

Materials Challenges in Alternative and Renewable Energy

Ceramic Transactions, Volume 224

A Collection of Papers Presented at the Materials Challenges in Alternative and Renewable Energy Conference February 21–24, 2010, Cocoa Beach, Florida

> Edited by George Wicks Jack Simon Ragaiy Zidan Edgar Lara-Curzio Thad Adams Jose Zayas Abhi Karkamkar Robert Sindelar Brenda Garcia-Diaz





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Preface

Materials Challenges in Alternative & Renewable Energy (Energy 2010) was an important meeting and technical forum held in Cocoa Beach, Florida, on February 21–24, 2010. This represented the second conference in a new series of intersociety meetings and exchanges, with the first of these meetings held in 2008, on "Materials Innovations in an Emerging Hydrogen Economy." The current Energy Conference- 2010 was larger in scope and content, and included 223 participants from more than 25 countries and included more than 160 presentations, tutorials and posters. The purpose of this meeting was to bring together leaders in materials science and energy, to facilitate information sharing on the latest developments and challenges involving materials for alternative and renewable energy sources and systems.

Energy 2010 marks the first time that three of the premier materials organizations in the US have combined forces, to co-sponsor a conference of global importance. These organizations included The American Ceramic Society (ACerS), ASM International, and the Society of Plastics Engineers (SPE), representing each of the materials disciplines of ceramics, metals and polymers, respectively. In addition, we were also very pleased to have the support and endorsement of important organizations such as the Materials Research Society (MRS) and the Society for the Advancement of Material and Process Engineering (SAMPE), in this endeavor.

Energy 2010 was highlighted by nine "tutorial" presentations on leading energy alternatives provided by national and international leaders in the field. In addition, the conference included technical sessions addressing state-of-the art materials challenges involved with Solar, Wind, Hydropower, Geothermal, Biomass, Nuclear, Hydrogen, and Batteries and Energy Storage. This meeting was designed for both scientists and engineers active in energy and materials science as well as those who were new to the field.

We are very pleased that ACerS is committed to running this materials-oriented conference in energy, every two years with other materials organizations. We believe the conference will continue to grow in importance, size, and effectiveness and provide a significant resource for the entire materials community and energy sector.

GEORGE WICKS Savannah River National Laboratory Energy Conference-2010 Co-Organizer/President-Elect of ACerS

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Hydrogen

HYDROGEN STORAGE TECHNOLOGIES – A TUTORIAL WITH PERSPECTIVES FROM THE US NATIONAL PROGRAM

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ABSTRACT

While the demand for electrical power generated by clean, efficient hydrogen fuel cells is rapidly growing, one of the key technical issues that remains to be resolved is the storage of hydrogen, or hydrogen-bearing fuels, to be available to the fuel cell within the design and performance constraints of the total power system. Criteria such as hydrogen storage capacity, weight, volume, lifetime and cycle-life, and certainly cost, become important factors in determining the best storage system for a particular application. In this paper we review the various storage approaches that are currently under investigation and provide a brief materials science tutorial on the storage mechanism for each approach.

Physical storage approaches store hydrogen as a compressed gas, a cryogenic liquid or as a cryo-compressed gas. Materials-based storage systems are based on storing hydrogen by adsorption, absorption or chemical bonding to various materials such as reversible or regenerable hydrides. Each of these storage systems will be discussed and the particular materials science challenges involved will be noted. At the present time no hydrogen storage approach meets all volume, weight and cost requirements for automotive fuel cell power systems across the full range of vehicle platforms. It is clear that materials science will play a key role in the ultimate solution of the hydrogen storage challenge.

INTRODUCTION

Hydrogen fuel cells are emerging as a leading candidate in the search for a clean, efficient alternate energy source. Fuel cells fueled with hydrogen are coming out of the Laboratory and moving toward commercialization in a variety of important applications. Initially fuel cells provided high-value power for both manned and unmanned spacecraft, but more recently they are being developed for "down to earth" applications such as back-up power for telecommunications and uninterrupted power systems (UPS), stationary power for residential, commercial and industrial uses, and portable power for hand-held instrumentation and military applications. Longer term transportation deployments are targeted toward the personal automobile market with specialty vehicles (e.g., forklifts), transit buses, and fleet vehicles leading with early market entry. In 2008 world-wide cumulative shipments of fuel cells exceeded 50,000 units (see Figure 1).

As hydrogen fuel cells become a viable contender in the alternative energy arena, attention is being focused on overcoming the major technical challenges that may ultimately impact introduction in potential early markets. For example, fuel cell cost is a significant factor that must be addressed for this technology to be competitive with conventional, petroleum-based power systems. Likewise the availability of hydrogen to fuel the system is a technical challenge. For the ultimate transportation application – the consumer automobile – a sufficient amount of hydrogen must be stored on-board the vehicle to allow a 300-mile driving range.



Figure 1. Worldwide Cumulative Fuel Cell Shipments. (Source Fuel Cells Today)

Hydrogen continues to receive intense study and support as a leading candidate to provide clean, safe and efficient power as an alternative to petroleum/hydrocarbon sources. Like all potential fuels hydrogen has both advantages and disadvantages. It is the lightest of all the elements. Based on its lower heating value (LHV) hydrogen has a very attractive specific energy of 120 kJ/g or 33.3 kWh/kg – approximately three times that of gasoline. Of course, with a normal boiling point of 20 K, hydrogen is a gas in its normal state with a density of ~0.09 g/L or 11 L/g. So while hydrogen has a high specific energy, due to its low density it has a normal energy density of only 10 kJ/L compared to gasoline at ~32,000 kJ/L. Therefore the challenge for hydrogen state is to increase its normal energy density, thus it is normally stored either at high pressure or as a cryogenic liquid. Its storage is further problematic due to its ability to diffuse through many containment materials and can cause embrittlement, resulting in diminished material strength and lifetime challenges. On the other hand hydrogen combustion products from fuel cells are only water and heat making it a non-polluting energy carrier. Additionally hydrogen can be derived from various liquid fuels that can be reformed either internally within or externally to the fuel cell, and it can also be produced using alternative energy sources (such as solar, wind, nuclear, etc.).

The U. S. Department of Energy has identified several key characteristics for viable hydrogen storage systems. Key storage system characteristics include: gravimetric and volumetric capacities (i.e. system weight and volume per unit H₂); operating temperature and pressure; transient response (startup and shut-down times and load following); refill time; dormancy (i.e. length of idle time before H₂ loss occurs); cycle life and costs (capital, maintenance and refueling). The actual values of these characteristics will vary depending on the specific needs of the particular application. However the most challenging requirements, by far, are those for the \geq 300-mile range, on-board hydrogen storage system for automobiles. A complete list of the DOE system performance targets for vehicular, onboard hydrogen storage can be found on the DOE website.¹ The performance targets are system targets and must be achieved simultaneously. Presently extensive research, development and testing are underway to address the challenge of hydrogen storage for fuel cell power systems. Material science is the key to the long-term development of practical hydrogen storage systems that meet the established performance and cost targets. Hydrogen storage concepts are based on physical storage systems and materials-based approaches; each is summarized in the following sections of this paper.

PHYSICAL STORAGE

Physical storage techniques generally involve storing hydrogen as a compressed gas or as a cryogenic liquid in a qualified container. High pressure storage vessels are the present state-of-the-art in hydrogen storage. Most commercially available fuel cell power systems operate on high pressure compressed hydrogen stored in certified tanks. Storage at cryogenic temperatures allows hydrogen to be stored at liquid densities and cryo-compressed storage concepts attempts to take advantage of both high pressure and cryogenic temperatures.

Compressed Storage

For compressed gas storage the higher the pressure the higher the density of stored gas. While merchant hydrogen is typically delivered for industrial uses in the pressure range from 150 to 250 bar, automotive storage systems commonly operate at 350 bar with the goal of increasing the operating pressure to 700 bar. Clearly for on-board storage the higher the pressure the greater quantity of hydrogen that can be contained in a fixed volume. However as the pressure increases the cost and weight of the storage tank increases and ultimately a point of diminishing returns is reached. The walls of all-metal storage tanks (Type I) must contain all of the stress from the high pressure, thus the wall thickness of the containment vessel increases rapidly with pressure. Since the wall thickness relates to the operating pressure and ultimate tensile and yield strength of the metal, higher strength metals could lead to lighter cylinders, however current standards and regulations limit the ultimate tensile strength of steels used in hydrogen service to 950 MPa due to hydrogen embrittlement issues.² The materials R&D challenges for all-metal hydrogen storage cylinders therefore include the development of high strength metals that are not susceptible to hydrogen storage operating conditions.

Fiber reinforced composite cylinders are also being developed for hydrogen storage. These include hoop-wrapped (Type II) and fully wrapped with either metal liners (Type III) or non-metal liners (Type IV). These composite tanks can either share the strain load between the liner and fiber layers (Type II and III) or have the fiber layer fully bear the strain load (Type IV). Composite cylinders generally allow higher pressure operation resulting in higher gravimetric capacities (>5 wt.%) compared to more conventional Type I metal vessels (typically <2 wt.%). However cost is an important issue with composite tanks and current analyses indicate approximately 75% of the cost is due to the carbon fiber layer.³ The key material R&D challenge for composite storage vessels is the development of low-cost, high-strength carbon fiber suitable for reinforcing these vessels.

Liquid Hydrogen Storage

Hydrogen for industrial applications is often transported and stored as a cryogenic liquid. Several automotive manufacturers have incorporated liquid hydrogen storage into fuel cell concept vehicles. The cryogenic temperatures (33 K hydrogen critical temperature, 20 K normal boiling point) required for liquefying hydrogen necessitates double-walled containment with multi-layer vacuum super insulation (MLVSI). These vessels are designed to minimize conductive, convective and radiative heat transfer between the inner and outer vessel walls to maximize the dormancy before pressure buildup due to boil-off causes venting and loss of hydrogen. Storage system capacities in the range of 5-6 wt.% have been projected for liquid hydrogen storage. In addition to a problem with dormancy, the energy required for hydrogen liquefaction results in an efficiency penalty that must be addressed; the total liquefaction energy is approximately 30% of the stored hydrogen energy. The development of low-cost materials of construction including super insulation is a material R&D challenge.³

Cryo-Compressed Storage

Cryo-compressed hydrogen gas storage uses temperature along with pressure to increase the density of stored hydrogen. At temperatures slightly above the critical temperature, hydrogen density increases rapidly with pressure. Densities greater than the liquid density (71 g/L) are possible with sufficiently low temperature and high pressure. Storage capacities of >6 wt.% are projected to be achievable with a doubled-walled tank with a high-pressure Type III inner vessel and MLVSI.⁴ Cryo-compressed hydrogen storage systems are similar in design to liquid storage tanks with the inclusion of a high-pressure capable inner vessel. If filled using liquid hydrogen, this storage concept still has the liquefaction energy penalty and system costs are still a significant issue. Cryogenic compatible materials of construction, including high-pressure seals, are material R&D challenges for this storage concept.

MATERIALS-BASED STORAGE

Hydrogen can be stored on the surfaces of solids (adsorption) or within solids (absorption). In adsorption, hydrogen attaches to the surface of a material either as hydrogen molecules (H_2) or hydrogen atoms (H). In absorption, hydrogen molecules dissociate into hydrogen atoms that are incorporated into the solid lattice framework. Finally, hydrogen can be strongly bound within molecular structures, as chemical compounds containing hydrogen atoms. These materials-based approaches may make it possible to store larger quantities of hydrogen in smaller volumes at low pressure and at temperatures closer to room temperature than is possible through physical storage methods. Materials for hydrogen storage being investigated include high surface area adsorbents, intermetallic hydrides, complex hydrides and chemical hydrogen storage materials, each of which will be discussed in the following sections of this paper.

Figure 2 shows the density of hydrogen at several temperature and pressure configurations and in various materials. For the materials, the densities are at near-room temperature and relatively low-pressures (0 to 1 MPa). The high hydrogen densities at low to moderate conditions of the materials shown in the middle portion of the figure clearly indicate why they are very attractive candidates for hydrogen storage.

The nature of how hydrogen is bound within materials is an important property for potential hydrogen storage materials. Storage characteristics such as hydrogen uptake and release temperatures and pressures are strongly dependent on the binding energies. For sorbents, the primary binding type is weak van der Waals attractions between the sorbent substrate and the diatomic hydrogen molecule. For carbon-based substrates the binding energy is typically 4-6 kJ per mole hydrogen, meaning there is only significant adsorption at cryogenic temperatures. The goal is to increase the binding energy to around 15-20 kJ per mole hydrogen for ambient temperature adsorption. For interstitial or intermetallic hydrides, the binding energy type is primarily metallic and a range of binding energies is possible; materials developed for most practical applications have a range of about 20 to 40 kJ per mole hydrogen. Complex hydrides generally have hydrogen covalently bonded to a metal forming a complex anion with the charged balanced by a metal cation. Some complex hydrides have additional ionic-bound hydrogen as well. The strong covalent bonds are often greater than 40 kJ per mole hydrogen, which will typically lead to high hydrogen release temperatures. Like complex hydrides, chemical hydrogen storage materials have primarily strongly covalent bound hydrogen. Since with chemical hydrogen storage materials, hydrogen is not released through equilibrium processes, the strong binding is not necessarily a disadvantage. For materials-based hydrogen storage, the key

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Figure 2. Hydrogen density at various temperatures and pressures or in various materials.

research areas include increasing the hydrogen capacity (both by weight and volume) and optimizing both the energetics and rates of hydrogen uptake and release.

Hydrogen Sorbents

Hydrogen adsorption is typically characterized by the formation of a dense physisorbed layer of diatomic hydrogen molecules on the surface of the sorbent material; thus the adsorption capacity is usually a function of the material's surface area. The increased hydrogen content of the dense surface layer over and above hydrogen gas at the corresponding pressure is known as the excess surface capacity. The total capacity is the sum of surface excess capacity plus the gas stored in the void space of a sorbent material. Research to discover effective hydrogen sorbents focuses on high surface area materials, such as various graphite nanostructures and metal-organic frameworks (MOF), as good potential candidate sorbents. Graphite nanostructures (nanotubes, nanohorns, fullerenes and aerogels), due to their lightweight and open structure (high void volume), have been studied extensively. MOFs are synthetic, highly porous, crystalline materials composed of metal clusters linked by organic molecules to form highly ordered three dimensional structures. The resulting material can have very large surface areas. Figure 3 shows a schematic of hydrogen adsorbed within MOF-74, as determined by neutron diffraction experiments, with an exceptionally high hydrogen density.⁵ In addition to traditional MOFs, there are a number of related highly ordered synthetic materials (e.g. covalent organic frameworks (COFs), porous coordination networks (PCNs), zeolitic imidazolate frameworks (ZIFs)) that are being investigated as well.

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Figure 3. Hydrogen Filling in MOF-74 (only part of the MOF-74 backbone shown, hydrogen atoms represented by the green balls).⁶

Figure 4 shows H_2 uptake as a function of pressure for a typical MOF (MOF-177). Note that the adsorption at 77 K is shown; low temperatures are required to optimize adsorption due to the low binding energy between hydrogen and the sorbent material.



Figure 4. Hydrogen Capacity of MOF-177.7

One area of active research with hydrogen sorbents is to increase the binding energy of hydrogen to the substrate from the typical binding energy of 4-6 kJ/mol of hydrogen on carbon materials to 15 kJ/mol or higher. Several approaches that are being investigated include doping of carbon structures with metals or elements such as boron; developing materials that contain unsaturated metal centers and developing materials with void spaces with narrow size distribution of specific size.⁸ While the first two approaches have been found to increase the binding energy of the initial hydrogen adsorbed, the binding typically is found to become lower as more hydrogen is adsorbed. More constant binding energy for a greater portion of the absorbed hydrogen has been found with materials with narrow pore size distribution of appropriate size.⁹ The materials R&D challenge is the development of

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new sorbent materials tailored to have high surface area and high pore volume with a narrow size distribution.

Reversible Metal Hydride Storage

Reversible interstitial or intermetallic metal hydrides are a class of metal alloys that absorb hydrogen under pressure and then release the absorbed hydrogen when the pressure is released. As shown in Figure 5, the hydriding process involves several steps: hydrogen adsorption, disassociation of the hydrogen molecule and dissolution of the hydrogen atoms into the metal lattice. Initial dissolution of hydrogen into the metal forms what is known as the -phase. As further hydrogen dissolves into the metal, a -phase nucleates and grows. The co-existence of the two phases results in a plateau in plots of isothermal measurements of the equilibrium hydrogen concentration as a function of pressure (known as PCT or PCI plots). Since an equilibrium condition exists between the free hydrogen gas and hydrogen capacity is fairly low, approximately 2 wt.% for many interstitial hydrides. The stored hydrogen capacity is fairly low, approximately 2 wt.% for many interstitial hydrides. The phase is typically characterized by an increase in the distance between metal atoms, and thus results in a swelling of the solid. Many interstitial hydrides will swell by 20-25%, which often leads to the



Figure 5. Schematic of Hydrogen Diffusion into the Lattice of a Reversible Metal Alloy.

breakdown of the solid into fine powders, a phenomenon called decrepitation. Along with system engineering challenges, material R&D challenges include the discovery of new lightweight, low-cost hydride formers that are tolerant to air exposure.

Complex Hydride Storage

Complex hydrides are materials with hydrogen covalently bonded to a metal to form a multiatom (complex) anion with an ionically-bound cation to balance the charge. For example sodium alanate (Na AlH₄) can be written $Na^+(AlH_4)^-$. The strong covalent bonds between hydrogen and the



Figure 6. Generalized enthalpy diagram showing transition between hydrogenated and dehydrogenated states and how enthalpy change is reduced through formation a binary alloy upon dehydrogenation.

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metal result in high hydrogen release temperatures. To achieve reversible hydrogen release at low to moderate temperatures requires other strategies to facilitate release from the complex hydrides. An approach that has shown promise is to alter the reaction pathway by adding additional phases so that products closer in energy to the complex hydride phase are formed on release of hydrogen. This approach is shown schematically in Figure 6. In addition to high release temperatures, complex hydrides tend to have slow sorption kinetics. The use of additives to catalyze the hydrogen uptake or release reactions has been successful in a number of complex hydrides. One of the best examples demonstrating the positive effect that an additive can have on hydrogen release from complex hydrides is the addition of titanium to sodium alanate.¹⁰ The enhanced release of hydrogen from titanium-doped sodium alanate at relatively moderate conditions has opened up new interest and activity in the discovery of new complex hydride materials along with development of appropriate additives and/or catalysis. Figure 7 shows an example of the additive effect on a metal hydride resulting in improved hydrogen release



Figure 7. Example of the Use of Additives to Destabilize Complex Hydrides¹¹

The following table compares important characteristics of representative interstitial and complex hydrides. As illustrated by the table complex hydrides demonstrate substantially higher stored hydrogen capacity and lighter weight which are attractive attributes for hydrogen storage systems. Unfortunately the complex hydrides suffer from slow hydrogen sorption rates and require

	Interstitial Hydrides	Complex Hydrides
Gravimetric capacity	1-4 wt.%	5-18 wt.%
Material bulk density	4-9 g/cc	<5 g/cc
Enthalpy (H)	<20 - >40 kJ/mol	>35 kJ/mol
Sorption kinetics	fast	Slow
Cycle-life	moderate-good	poor-moderate
Other issues	decrepitation	volatile species (e.g. B ₂ H ₆ , NH ₃)

Table I. Comparison of Interstitial Metal and Complex Hydrides for Hydrogen Storage.

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higher temperature for hydrogen release. On the other hand the interstitial metal hydrides display faster sorption kinetics and release stored hydrogen at lower temperature but suffer from low storage capacity and higher weight. Advances in materials science may improve the feasibility of both of these types of hydride materials for hydrogen storage in the future. The material R&D challenges for complex hydrides are the development light-weight, high capacity hydride materials with low sorption enthalpies and fast kinetics. Additives/dopants, and catalysis are needed that will complement the hydrogen release and sorption kinetics of the complex hydride storage materials are also needed.

Chemical Hydrogen Storage

In this concept hydrogen is released irreversibly from a hydrogen-rich storage material. Hydrogen is stored in these materials via strong chemical bonds and is released by thermal decomposition or other chemical reaction such as the catalyzed reaction of sodium borohydride with water to produce sodium borate and gaseous hydrogen. The reaction by-products must then be regenerated back to the original hydrogenated material requiring a separate process. The hydrogen release mechanisms and thermodynamics of candidate chemical hydrogen storage materials vary widely and can range from strongly exothermic (e.g., hydrolysis reactions of LiH or NaBH₄) to endothermic decomposition of liquid or solid compounds assisted by catalysis and heating. Due to their high gravimetric storage capacities (>10 wt.%) and fast desorption kinetics at near-ambient temperatures, these systems are ideal for single-use applications where disposal of the spent fuel is acceptable or in situations where efficient fuel regeneration schemes exist. The configurations of chemical hydrogen storage systems are thus highly dependent on the nature of these reactions as well as the characteristics of the materials.¹²

Research and development of these materials has focused on catalysts to control hydrogen release rate and to increase the usable hydrogen yield from the chemical reaction. Figure 8 shows catalyst development progress on a typical chemical hydrogen storage material – ammonia borane (NH_3BH_3) (AB).



Figure 8. Catalyst development has increased the kinetics for hydrogen release and enhanced the usable hydrogen obtained for AB.¹³

Likewise solvents are being studied as a means to achieve full thermal decomposition at reduced temperatures (See Figure 9). In this example the hydrogen evolution rate of the chemical

hydrogen storage material, alane – AlH₃, is shown first as a dry powder. Next the AlH₃ is dissolved in the hydrocarbon solvent, $C_{10}H_{22}O_2$, and an increase in hydrogen release is observed, particularly at lower temperature. Finally titanium is added to the mixture and a significant increase in the rate of hydrogen release is obtained. This example showing both the effect of solvents and additives on the performance of hydrogen storage materials moves toward the goal for chemical hydrogen storage materials of full decomposition of the material at reasonable, acceptable temperatures.



Figure 9. The Effect of Added Solvent on Hydrogen Release in Chemical Hydrogen Storage Materials.¹⁴

The technical issues associated with chemical hydrogen storage materials include the total cycle energy efficiency of the entire reaction process including the regeneration of the hydrogenated starting materials. Likewise the overall cost of hydrogen production/storage, again including regeneration, must be reduced so that the costs are competitive with conventional fuels. The many material R&D challenges include new high-capacity hydrogen materials, new release catalysts, and regeneration methods that are energy efficient and cost effective.

CONCLUSIONS

Figures 10 and 11 summarize the status of the state-of-the-art in hydrogen storage systems. The capacities shown are for complete systems based on experimental capacities for the basic materials. Thus engineering design and analysis has been applied to project system characteristics and properties based on the basic material measurements. The system analyses have been based on a total system capacity of 5.6 kg of hydrogen – the estimated nominal amount of hydrogen required for a 300-mile range for a conventional-type passenger automobile. The performance targets for system capacities depend strongly on the particular fuel cell system and the specific application (portable, stationary CHP, back-up, auxiliary, etc.).



Figure 10. Estimates of gravimetric capacities projected for on-board storage systems that can supply 5.6 kg of usable hydrogen (based on engineering analyses at Argonne National Laboratory).

The system capacities shown in Figures 10 and 11 include the hydrogen, storage media (i.e., metal hydrides, chemical hydrides, or sorbents), the containment vessel, as well as associated plumbing, valves, and auxiliary components required to supply hydrogen to the inlet of the fuel cell power system. The engineering assessments of these hydrogen storage systems were based on information from prototypes (when publicly available), publicly released reports and documents on candidate storage materials and schematic designs of proposed system configuration.¹⁵

The figures show a steady trend of increasing capacities resulting from the dedicated efforts of many researchers and organizations, however it is also clear that there is still considerable work to be done. While significant progress has been made in the development of hydrogen storage systems, none currently meet all of the stringent performance requirements for the most demanding applications, such as on-board vehicle storage. The materials-based approaches require further development to improve sorption kinetics, less extreme operating temperatures and pressures, and higher volumetric and gravimetric capacities. Additionally there are significant engineering challenges for the materials-based and physical storage methods, not the least of which is to reduce the costs. Material science is the key to answering the challenge of hydrogen storage and enabling the commercialization and economic and societal benefits of fuel cells as a credible alternative energy source.



Figure 11. Estimates of volumetric capacities projected for on-board storage systems that can supply 5.6 kg of usable hydrogen (based on engineering analysis at Argonne National Laboratory).

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