of the lower heating value of hydrogen) and heat management requirements during refilling also need to be considered [8].

The cost of high-pressure compressed gas tanks is essentially dictated by the cost and the amount of the carbon fiber that must be used for structural reinforcement for the composite vessel. Efforts are underway to identify lower-cost carbon fiber that can meet the required stress, strain and safety specifications for high-pressure hydrogen gas tanks. However, lower-cost carbon fiber must still be capable of meeting tank thickness constraints in order to help meet volumetric capacity targets. Thus an optimization is required among cost, weight and volume that is a function of the amount and cost of carbon fiber used in the composite tank.

Two approaches are being pursued to increase the gravimetric and volumetric storage capacities of compressed gas tanks from their current levels. The first approach involves "cryo-compressed" tanks, i.e. compressed cryogenic hydrogen or a combination of liquid hydrogen and high pressure hydrogen in the headspace [9]. At a given pressure, hydrogen gas becomes more dense as the temperature decreases allowing more hydrogen to be stored in a given volume. Thus, by cooling a tank from room temperature to liquid nitrogen temperature (77 K), its volumetric media capacity will increase by approximately a factor of three. The overall increase in system volumetric capacity will be somewhat less than this because the pressurized tank will now include thermal insulation.

The second approach involves the development of conformable tanks [9]. Present liquid gasoline tanks in vehicles are conformable in order to take maximum advantage of vehicle space restrictions. Today's compressed gas tanks are limited in terms of size and shape (generally cylindrical) and do not offer flexibility in terms of vehicle packaging. Semi-conformable tank structures could have internal structural supporting walls,

and may offer more options for overall tank shape. Internal cellular-type load bearing structures may also be a possibility for greater degrees of conformability. Such approaches are also applicable to materials-based storage technologies that may require moderate pressure. For example, internal skeletal structures may be made with high thermal conductivity materials to allow for more rapid heat flow during hydrogen charging and discharging of the hydrogen storage material. Thus tanks could be designed to provide both structural support and thermal management functions.

5.2. Liquid hydrogen tanks

Liquid hydrogen (LH_2) tanks can, in principle, store more hydrogen in a given volume than compressed gas tanks, since the volumetric capacity of liquid hydrogen is 0.070 kg/L (compared to 0.039 kg/L at 700 bar) [10]. Key issues with LH_2 tanks are hydrogen boil-off, the energy required for hydrogen liquefaction, as well as tank cost. However, the driving range for vehicles using liquid hydrogen, excluding the effects of boil-off, can be longer than that for compressed hydrogen. For example, the General Motors HydroGen3 Opel Zafira minivan is specified with a driving range of 400 km (249 mile) with 4.6 kg liquid hydrogen, versus 270 km (168 mile) described above for the 700 bar tank [7].

Hydrogen loss due to boil-off must be minimized or eliminated to get the maximum possible driving range. Hydrogen boil-off is also considered an issue in terms of refueling frequency, cost, energy efficiency and safety, particularly for vehicles parked in confined spaces such as parking garages. The amount and rate of hydrogen boil-off depends on a number of factors including the amount of hydrogen stored, effectiveness of the thermal insulation, ambient conditions, geometry of the vessel, and length of time between driving. The amount of thermal insulation affects the system-level gravimetric and volumetric capacity, so there are trade-offs to consider among all of these different factors. Examples of typical boil-off rates range from slightly less than 1% to a few percent per day. Hydrogen is lost when the system has been dormant (without driving) and the pressure within the liquid tank reaches the boil-off pressure. System designs that have a capacity for higher levels of gas pressure ("cryo-compressed" tanks, mentioned above) can greatly improve the degree of dormancy and reduce boil-off loss. However, even with minimal or no boil-off, the energy required to liquefy hydrogen, over 30% of the lower heating value of hydrogen, remains a key issue and impacts fuel cost as well as fuel cycle energy efficiency. New approaches that can lower these energy requirements and thus the cost of liquefaction are needed.

5.3. Metal hydrides

Some metal hydrides have the potential for reversible on-board hydrogen storage and release at the relatively low temperatures and pressures required for fuel cell vehicles [11]. Fig. 4 shows that the optimum "operating P–T window" for PEM fuel cell vehicular applications is in the range of 1–10 atm
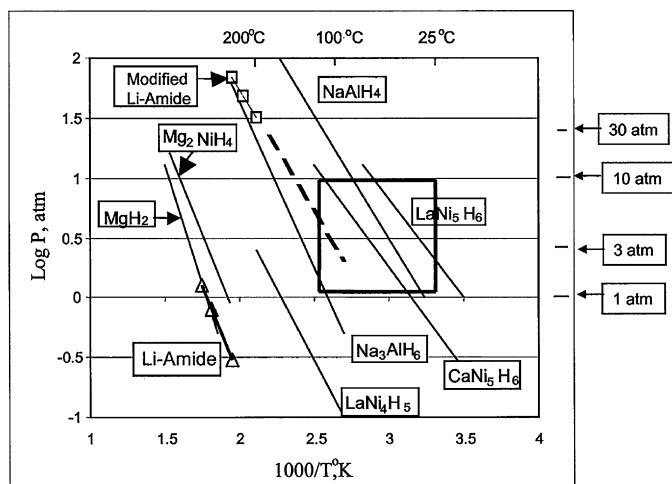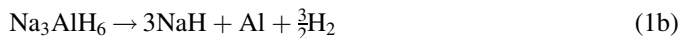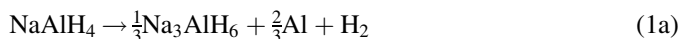
Fig. 4. Equilibrium pressure–temperature curves for various metal hydride materials [12]. The "*P–T* operating window" for PEM fuel cell vehicular applications is indicated by the highlighted box. This operating window indicates conditions of operation that may use the waste heat available from a PEM fuel cell power plant for storage system thermal management.

and 25–120 °C [12]. This represents the hydrogen delivery pressure required by the fuel cell and the temperature of waste heat available from the fuel cell for use by the storage system for hydrogen release. A simple metal hydride such as $LaNi_5H_6$, that incorporates hydrogen into its crystal structure, can function in this range, but its gravimetric capacity is too low and its cost too high for vehicular applications. However, at the present time, $LaNi_5H_6$ is one of the few metal hydrides commercially available.

Complex metal hydrides such as alanates have the potential for higher gravimetric hydrogen capacities in the operational window than conventional metal hydrides such as $LaNi_5H_6$. Sodium alanate can store and release hydrogen reversibly through chemical reactions conducted at modest temperature and pressure when catalyzed with titanium dopants, as discovered by Bogdanovic and co-workers, according to the following reactions [13,14]:

$$NaAlH_4 \rightarrow \tfrac{1}{3}Na_3AlH_6 + \tfrac{2}{3}Al + H_2 \qquad (1a)$$

$$Na_3AlH_6 \rightarrow 3NaH + Al + \tfrac{3}{2}H_2 \qquad (1b)$$

At 1 atm pressure, the first reaction becomes thermodynamically favorable at temperatures above 33 °C and can release 3.7 wt.% hydrogen, while the second reaction takes place above 110 °C and can release 1.8 wt.% hydrogen [13]. In practice, reaction kinetics dictates that higher pressure and temperature are typically required for both hydrogen uptake and release. The amount of hydrogen that a material can release in an absorption/desorption cycle, rather than only the amount the material can hold theoretically by formula weight, is the key parameter used to determine system (net) gravimetric and volumetric capacities.

Examples of issues with complex metal hydrides include low hydrogen capacity and slow hydrogen uptake and release kinetics. The maximum theoretical material (not system) gravimetric capacity of sodium alanate is 5.5 wt.% hydrogen

and is below the 2010 system target of 6 wt.%. In practice, material (not system) gravimetric capacities are currently only 3–4 wt.% [15]. Hydrogen release kinetics are too slow for vehicular applications and the packing density of powder is low (for example roughly 50% of theoretical crystal density) making the system volumetric capacity a challenge. For these reasons, sodium alanate, which has received a significant amount of study to date, will not meet the DOE 2010 targets and is no longer a focus of the DOE program. However, a fundamental understanding of the mechanisms involved in doped sodium alanate materials as well as system engineering issues can be applied to the development of improved types of metal hydrides and systems.

More recently, metal hydride systems based on lithium amide are being investigated within the DOE program and by others [16,17]. In this system, the following reversible reaction takes place at 285 °C and 1 atm [16]:

$$Li_2NH + H_2 = LiNH_2 + LiH \qquad (2)$$

In this reaction, 6.5 wt.% hydrogen can be reversibly stored. However, the temperature is outside of the vehicular operating window using the waste heat of a PEM fuel cell. Methods to produce high temperature heat or a portion of the hydrogen would have to be used to drive the reaction (e.g. burned to generate the required temperature), with resultant penalty in system cost, volume, weight and efficiency. It has been found that magnesium substitution can enhance the dehydriding reaction of $LiNH_2$ [17] and lower the reaction temperature to 200 °C, although with a moderate reduction in hydrogen capacity. Another issue with the lithium/nitrogen system is that ammonia is formed as a reaction by-product during hydrogen release. In order to avoid poisoning of PEM fuel cells, ISO standards dictate that less than 0.1 ppm of ammonia is allowed in the effluent of the storage system [18]. Current research is focusing on improving the reversible hydrogen available at lower temperatures while reducing and/or eliminating ammonia formation.

Another example of a system that has received significant attention since the recent work of Vajo et al. is "destabilized" lithium borohydride ($LiBH_4$), with over 9 wt.% material capacity demonstrated [19,20]. This approach is shown in Fig. 5. The formation of dehydrogenated alloy MgB_2 can reduce the temperature for hydrogen release by approximately 240 °C as compared to pure $LiBH_4$. However, the hydrogen release or dehydrogenation temperature is still high at approximately 375 °C and the kinetics are slow. Further improvements will be pursued by nanoengineering and catalyst development.

Finally, one of the major issues with many metal hydrides, due to the reaction enthalpies involved (e.g. ∼40 kJ/mol H_2), is thermal management during refueling. Depending on the amount of hydrogen stored and refueling times required (e.g. 2010 target of 3 min for 5 kg of hydrogen), approximately 0.5–1 MW of heat must be rejected during recharging on-board vehicular systems. Reversibility and durability of these and other new materials also needs to be demonstrated for more than a thousand cycles. Issues with material handling,
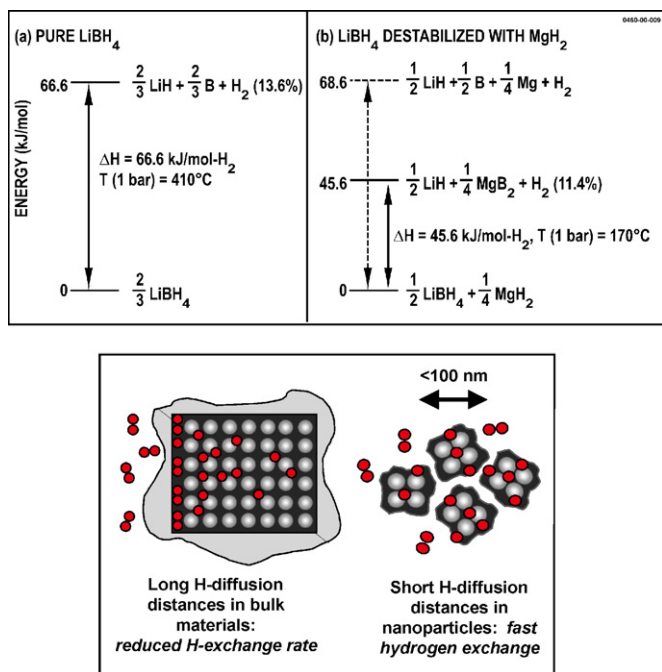
Fig. 5. Destabilization of LiBH$_4$ with MgH$_2$ [4,19,20].

pyrophoricity, and exposure to air, humidity and contaminants also need to be addressed.

5.4. High surface area sorbents and carbon-based materials

While metal hydrides offer high volumetric capacities through dissociative absorption of hydrogen, high surface area sorbents offer the advantages of fast hydrogen kinetics and low hydrogen binding energies and, hence, potentially fewer thermal management issues during hydrogen charging and discharging. Single-walled carbon nanotubes (SWNTs), among several other high surface area sorbents (e.g. carbon nanofibers, graphite materials, metal-organic frameworks, aerogels, etc.) are being studied for hydrogen storage within the DOE program and by others.

One of the issues with carbon nanotubes has been the lack of reproducibility in hydrogen storage capacity data around the world for more than a decade. A recent DOE-sponsored external peer review of hydrogen storage in single-walled carbon nanotubes has shown that experimental techniques (both temperature programmed desorption and Sievert's volumetric methods) used to quantify hydrogen storage in carbon nanotubes are reproducible. Based on experiments observed by the peer review, there was essentially no hydrogen stored on/ in pure SWNTs at room temperature, while metal alloy-doped SWNTs were observed to store 2–3 wt.% hydrogen [21]. DOE-sponsored work in this area has been expanded to include hydrogen storage in metal-doped carbon nanostructured materials, other than SWNTs, both at room temperature and at low temperature (e.g. 77 K).

Modeling of binding energies and theoretical predictions of optimum compounds for hydrogen storage are under way. For example, transition metal atoms bound to fullerenes have recently been proposed by the National Renewable Energy Laboratory (NREL) and NIST as potential adsorbents for the high density, room temperature and ambient pressure storage of hydrogen based on theoretical studies [22,23]. It is indicated that stable scandium-based organometallic buckyball full-erenes might adsorb and desorb as many as 11 hydrogen atoms per scandium atom, leading to a theoretical maximum reversible hydrogen storage density of close to 9 wt.%. Examples of these theoretical structures are shown in Fig. 6. These materials have yet to be synthesized to confirm the theoretical predictions.

6. Chemical hydrogen storage: regenerable off-board

Chemical hydrogen storage may offer options with high energy densities and potential ease of use, particularly if systems involve liquids that may be easily dispensed using infrastructure similar to today's gasoline refueling stations. Most of these reactions are irreversible, so the spent storage material would have to be regenerated off-board the vehicle because they cannot be reconstituted simply by applying an overpressure of hydrogen gas at modest temperature and pressure. A number of chemical systems, both exothermic and endothermic hydrogen release, are currently under investigation in the DOE program.

6.1. Hydrolysis reactions

Hydrolysis reactions involve the reaction of chemical hydrides with water to produce hydrogen. The reaction of sodium borohydride solutions has been the most studied to date [24]. This reaction is

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \qquad (3)$$
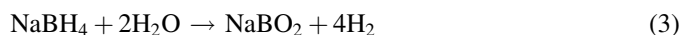
The exothermic reaction can be controlled in an aqueous medium via pH and the use of a catalyst. While the material hydrogen capacity can be high and the hydrogen release kinetics are fast, current borohydride production from borate requires multi-step conditions that are difficult on-board a vehicle and thus regeneration must take place off-board. A NaBH$_4$-based system has been reported to possess a system gravimetric capacity of approximately 4 wt.% [25]. In addition to increasing system capacity, regeneration energy requirements, novel approaches to regeneration and cost are major issues that are currently being investigated [26]. The key to successful implementation of this system centers around a more energy efficient regeneration process converting spent borate back to boron-hydride materials.

Another hydrolysis reaction that is presently being investigated is the reaction of MgH$_2$ with water, to form Mg(OH)$_2$ and H$_2$ [27]. In this case, particles of MgH$_2$ are contained in a non-aqueous slurry to inhibit premature water reaction when hydrogen generation is not required. Material-based capacities for the MgH$_2$ slurry reaction with water can be as high as 11 wt.%. However, water must also be carried on-board the vehicle in addition to the slurry and the Mg(OH)$_2$ must be regenerated off-board.
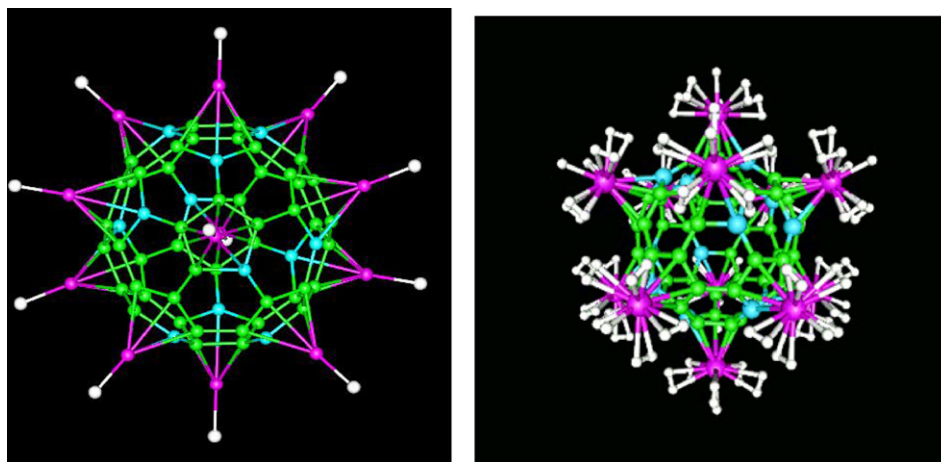
Fig. 6. Theoretical prediction of hydrogen storage in novel organometallic buckyballs [4,22].

In all these cases, it cannot be assumed that water is available from the fuel cell subsystem at all operating conditions of the vehicle. Hence the system gravimetric and volumetric capacities must include water that must be carried on-board as well as the spent fuel that may even be heavier than the starting material. Through the FreedomCAR and Fuel Partnership, a simple tool to estimate the amount of water available from the fuel cell has been developed and is available [28].

6.2. Hydrogenation/dehydrogenation reactions

The hydrogenation and dehydrogenation of organic liquids offers a potential advantage by not requiring water on-board as a co-reactant. For simple organic compounds, dehydrogenation is endothermic, so external heat must be applied. One early example is the decalin-to-napthalene reaction, which can release 7.3 wt.% hydrogen at 210 °C via the reaction [29]:

$$C_{10}H_{18} \rightarrow C_{10}H_8 + 5H_2 \qquad (4)$$

A platinum-based or other noble metal catalyst is required to enhance the kinetics of hydrogen evolution.
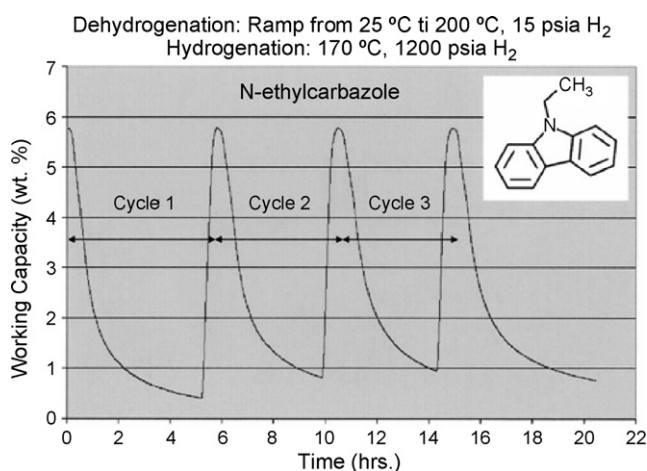

Fig. 7. Cyclic desorption of hydrogen from *N*-ethyl carbazole [4,30].

Recently, new organic liquid hydrogen storage media have been developed by Air Products [30] that demonstrate the beneficial effect of heteroatom substitution on the thermodynamics of dehydrogenation. These liquids, including an example of *N*-ethyl carbazole, have shown 5–7 wt.% gravimetric hydrogen storage capacity and greater than 0.050 kg/L hydrogen volumetric capacity (material capacities only). Fig. 7 shows the hydrogen evolution from *N*-ethyl carbazole with cycling at 197 °C. Because this hydrogen release reaction is endothermic, it can use waste heat from the fuel cell (or internal combustion engine) and on-board heat rejection may not be an issue. Furthermore, the spent fuel regeneration (hydrogenation) reaction is exothermic, so it may be possible to couple the reaction efficiently at the regeneration plant to optimize energy recovery and to reduce cost.

While hydrogenation/dehydrogenation reactions show promise, particularly in terms of ease of refueling, issues include kinetics of dehydrogenation, ensuring the required hydrogen purity levels and demonstrating the number of regeneration cycles needed to achieve the cost targets consistent with the hydrogen cost goal ($2 to $3 per kg by 2015, untaxed, delivered).

6.3. Ammonia borane and other boron hydrides

There are a number of boron hydride materials that have a high hydrogen content. Ammonia borane (AB, NH_3BH_3), is isoelectronic with ethane and has a high hydrogen storage capacity (up to 19.6 wt.% for release of three hydrogen molecules). Unlike ethane, hydrogen release from AB is exothermic. Products of dehydrogenation can include compounds such as cyclotriborazane (one hydrogen molecule released), borazine (two hydrogen molecules released), and polymeric analogues(as shown in Fig. 8). The thermodynamics of these pathways is being determined both theoretically [32] and experimentally.

Autrey and co-workers [31] have shown that incorporating solid ammonia-borane into a mesoporous silica scaffold (as shown in Fig. 9) enhances hydrogen release through the
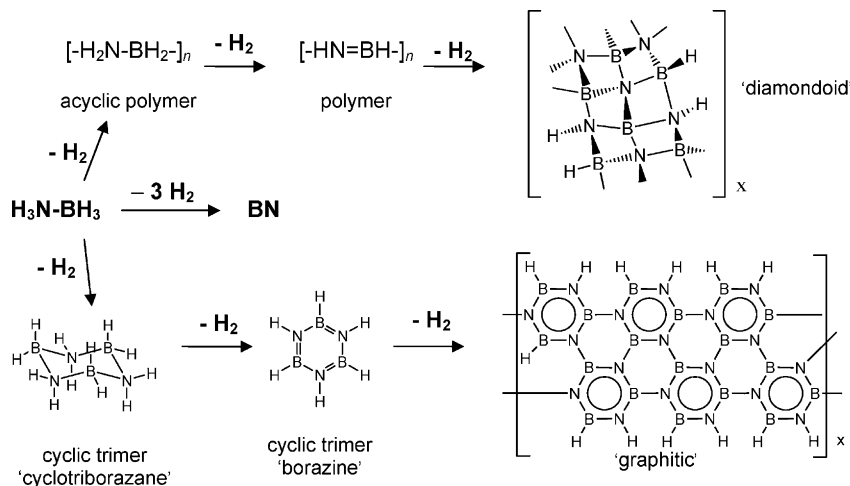
Fig. 8. Products of ammonia borane dehydrogenation [4].

formation of $(NH_2BH_2)_n$ and $(NHBH)_n$ compounds at relatively low temperature (even at 80 °C, with a 6 wt.% material capacity, including the scaffold). Due to the promise of high hydrogen storage capacity, the Chemical Hydrogen Storage Center of Excellence is developing a number of processes to release hydrogen from ammonia borane in the solid state and in solution. Catalysts, including a range of acids and transition metal

Fig. 9. Improved release of hydrogen from NH_3BN_3 via a mesoporous silica scaffold arrangement [4,31].

complexes, have been demonstrated [33,34] and are being optimized to enhance the amount of hydrogen released as well as the overall kinetics for hydrogen release. However, efficient and cost effective regeneration of the spent fuel resulting from the dehydrogenation of ammonia-borane is critical to the successful application of ammonia-borane as an on-board hydrogen storage material. Several concepts are being advanced and progress is being made towards off-board regeneration. Other boron hydride systems are also being examined.
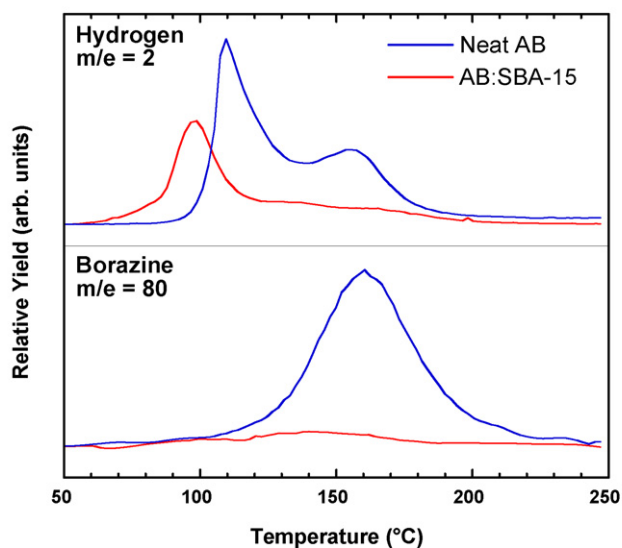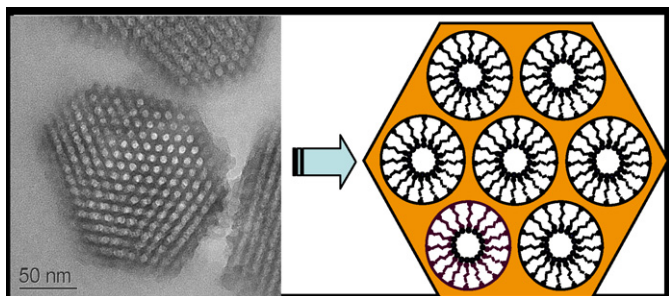
6.4. Ammonia

Ammonia, NH_3, which has a boiling point of −33.5 °C, has a high capacity for hydrogen storage, 17.6 wt.%. However, in order to release hydrogen from ammonia (an endothermic reaction), high fuel processing temperatures, and therefore large reactor mass and volume would be required. Other considerations include safety and toxicity issues, both actual and perceived, as well as the incompatibility of PEM fuel cells in the presence of trace levels of ammonia (>0.1 ppm).

Given the state-of-the-art in decomposing or 'cracking' ammonia to produce hydrogen, the total system performance of on-board ammonia reactors (weight, volume, start-up time, etc.) would not meet the requirements for commercially viable hydrogen-powered fuel cell vehicles. However, ammonia is being considered as a means for delivering hydrogen. Reforming ammonia to produce hydrogen may then take place at the refueling station or at stationary sites, without the weight and volume constraints dictated by on-board hydrogen storage. Overall well-to-wheels efficiency, emissions and cost need to be compared to other options. DOE has developed a position paper on the use of ammonia for on-board storage [35].

6.5. Alane

Alane, AlH_3, is another metal hydride being investigated as a material for hydrogen storage. The chemical formula of alane contains a theoretical 10 wt.% of H_2, and a theoretical density of hydrogen in the compound (148 g H_2/L) that is more than
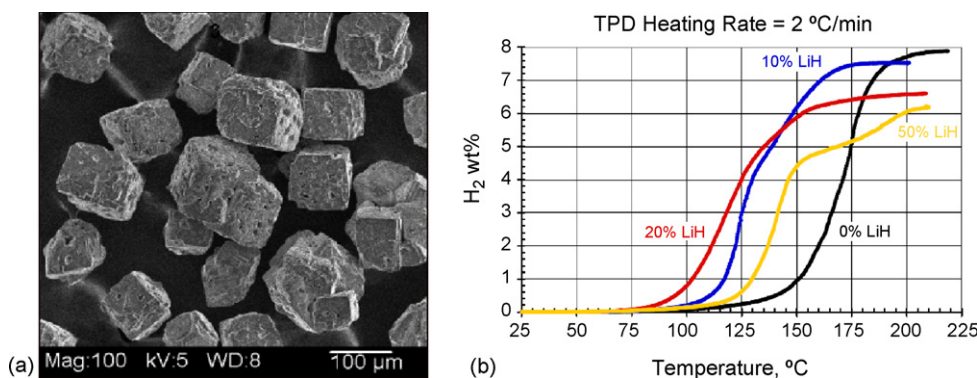
Fig. 10. (a) AlH_3 metal hydride particles and (b) H_2 desorbed vs. temperature for AlH_3 doped with LiH. The doped samples (yellow, blue, and red curves) show significantly lower temperatures of desorption than the undoped samples (black curve) [4,36]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

double the density of liquid H_2. In a collaborative effort at Brookhaven National Laboratory [36], it was found that the addition of LiH reduces the desorption temperature. As shown in Fig. 10, the onset of hydrogen desorption of alane has been lowered to below 125 °C, with hydrogen yields of 7–8 wt.% (based on material only) below 175 °C. However, in order to utilize AlH_3 as an on-board storage technology, significant issues need to be resolved. First of all, the desorption temperature should be lowered further to make the release of H_2 compatible with the waste heat generated by a PEM fuel cell system (∼80 °C). Secondly, there is no practical, low-cost method to regenerate the spent Al powder back into AlH_3. Finally, the infrastructure implications of a solid-state hydride storage option that is not rechargeable on-board the vehicle have yet to be fully explored.

7. Hydrogen storage testing and analysis

As a part of the National Hydrogen Storage Project, DOE has established activities for independent testing/validation of hydrogen storage materials as well as independent systems analyses [3,4]. Independent hydrogen storage capacity evaluations of hydrogen storage materials being developed under the project are being conducted at Southwest Research Institute. Sandia National Laboratory has built a facility to measure engineering properties, such as thermal conductivity, expansion, etc., of hydride materials and has used these data to model the heat and mass flow in hydride beds. Argonne National Laboratory has used engineering models to estimate the performance of storage technologies at an early stage of development, such as what a carbon adsorption-based fuel system might look like in terms of volume, weight and capacity. TIAX LLC has used a similar approach to benchmark a complex hydride system built by United Technologies Research Center and has made an engineering cost estimate. These system analysis studies have provided important information on the performance expected from materials currently under study. They also have provided insight into subsystem and component properties that will be needed to minimize overall system weight, volume and cost. Overall system analyses of life cycle efficiency, cost and environmental

impact are also underway and will play a key role in down-selecting hydrogen storage options.

8. International activities

A number of international collaborations focused on hydrogen storage have been supported by DOE over the years, most notably the IEA (International Energy Agency) Hydrogen Implementing Agreement's Hydrogen Storage Task 17 [37]. In June 2005 the International Partnership for the Hydrogen Economy (IPHE) organized a workshop on hydrogen storage through the DOE, the Italian Ministry of Environment and Territory, the Russian Ministry of Science and the European Commission and various topics were proposed for international collaboration in hydrogen storage [38]. The first IPHE project, led by the Russian Academy of Sciences, was established in 2005, focused on integration of solid-state hydrogen storage systems with a hydrogen fuel cell. Other large scale projects include StoreHy, with 13 countries involved in both physical as well as materials-based hydrogen storage, and NessHy, with 22 partners from 12 countries, focused primarily on solid hydrides. New projects on materials safety and testing, as well as various topics in metal hydrides, chemical hydrides and high surface area sorbents are currently under negotiation with multiple countries and expertise around the world.

9. Summary

The focus of the DOE National Hydrogen Storage Project is on materials-based technologies to meet DOE's 2010 performance targets and with potential to meet 2015 targets. It is important to emphasize that to achieve system-level capacities of 2 kWh/kg (6 wt.% hydrogen) and 1.5 kWh/L (0.045 kg hydrogen/L) in 2010, the gravimetric and volumetric capacities of the material alone must clearly be higher than the system-level targets. There are also several important targets besides weight, volume and cost, such as hydrogen charging and discharging rates, durability, safety, and operability over temperatures and pressures defined by vehicular requirements. While the long term targets represent what is required for vehicles to have similar performance to today's gasoline

internal combustion engine vehicles and for complete market penetration based on consumer demand in the North American market, it is clear that vehicles in the transition to a hydrogen economy may not require the stringent hydrogen storage requirements represented by the 2015 targets. However, it is also recognized that completely new materials with high hydrogen storage capacity have been developed in the last few years and it is still too early to select today's materials or systems as the potential hydrogen storage technology for the long term. Continued basic and applied research and development of new concepts for materials as well as systems are required. In conclusion, DOE agrees with the National Academies' recent recommendation that "…DOE should continue to elicit new concepts and ideas, because success in overcoming the major stumbling block of on-board storage is critical for the future of transportation use of fuel cells" [39].

References

[1] DOE Annual Energy Outlook, 2006, available at: http://www.eia.doe.gov/oiaf/aeo/.

[2] DOE Office of Energy Efficiency and Renewable Energy Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (http://www.eere.energy.gov/hydrogenandfuelcells/mypp), DOE Office of Fossil Energy Hydrogen from Coal Program Research, Development and Demonstration Plan (http://www.fossil.energy.gov/programs/fuels/publications/programplans/2005/Hydrogen_From_Coal_RDD_Program_Plan_Sept.pdf), DOE Office of Nuclear Energy, Science & Technology Nuclear Hydrogen R&D Plan (http://www.hydrogen.energy.gov/pdfs/nuclear_energy_h2_plan.pdf), DOE Office of Science Basic Research Needs for the Hydrogen Economy (http://www.sc.doe.gov/bes/hydrogen.pdf), and the DOE Hydrogen Program Posture Plan (http://www.hydrogen.energy.gov/pdfs/hydrogen_posture_plan.pdf) and references therein.

[3] DOE Office of Energy Efficiency and Renewable Energy Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, available at: http://www.eere.energy.gov/hydrogenandfuelcells/mypp. [2005FY] Annual Progress Report for the DOE Hydrogen Program, November 2005, available at: http://www.hydrogen.energy.gov/annual_progress05.html.

[4] S. Satyapal, C. Read, G. Ordaz, G. Thomas, DOE Hydrogen Program Annual Merit Review Proceedings (2006) http://www.hydrogen.energy.gov/annual_review06_plenary.html.

[5] http://www.eere.energy.gov/vehiclesandfuels/about/partnerships/freedomcar/index.shtml.

[6] Quantum Fuel Systems Technologies Worldwide Project Report, FY2005 Annual Progress Report for the DOE Hydrogen Program, November 2005, available at: http://www.hydrogen.energy.gov/annual_progress05_storage.html.

[7] http://www.gm.com/company/gmability/adv_tech/400_fcv/fact_sheets.html.

[8] A. Zuttel, Naturwissenschaften 91 (2004) 157.

[9] Lawrence Livermore National Laboratory Project Report, FY2005 Annual Progress Report for the DOE Hydrogen Program, November 2005, available at: http://www.hydrogen.energy.gov/annual_progress05_storage.html.

[10] R.D. McCarty, J. Hord, H.M. Roder, Selected Properties of Hydrogen (Engineering Design Data), Center for Chemical Engineering, National Engineering Laboratory, National Bureau of Standards, Boulder, Colorado, NBS Report No. 168, February 1981.

[11] R.C. Bowman Jr., B. Fultz, MRS Bulletin September 2002 (2002) 688.

[12] Sandia National Laboratories Project Report, FY2005 Annual Progress Report for the DOE Hydrogen Program, November 2005, available at: http://www.hydrogen.energy.gov/annual_progress05_storage.html.

[13] K.J. Gross, G.J. Thomas, C.M. Jensen, J. Alloys Compd. 330–332 (2002) 683.

[14] B. Bogdanovic, G. Sandrock, MRS Bulletin September 2002 (2002) 712.

[15] United Technologies Project Report, FY2005 Annual Progress Report for the DOE Hydrogen Program, November 2005, available at: http://www.hydrogen.energy.gov/annual_progress05_storage.html.

[16] P. Chen, Z. Xiong, J. Luo, J. Lin, K.L. Tan, Nature 420 (2002) 302.

[17] W. Luo, J. Alloys Compd. 381 (2004) 284.

[18] http://www.iso.org/iso/en/CatalogueDetailPage.CatalogueDetail?CSNUMBER=43994&scopelist=PROGRAMME.

[19] J.J. Vajo, et al. J. Phys. Chem. B 108 (2004) 13977.

[20] J.J. Vajo, S. Skeith, F. Mertens, J. Phys. Chem. B 109 (2005) 3719.

[21] NREL Project Report, FY2004 Annual Progress Report for the DOE Hydrogen Program, November 2004, available at: http://www.hydrogen.energy.gov/annual_progress04_storage.html#carbon.

[22] Y. Zhao, Y.-H. Kim, A.C. Dillon, M.J. Heben, S.B. Zhang, Phys. Rev. Lett. 94 (2005) 155504.

[23] T. Yildirim, S. Ciraci, Phys. Rev. Lett. 94 (2005) 175501.

[24] S.C. Amendola, et al. Int. J. Hydrogen Energy 25 (2000) 969.

[25] Millennium Cell Project Report, FY2005 Annual Progress Report for the DOE Hydrogen Program, November 2005, available at: http://www.hydrogen.energy.gov/annual_progress05_storage.html.

[26] Z.P. Li, N. Morigazaki, B.H. Liu, S. Suda, J. Alloys Compd. 349 (2003) 232.

[27] Safe Hydrogen Project Report, FY2005 Annual Progress Report for the DOE Hydrogen Program, November 2005, available at: http://www.hydrogen.energy.gov/annual_progress05_storage.html.

[28] V. Hovland, A. Pesaran, R.M. Mohring, I.A. Eason, G.M. Smith, D. Tran, R. Schaller, T. Smith, Water and Heat Balance in a Fuel Cell Vehicle with A Sodium Borohydride Hydrogen Fuel Processor, SAE Future Transportation Technology Conference, SAE Technical Paper #2003-01-2271, 2003.

[29] S. Hodoshima, H. Arai, Y. Saito, Int. J. Hydrogen Energy 28 (2003) 197.

[30] Air Products and Chemicals Project Report, FY2005 Annual Progress Report for the DOE Hydrogen Program, November 2005, available at: http://www.hydrogen.energy.gov/annual_progress05_storage.html.

[31] C. Aardahl, et al., Pacific Northwest National Laboratory, FY2005 Annual Progress Report for the DOE Hydrogen Program, November 2005, available at: http://www.hydrogen.energy.gov/annual_progress05_storage.html.

[32] D.A. Dixon, M Gutowski, Thermodynamic properties of molecular borane amines and the [BH{sub}][NH{sub 4}{sup-}] salt for chemical hydrogen storage systems from ab initio electronic structure theory, J. Phys. Chem. 109 (2005) 5129.

[33] M.E. Bluhm, M.G. Bradley, R. Butterick III, U. Kusari, L.G. Sneddon, Aminoborane based chemical hydrogen storage: enhanced ammonia borane dehydrogenation in ionic liquids, J. Am. Chem. Soc. 128 (2006) 7748–7749.

[34] M.E. Bluhm, M.G. Bradley, J.G. Sneddon, Promoted hydrogen release from aminoborane, Prepr. Sym., Am. Chem. Soc. Div. Fuel Chem. 51 (2006) 571–572.

[35] Potential Roles of Ammonia in a Hydrogen Economy: A Study of Issues Related to the Use of Ammonia for On-Board Vehicular Hydrogen Storage, U.S. Department of Energy, available at: http://www1.eere.energy.gov/hydrogenandfuelcells/hydrogen_publications.html#h2_storage.

[36] G. Sandrock, J. Reilly, J. Graetz, W.-M. Zhou, J. Johnson, J. Wegrzyn, Appl. Phys. A 80 (2005) 687.

[37] http://www.iea.org/.

[38] http://www.iphe.net/.

[39] The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs, National Research Council Report, 2004, p. 44, available at: http://www.nap.edu/catalog/10922.html.