IV.0 Hydrogen Storage Sub-Program Overview

Introduction

Hydrogen Storage activities in Fiscal Year 2009 continue to focus on research and development (R&D) of low-pressure, materials-based technologies suitable to both stationary and transportation applications to allow for a driving range of more than 300 miles (500 km) while meeting packaging, cost, safety, and performance requirements to be competitive with current vehicles. Figure 1 shows the framework for DOE's National Hydrogen Storage Project. It includes independent projects and Centers of Excellence (CoEs) in applied hydrogen storage R&D as well as DOE Office of Science basic research in hydrogen storage. Materials projects are focused in three main areas: metal hydrides, chemical hydrogen storage materials, and hydrogen sorbents. The Hydrogen Storage Engineering CoE was initiated in FY 2009 to provide a coordinated approach to the engineering R&D of on-board storage and refueling systems; and marked an enhanced programmatic emphasis on systems integration, design, and prototype development. Accelerated and strengthened system analysis efforts in 2009, as well as the continuing activities in material chemical and environmental reactivity, are contributing to this programmatic emphasis.

DOE is continuing close coordination with other national and international efforts to leverage technical talent worldwide, to avoid duplication and to help accelerate progress in hydrogen storage R&D. Figure 2 shows the progress in collaborative activities and how DOE's applied R&D program (Office of Energy Efficiency and Renewable Energy, EERE) interfaces with key partners to enable the ultimate development of commercially viable hydrogen storage technologies.

FY 2009 also saw a continued close coordination with the DOE Office of Science basic research activity as well as growth in the applied R&D portfolio. Twenty nine fundamental studies on hydrogen



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

FIGURE 1. Framework for the U.S. National Hydrogen Storage Project



FIGURE 2. Hydrogen Storage Collaborations

storage materials are being supported by the Office of Science. Within EERE, 10 new projects competitively selected in FY 2008 that focus on both new materials and new concepts were initiated this year. The organizations (and R&D topics) were: Northwestern University (multicomponent hydride mixtures), Northwestern University (porous carbons with higher hydrogen binding energy), Ohio State University (aluminoboranes), Pennsylvania State University (hydrogen spillover materials), U.S. Borax (amine borane regeneration), University of Missouri (nanoporous monolithic carbons), University of Oregon (carbon-boron-nitrogen heterocycle materials), University of California, Los Angeles (covalent organic framework and zeolite imadazolate framework nanostructured materials), Los Alamos National Laboratory (capacitive H_2 storage with dielectrics), and Sandia National Laboratories (nanoparticle synthesis via ordered polymer templates. In summary, the storage portfolio is currently comprised of 41 universities, 15 companies and 14 federal laboratories.

Goals

The sub-program's primary objective in 2009 is to develop and demonstrate viable hydrogen storage technologies for transportation and stationary fuel cell applications. There are many requirements to achieve technical success: volume, weight, cost, durability, cycle life, and transient performance as examples. Several of the original performance targets for light-duty vehicles were revised in 2009 as scheduled based on real-world experience with hydrogen fuel cell vehicles. The original 2010 and 2015 targets are compared to the new 2010, 2015, and "Ultimate" targets in Table 1. The ultimate targets are intended to facilitate the introduction of hydrogen-fueled propulsion systems across the majority of vehicle classes and models. While these targets continue to be based upon application requirements and not current storage technology capabilities, they have been updated to account for differences in vehicle architecture between gasoline internal combustion engines and fuel cell vehicles. The revised targets are based upon the packaging, design, and fuel economy of current fuel cell vehicles. These revised targets can be found at: http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf

Although automakers have recently demonstrated progress with some vehicles that can travel more than 300 miles on a single fill, this driving range must be achievable across different vehicle models and without compromising space, performance or cost. Storage materials and concepts are needed to meet

Target	2010	2010	2015	2015	Ultimate
	old	new	old	new	new
System Gravimetric Density [% wt.] (kWh/kg)	6	4.5	9	5.5	7.5
	(2.0)	(1.5)	(3.0)	(1.8)	(2.5)
System Volumetric Density [g/L] (kWhr/L)	45	28	81	40	70
	(1.5)	(0.9)	(2.7)	(1.3)	(2.3)
System fill time for 5-kg fill [min] (kg H_2/min)	3	4.2	2.5	3.3	2.5
	(1.67)	(1.2)	(2.0)	(1.5)	(2.0)
System cost (\$/kg H ₂) (\$/kWhr _{net})	133 (4)	133* (4)*	67 (2)	67* (2)*	tbd

TABLE 1. Performance Targets as Revised in 2009

*Cost targets are still being considered as other H2-fuel call vehicle targets are assessed.

the 2015 and ultimate targets to enable market penetration of hydrogen-fueled vehicles that can achieve greater than a 300-mile driving range without compromising packaging, cost, safety, and performance.

In 2009 DOE will also address storage options to facilitate EERE objectives for deployment and market growth of fuel cell power packs for early market applications with stationary, portable, and back-up power systems. Efforts will be initiated to identify key challenges, priorities and needs for these applications.

FY 2009 Technology Status

Hydrogen storage for on-board transportation applications remains one of the most technically challenging barriers to the widespread commercialization of hydrogen vehicles. On-board hydrogen storage approaches under investigation include high capacity metal hydrides, high surface area sorbents, chemical hydrogen storage carriers, low-cost and conformable tanks, compressed/cryogenic hydrogen tanks, and new materials or processes, such as conducting polymers, spillover materials, metal organic frameworks (MOFs), and other nanostructured materials. There are two principal classes of on-board storage systems. "On-board reversible" systems can be refueled on-board the vehicle from a hydrogen supply at the fueling station. These include physical storage systems, such as compressed/ cryogenic tanks, as well as on-board reversible material systems such as metal hydrides and high surface area sorbents. "Regenerable off-board" systems involve materials that are not easily and quickly "refilled" or regenerated with hydrogen while on-board the vehicle. These include chemical hydrogen storage materials and certain metal hydrides where the temperature, pressure, kinetics, and/or energy requirements are such that the processes must be conducted off-board the vehicle.

The current storage system status values are shown relative to the revised 2015 and ultimate targets in Figure 3. The points and ranges shown are estimates provided by developers and by the R&D community and continue to be updated as new data become available. Because a very limited number of publicly available complete full-scale systems have been fabricated, most of the data shown are projections based on system design analysis or on laboratory sub-scale prototypes. Key exceptions to this are the ranges for 350 and 700 bar compressed hydrogen tanks, which show actual system data from the DOE Learning Demonstration Project, part of the Technology Validation sub-program involving 140 hydrogen fuel cell vehicles. The majority of these vehicles used 5,000 psi (350 bar) hydrogen tanks (system gravimetric and volumetric capacities of 2.8-3.8 wt% and 17-18 g/L, respectively). Over 30 demonstrations used 10,000 psi (700 bar) where the storage system capacities ranged from 2.5-4.4 wt% and 18-25 g/L. The driving range for many second generation demonstration vehicles, based on Environmental Protection Agency driving cycle data, was 196 to 254 miles. Although cryogenic systems (e.g. cryo-compressed and liquid H₂) are approaching or meeting the revised 2010 targets, it is clear that none of the current systems actually meet the combined gravimetric and volumetric system targets for 2015. It should also be reiterated that there are several other requirements such as cost, hydrogen charging and discharging rates, durability, etc., that are not illustrated in Figure 3 and that must be met simultaneously with the capacity targets.



FIGURE 3. 2009 Status of Hydrogen Storage Systems versus Revised 2015 Targets

FY 2009 Accomplishments

During FY 2009, a number of new materials were developed and the performances of earlier materials improved through the materials CoE and independent projects. Down-select decisions were made and materials eliminated based on performance criteria so that work could be focused on more promising directions. At the end of FY 2007 approximately 55 materials were considered within the Metal Hydride CoE (MHCoE) and work on about 60% of those was discontinued based on criteria developed by the MHCoE that included material reversible capacity, sorption thermodynamics and kinetics.¹ During the past year, the down selection process was continued by the MHCoE as more materials were prepared and characterized. Examples of the criteria for discontinuing evaluation of several of these materials include: unacceptably high desorption temperature (Ca(BH₄)₂); irreversibility (Na₂Zr(BH₄)₆, Li₂Zr(BH₄)₆, NaMn(BH₄)₆, LiSc(BH₄)₄); and excessive ammonia release (LiCa(BH₄)₃NH₃). The remaining hydride materials systems still under investigation by the MHCoE include: LiBH₄/MgH₂ in aerogels, LiMgN, Mg(BH₄)₂, Mg(BH₄)₂ (NH₃)₂, MgH₂-Ti, AlH₃, LiAlH₄, LiBH₄/Mg₂NiH₄, and other new systems involving combinations of NH₂, BH₄, AlH₄, and NH₃ species.

The Chemical Hydrogen Storage CoE (CHSCoE) completed an initial down-select process during FY 2008 in which more than 60 materials were evaluated and about 50% of these materials were discontinued.² This process has continued through FY 2009 with a total of about 120 material/ combinations examined and approximately 85% discontinued. Investigations of these materials or release concepts have been discontinued for reasons of low capacity, poor release kinetics, high release temperatures, or inefficient spent fuel regeneration. The remaining materials still under investigation include many derivatives of ammonia borane (AB) or mixtures of AB with additives. During FY 2009, CHSCoE research efforts have focused on improving the kinetics and capacities for hydrogen release

¹L. Klebanoff, Materials Go/No-Go Decisions Made Within the Department of Energy Metal Hydride Center of Excellence (MHCoE) In fulfillment of the end of Fiscal Year 2007 Project Milestone on Materials Down-selection, September/October 2007, published on DOE HFCIT Website, http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/mhcoe_materials_downselect_report_fy07.pdf

² "Down Select Report of Chemical Hydrogen Storage Materials, Catalysts, and Spent Fuel Regeneration Processes," May 2008, published on DOE HFCIT Website, http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/chs_coe_ down_select.pdf

through the use of catalysts and other additives for both solid and liquid phases in various AB systems. In addition, considerable effort was focused in 2009 on the continued improvement towards an energy efficient and cost-effective AB regeneration scheme. To identify areas for improvement, a major effort was made to estimate the costs for regeneration of AB from spent fuel at large-scale using the thiol process. The cost study identified the equipment and energy required for the multiple separation steps to be the dominant cost factor. Subsequently, mechanisms of various reactions of the AB regeneration process) with the potential to reduce the number of necessary separations to improve efficiency and lower costs were identified.

A down-select process was completed by the Hydrogen Sorption CoE (HSCoE) during FY 2009 on approximately 60 materials with about 40 being discontinued. A report on these results is now in preparation. In depth modeling studies were performed within the HSCoE to better characterize the hydrogen spillover process and understand the mechanisms in order to facilitate the diffusion and transfer processes between the metal catalysts and substrates. Improved capacities and kinetics were obtained in some systems although reproducibility remains a challenge that is being addressed. The maximum room temperature capacity reproduced to date for spillover on activated carbon is 1.2 wt%. New carbon materials with narrow pore size distributions (i.e., pores in range of 0.5 - 1.0 nm) and larger binding energies were prepared and evaluated.

Significant R&D is needed to modify or "tune" the properties of high hydrogen capacity materials towards the required range of operating temperature and pressure. The optimum scenario is to utilize the waste heat of the powerplant (e.g. fuel cell or internal combustion engine). For example, if H₂ could be released at acceptable rates at less than 80°C, the waste heat of the fuel cell could be utilized for endothermic desorption, i.e., avoiding the need to burn H, to generate the needed temperature. A useful alternative to the gravimetric versus volumetric capacity depiction is to show capacity as a function of temperature. Figure 4 shows the current status of materials development for the applied R&D Storage activity in terms of material-based capacity on a weight basis as a function of release or uptake temperature. The system level requirements for weight and temperatures are defined by the dashed lines (greater than 5.5 wt% and 7.5 wt% H₂ for the new 2015 and ultimate targets, respectively, and 0-100°C) to put the material-based capacities in perspective (i.e., ignoring system weight additions). The limitations in temperature are mainly due to thermodynamic properties (e.g., enthalpies or binding energies that are either too high or too low) and kinetics (e.g., hydrogen absorption or release rates are too slow at the required operating temperatures). It should also be noted that there is typically a range of temperature across which hydrogen is discharged (or charged). The values shown in Figure 4 have been updated for new candidates identified during FY 2009 and will be further modified by DOE as advancements are made in this rapidly progressing field.

Selected Examples of FY 2009 Accomplishments

Advanced Metal Hydrides

- High yields of gram quantities of pure alane (AlH₃) have been synthesized electrochemically bypassing expensive thermodynamics routes for its reversible regeneration and thereby making this hydride a more viable storage candidate. (R. Zidan, Savannah River National Laboratory member of the Metal Hydride CoE)
- A simple and energy-efficient single-stage procedure has been shown to rehydrogenate Ti-doped LiAlH₄ at ambient temperature and a moderate hydrogen pressure of 100 bars with a dimethyl ether (DME) solvent. (S. McGrady, University of New Brunswick, and C. Jensen, University of Hawaii, members of the Metal Hydride CoE) Preliminary thermodynamic analyses of the regeneration process from LiH, Al, and H₂ in the DME solvent showed the energy requirement to depend upon the molar ratio of DME to LiAlH₄ and to have the potential of achieving a 60 % well-to-tank (WTT) efficiency. (R. Ahluwalia, Argonne National Laboratory)
- A low temperature homogeneous organometallic approach has been used to incorporate about five times higher amounts of MgH₂ into carbon aerogels than was achieved via molten Mg metal. Both methods had similarly enhanced desorption kinetics compared to ball milled MgH₂ powders.



FIGURE 4. Hydrogen storage capacity for materials developed by the sub-program as a function of temperature. The open symbols represent new materials and/or data for FY 2009.

While $LiBH_4$ could be added to the aerogel after the MgH₂, the subsequent desorption behavior indicated independent decomposition of the two hydrides presumably due to separate filling of the nano-pores rather than promoting the desired destabilization reactions. Variations in the filling and processing conditions are being explored to promote simultaneous occupancy of both hydrides into the pores. (C. Jensen, University of Hawaii, and J. Vajo, HRL, members of the Metal Hydride CoE)

The aluminoborane compound AlB₄H₁₁ has been found to start releasing hydrogen at 125°C and can desorb 10.5 wt% H₂ by heating to 325°C. Substantial reversibility was also observed when TiCl₃-catalyzed AlB₄H₁₁ was exposed to ~90 bar of H₂ at 200°C. This suggests that this material and related species may be attractive candidates for on-board hydrogen storage if the reaction temperatures can be lowered. (Collaborative effort of the Metal Hydride CoE partners Ohio State University, Oak Ridge National Laboratory, Jet Propulsion Laboratory, and California Institute of Technology)

Chemical Hydrogen Storage

- A detailed cost estimate for the regeneration of AB using the current thiol-based route indicated a cost of \$7-8/kg H₂ for large-scale production. Capital equipment recovery costs and cost of utilities were found to be the dominant components and were caused by the high volume process flows and multiple separations required for this pathway. This analysis suggested substantial cost reductions may be possible via alternative chemical reactions to lower processing and separation costs. (S. Linehan, Rohm & Hass Co., a member of the Chemical Hydrogen Storage CoE)
- A new approach using hydrazine to form the BH₃-containing species may regenerate decomposed AB in just one or two steps, which would be much simpler and reduce the mass of this reductant compared to the current baseline using Bu₃Sn-H as the reductant. The estimated thermodynamic

efficiencies are 83% and 65% for the hydrazine and Bu_3Sn-H processes, respectively. (K. Ott, Los Alamos National Laboratory, member of the Chemical Hydrogen Storage CoE)

- Several approaches including scaffolds, nano-BN, methylcellulose, and metal substitutions (i.e., Li, Na) have been found to mitigate foaming during hydrogen desorption from AB. However, there are issues with excessive impurity levels (i.e., ammonia and borazine) that still need to be better controlled. (T. Autrey, Pacific Northwest National Laboratory, member of Chemical Hydrogen Storage CoE).
- Progress continued on increasing the hydrogen release rates from several ionic liquid/AB mixtures at temperatures below 120°C along with a total release that exceeded 10 wt%. A variety of catalysts were found to be effective. (L. Sneddon, University of Pennsylvania, and A. Burell, Los Alamos National Laboratory, members of the Chemical Hydrogen Storage, CoE).

Hydrogen Sorption

- Substantial efforts were devoted within the Hydrogen Sorption CoE towards gaining a better understanding of the mechanisms for the hydrogen spillover effects of metal particles on sorbent surfaces with the goal of improving both kinetics and storage capacity. Recent modeling studies have provided several new insights: (1) Hydrogen hopping between carbon surfaces is faster than diffusion on the surface; (2) Creation of holes in the valence band by either doping or defects lowers diffusion energy barriers to enable faster transport; (3) Non-precious metals components such as BC₃ can catalyze H₂ dissociation to serve as a less expensive spillover catalyst. (Hydrogen Sorption CoE members National Renewable Energy Laboratory, Air Products, and Rice University)
- A sample of Pd/Hg-doped carbon foam (CF) was reported to have an 8 wt% reversible hydrogen storage capacity at room temperature and 80 bar pressure from a collaborative assessment between the Southwest Research Institute[®] and the "Demokritos" Research Center in Greece. During the continuation of this joint study, the maximum room temperature capacity obtained on new preparations of the Pd/Hg-CF has not exceeded 2.1 wt% at 88 bar, which might be attributed to different segregation of the catalyst during processing. On the other hand, laser induced chemical desorption mass spectrometry measurements have indicated hydrogen can bind to oxygen-bearing carbons leading to water evolution during desorption. Further studies are underway to resolve this issue. (M. Miller, Southwest Research Institute[®]).
- Layered carbon structures are being explored as one means to increase the hydrogen sorption enthalpy (Δ H) from the nominal range of 4-6 kJ/mole for most carbon sorbents (i.e., activated AX-21 carbon and MOF-155) to larger values for increased adsorption above liquid nitrogen temperature. One clear example of this effect occurs with the compound CsC₂₄ where Δ H = 13 kJ/mole for a broad range of hydrogen content such that this material retained ~50 % of its 77 K capacity, which is 1.8 wt%, at 195 K. (C. Ahn, California Institute of Technology, member of the Hydrogen Sorption CoE)
- Catenation (i.e., intergrowth of two or more identical frameworks) in porous MOFs has led to a 41% improvement of apparent Langmuir surface area (3,800 m²/g for PCN-6 vs. 2,700 m²/g for PCN-6'), a 29% increase in excess gravimetric hydrogen uptake (1.74 wt% for PCN-6 vs. 1.35 wt% for PCN-6') at 77 K/760 torr, and a 263% increase in volumetric hydrogen uptake (9.19 kg/m³ for PCN-6 vs. 3.49 kg/m³ for PCN-6') in the catenation isomer pair of PCN-6/PCN-6'. In addition, increased isosteric heats of adsorption were observed with ΔH reaching 12.5 kJ/mole in some cases. (H. Zhou, Texas A&M University, member of the Hydrogen Sorption Center)

Compressed and Cryogenic Tanks

Updated projections of the performance levels and costs for high-volume (i.e., 500,000 units/yr) production levels have been made for composite tank systems with 350 bar and 700 bar gas storage at ambient temperature. These analyses included revised designs of the tank shape, changes in materials properties, and modified pressure safety factors. The gravimetric capacities for the 350 bar and 700 bar tanks rose to 5.9 wt% and 4.7 wt%, respectively, which are above or near the new 2015 target of 5.5 wt%. Although their volumetric capacities increased to 17.5 g-H₂/L and 25 g-H₂/L, they are still much lower than the 2015 target of 40 g-H₂/L. The costs of these systems

decreased to \$15.5 kWh (350 bar) and \$23.1 kWh (700 bar), which are 9-13% less than prior estimates since less carbon fiber material is required for the reduced pressure safety factors. These volumetric and costs results emphasize the need for low-pressure materials-based storage systems if targets are to be met. (TIAX, LLC and Argonne National Laboratory)

• A third generation (Gen 3) cryogenic vessel has been designed and fabricated for cryo-compressed hydrogen storage. Initial tests of the Gen 3 tank verified system capacities (7.4 wt% hydrogen and 45 g-H₂/L, exceeding the new 2015 targets); and indicated promising dormancy properties and costs relative to conventional liquid hydrogen tanks. (Lawrence Livermore National Laboratory)

Testing, Materials Properties and Analysis Cross-Cutting

- The document "*Recommended Best Practices for the Characterization of Storage Properties of Hydrogen Storage Materials*" December, 2008, was completed by K.J. Gross and K.R. Carrington and is now available. (http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/bestpractices_ h2_storage_materials.pdf) This document provides comprehensive assessments of the various volumetric and gravimetric methods that are most commonly employed to measure hydrogen storage capacities and kinetics. It addresses both the fundamentals of these techniques and issues that can arise when they are implemented for most hydrogen storage media. Hence it serves as a valuable resource for novice and experienced researchers in the hydrogen storage R&D community.
- Comprehensive analyses of performance parameters and the costs for large-scale production (i.e., 500,000 units/yr) were performed or updated on several on-board physical and chemical hydrogen storage systems. However, costs for all systems analyzed to date still greatly exceed the DOE 2010 target of \$4/kWhr reflecting the need for more innovations. (TIAX, LLC and Argonne National Laboratory)
- The WTT efficiencies for refueling several hydrogen storage systems were predicted for comparison to the DOE target of at least 60%. Estimates included: AB (~37% for the baseline regeneration process), liquid hydrogen (~40%), alane slurry (~40-55%, depending on low-grade waste heat available); the liquid carrier N-ethylcarbazole (~60%). Further analyses are in progress on alternative regeneration processes with lower energy requirements that should improve the WTT values for ammonia borane and alane. (Argonne National Laboratory)
- Three independent but coordinated projects are assessing the chemical reactivity and safety aspects of representative hydrogen storage materials (i.e., AlH₃, NaAlH₄, 2LiBH₄/MgH₂, NH₃BH₃, and the activated carbon AX-21), which correspond to the diverse range of candidates for future storage systems. Progress made during the past year encompasses qualitative and quantitative risk analyses for environmental exposures and potential accident scenarios; testing of materials properties (e.g., dust cloud flammability and pyrophoricity, reactivity during air and/or water exposures, and identification of product species formed); and development of possible mitigation methods such as fail-safe foams or organic liners that restrict air exposures in an accident. These studies have included the active participation by research groups in Canada, Germany, and Japan as part of international cooperative programs. (Savannah River National Laboratory, Sandia National Laboratory, United Technologies Research Center)

FY 2010 Plans

The technology portfolio for Hydrogen Storage emphasizes materials R&D to meet system targets for on-board applications with a focus on alternatives to high-pressure or cryogenic tanks. The three Materials CoEs will end in FY 2010 according to their five-year plans. Each center will thoroughly document and report their findings and conclusions. In particular, the performance capabilities and limitations of the various types of storage materials will be documented in order to facilitate development of viable hydrogen storage systems for vehicle and early market applications. This information will be accessible to researchers, the fuel cell industry, and the general public.

The sub-program will focus on improving material volumetric capacity, hydrogen uptake and discharge kinetics, overall system efficiency, durability and life cycle cost. The storage R&D portfolio will be adjusted to include the specification and development of advanced technologies for stationary,

portable, and back-up fuel cell power systems. The coordination with basic science, including theory, characterization and novel concepts, will continue during FY 2010.

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