

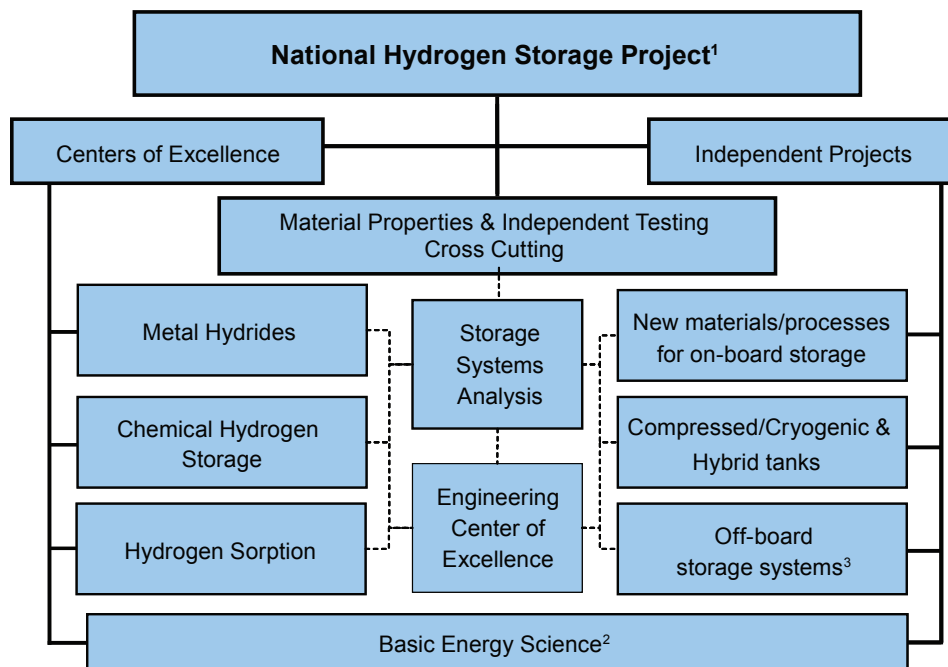
IV.0 Hydrogen Storage Sub-Program Overview

Introduction

Hydrogen storage for on-board transportation applications continues to be one of the most technically challenging barriers to the widespread commercialization of hydrogen-fueled vehicles. The Hydrogen Storage activity focuses primarily on the research and development (R&D) of low-pressure, materials-based technologies 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. While 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.

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. A new effort being initiated in Fiscal Year 2009 is the Hydrogen Storage Engineering CoE which will provide a coordinated approach to the engineering R&D of on-board storage and refueling systems. Crosscutting efforts on system analysis and material chemical and environmental reactivity are also included. In summary, the storage portfolio is comprised of approximately 47 universities, 15 companies and 14 federal laboratories.

The sub-program strongly agrees with the National Academy of Sciences' (NAS) 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."¹ This clear NAS observation is foremost in DOE's planning and execution of its storage R&D.



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

¹ The Hydrogen Economy, Opportunities, Costs, Barriers, and R&D Needs, p. 44, National Academy Press, Washington, D.C. (2004).

FY 2008 saw a continued strengthening of the applied sub-program’s portfolio and close coordination with the DOE Office of Science basic research activity. An annual solicitation is in place to ensure continued flexibility in adding promising new projects to complement the existing portfolio. As part of this annual call, ten new competitively selected individual projects were selected for negotiation of award, focusing on both new materials and new concepts. 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 H₂ storage with dielectrics), and Sandia National Laboratories (nanoparticle synthesis via ordered polymer templates).

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.

Goal

The sub-program’s overarching goal is to develop and demonstrate viable hydrogen storage technologies for transportation and stationary applications. There are many requirements to achieve technical success: volume, weight, cost, durability, cycle life, and transient performance as examples. Materials and concepts are sought to meet the 2010 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. Detailed targets can be found in the Multi-Year Research, Development and Demonstration Plan at: <http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/index.html>.

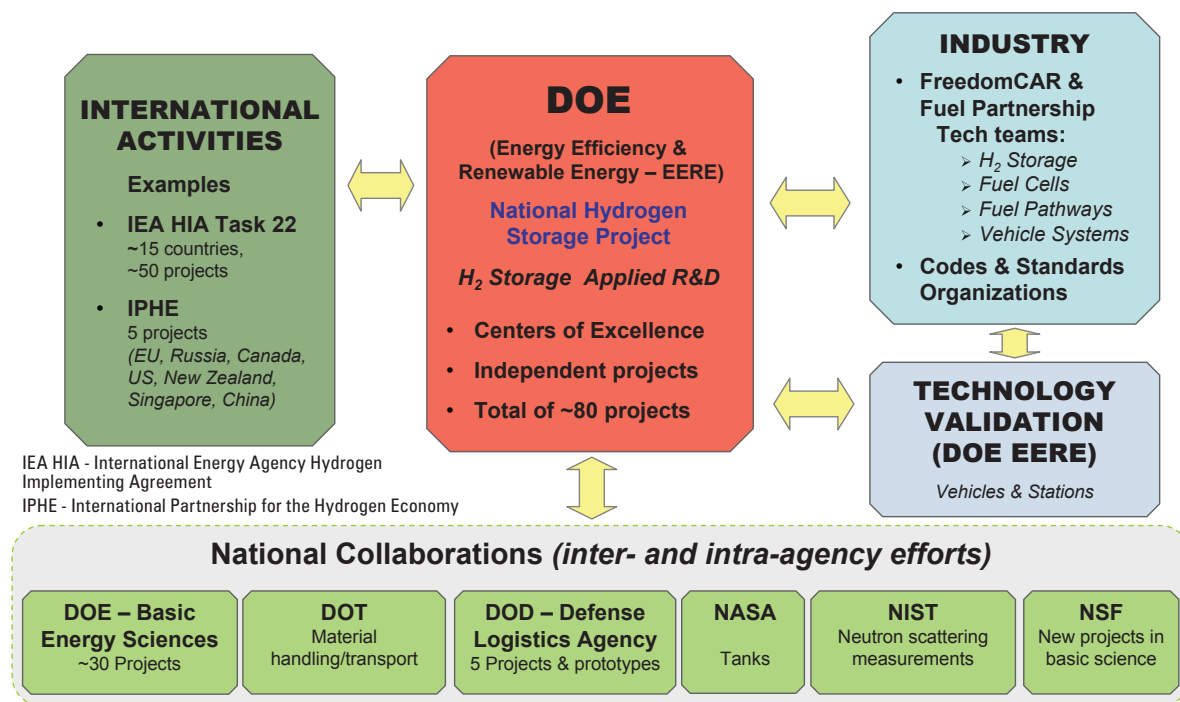


FIGURE 2. Hydrogen Storage Collaborations

FY 2008 Technology Status

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 in Figure 3. The points and ranges shown are estimates provided by developers and by the R&D community and will 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 92 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). A few 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 these demonstration vehicles, based on Environmental Protection Agency driving cycle data, was 103 to 190 miles. Although cryogenic systems (e.g. cryo-compressed and liquid H₂) are approaching the targets, it is clear that none of the current systems actually meet the combined gravimetric and volumetric system targets for 2010. 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.

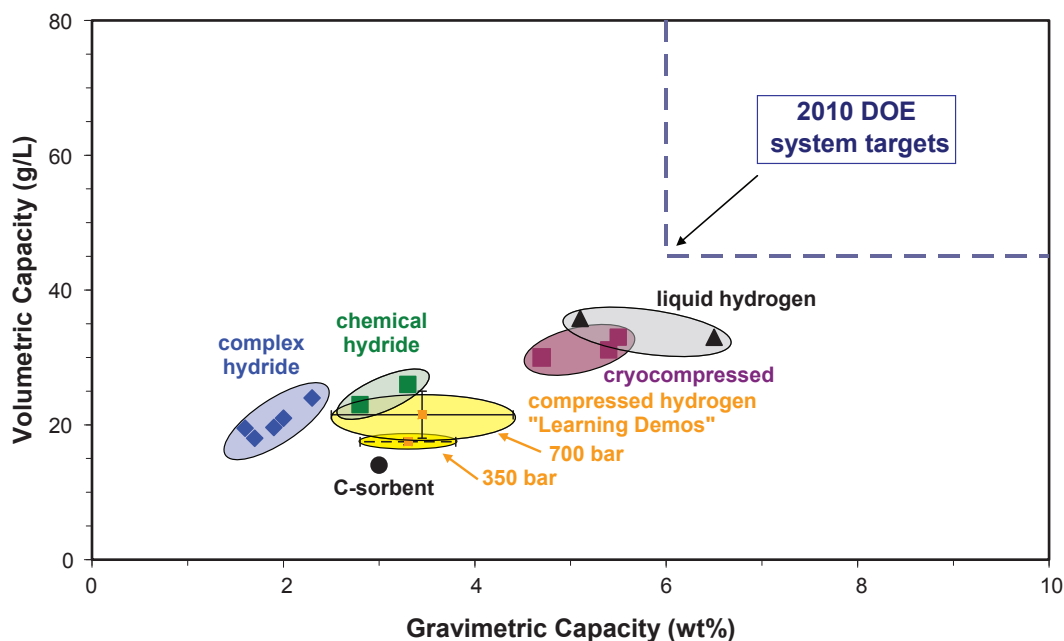


FIGURE 3. 2008 Status of Hydrogen Storage Systems versus 2010 Targets

FY 2008 Accomplishments

During FY 2008, 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 in some areas eliminating specific materials based on performance criteria so that work could be expanded in more promising directions. For example, more than 50 materials were considered within the Metal Hydride CoE (MHCoE) at the end of FY 2007, with work on about 50% of those discontinued based on criteria developed by the MHCoE that included material reversible capacity, sorption thermodynamics and kinetics.² Examples of a few of the materials discontinued are as follows (with prime criterion for discontinuation indicated): $\text{MgH}_2 + \text{Si}$ (not reversible), $2\text{LiNH}_2 + \text{MgH}_2$ (wt% limited), and $\text{Li}_2\text{Zn}(\text{BH}_4)_4$ (high diborane in desorbed H_2). Examples of materials continued include the following: $\text{LiBH}_4/\text{MgH}_2$ in aerogels, LiMgN , $\text{Li}_3\text{AlH}_6 + 3\text{LiNH}_2$, $\text{A}_x\text{Mn}(\text{BH}_4)_y$ [$\text{A}=\text{Li}, \text{Na}, \text{K}$], AlH_3 , and 22 other systems.

The Chemical Hydrogen Storage CoE also completed a down-select process during FY 2008. More than 60 materials were evaluated and about 50% of the materials were discontinued.³ The discontinued materials included endothermic imidazolines, nanoparticles and silicon clathrates, magnesium alkoxides, and polyhedral boranes. Certain hydrogen release concepts have also been discontinued, such as the use of Bronsted acid catalysis of hydrogen release from ammonia borane (AB), sub-stoichiometric $\text{LiH}/\text{ammonia borane}$ mixtures, and methylamine borane. Studies of these materials or release concepts are discontinued for reasons of either low capacity, poor release kinetics, high release temperatures, or inefficient spent fuel regeneration. Two examples of continued approaches are exothermic hydrogen release (e.g., AB, AB-scaffolds, AB-ionic liquid mixtures, and liquid amine boranes) and new materials (e.g., metal-boron-nitrogen materials) with potential thermoneutral hydrogen release reactions.

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 H_2 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_2 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 6 wt% H_2 and $0\text{--}100^\circ\text{C}$) 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 will be periodically updated by DOE as advancements are made in this rapidly progressing field.

Selected Examples of FY 2008 Accomplishments

Advanced Metal Hydrides

- In a cross-center collaborative effort, HRL and Lawrence Livermore National Laboratory have demonstrated incorporation of hydrogen storage materials, such as LiBH_4 , into carbon aerogel scaffolds with improvements in sorption properties. For example, LiBH_4 incorporated into a 13 nm scaffold achieved a 60-fold increase in desorption rates, an increase from 0.2 wt%/h for a bulk

² L. 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

³ “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

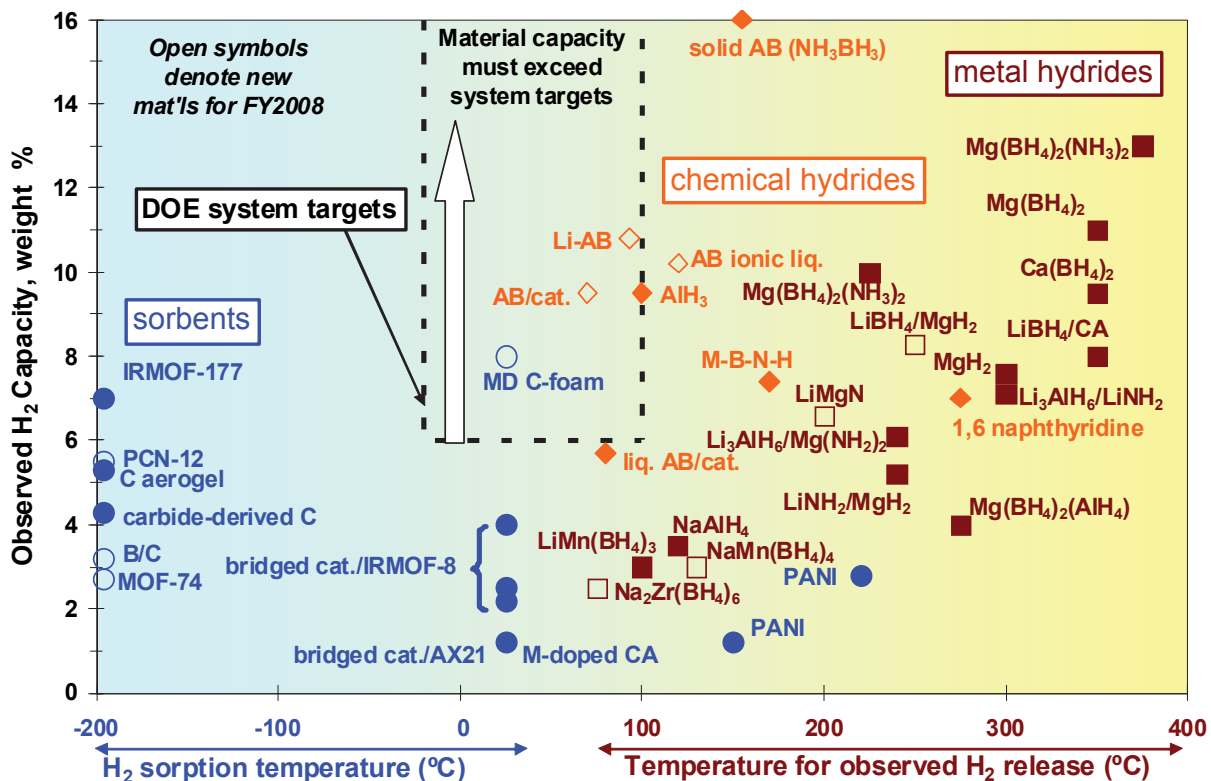


FIGURE 4. Hydrogen storage capacity for materials developed by the sub-program as a function of temperature. The open symbols represent new materials and/or data for FY 2008.

- reference sample to 12.5 wt%/h for the incorporated sample at 300°C, demonstrating that DOE rate targets could be achieved. (J. Vajo and P. Liu, HRL, member of the Metal Hydride CoE and T. Baumann, Lawrence Livermore National Laboratory, member of the Hydrogen Sorption CoE)
- Computer-based thermodynamic screening of hydriding reactions, using density functional theory, was greatly expanded during FY 2008. More than 20 million possible discreet reactant compositions have been screened to date. More than 40 single step reactions were predicted to have capacities >6 wt% H₂ with reaction enthalpies of 15-75 kJ/mol H₂. This is an example of how theoretical calculation can significantly reduce the experimental efforts required in new materials discovery research. It allows experimentalists to focus on the most promising thermodynamic options. (J.K. Johnson, University of Pittsburgh and D.S. Sholl, Georgia Tech, members of the Metal Hydride CoE)
 - An example of using the above thermodynamic predictive method during FY 2008 was the experimental confirmation of the existence and reversible H-storage properties of LiMgN. With calculated theoretical capacity of 8.2 wt% and ΔH of 34 kJ/mol H₂, LiMgN was experimentally shown to reversibly store 6.6 wt% recoverable at 200°C; see Figure 4. (Z. Fang, University of Utah, member of the Metal Hydride CoE).
 - Using nanoengineering and mechanical activation, the mixture of LiBH₄ and MgH₂ was shown to desorb 8.3 wt% H₂ at about 250°C; see Figure 4. The reaction is reversible. (L.L. Shaw, University of Connecticut)

Chemical Hydrogen Storage

- Mechanistic studies enabled the identification of non-platinum group metal heterogeneous catalysts that increased the hydrogen release rate from AB (NH₃BH₃) by a factor of two, which can meet the DOE target from a material perspective. The increased kinetics, especially for the release of the

- second equivalent of hydrogen, effectively increased the capacity to greater than 9 wt% H₂ at 70°C; AB/cat point in Figure 4. (T. Baker, Los Alamos National Laboratory, member of the Chemical Hydrogen Storage CoE)
- New metal amidoboranes (metal-boron-nitrogen compounds) that exhibit lower exothermicity of hydrogen release than AB materials were developed. They demonstrated greater than 7 wt% H₂ with rates of release meeting the DOE target from a material perspective and exhibited reduced impurities and foaming upon release of hydrogen. (A. Burrell, Los Alamos National Laboratory, T. Autrey, Pacific Northwest National Laboratory, members of the Chemical Hydrogen Storage CoE)
 - A Li-substituted AB (LiNH₂BH₃) has been synthesized and shown to desorb 10.8 wt% H₂ at 93°C; Li-AB point in Figure 4. This work was done as part of an International Partnership for the Hydrogen Economy (IPHE) collaboration. (T. Autrey, Pacific Northwest National Laboratory, member of the Chemical Hydrogen Storage CoE)
 - AB + 20% ionic liquid was demonstrated to desorb 10.8 wt% H₂ within 20 minutes at 120°C with reduced impurities and foaming; AB-ionic liquid point in Figure 4. (L. Sneddon, University of Pennsylvania, member of the Chemical Hydrogen Storage CoE)
 - Individual steps for three AB regeneration processes, each with a distinctive spent fuel digestion step using alcohol, thiol and superacid respectively, were demonstrated. Improvements were accomplished in all three spent fuel regeneration processes in yields and efficiencies resulting in overall improvements in regeneration efficiency of 22-35%. (F. Stephens, Los Alamos National Laboratory, D. Camaioni, Pacific Northwest National Laboratory, D. Dixon, University of Alabama, P. Power, University of California, Davis, L. Sneddon, University of Pennsylvania, members of the Chemical Hydrogen Storage CoE)

Hydrogen Sorption

- MOF materials with open-metal sites, designated PCN-12 and MOF-74 in Figure 4, have been demonstrated to have initial H₂ binding enthalpies of 12 and 8 kJ/mol, respectively. An activated carbon fiber material (without metal doping) was shown to have increased the initial H₂ binding enthalpy to ~10 kJ/mol through design of average pore dimensions and geometry. These binding energies may potentially increase the low-pressure H₂-capacity by up to 75% over adsorbents with typical physisorption binding enthalpies of ~5-6 kJ/mol. These tailored materials have volumetric hydrogen densities of 24-45 g/L (crystal, not system, densities). (H. Zhou, Texas A&M, formerly Miami University; C. Ahn, California Institute of Technology, members of the Hydrogen Sorption CoE; O. Yaghi, University of California, Los Angeles)
- DOE-funded work on the catalyzed “spillover” mechanism reported in FY 2007 (R. Yang, University of Michigan) has stimulated significant worldwide interest. A joint effort between Southwest Research Institute and the European Commission-funded NESSHY⁴ effort at the “Demokritos” Research Center (Greece) has led to the design of a spillover-catalyzed carbon-based foam that was reported to have 8 wt% reversible H-storage at room temperature and 80 bar pressure. While this result is preliminary, it represents a potential breakthrough in sorption materials. (M. Miller, Southwest Research Institute, Greece National Center of Scientific Research “Demokritos”)

Compressed and Cryogenic Tanks

- During FY 2008, an improved insulation method has led to doubling of the dormancy time for cryo-compressed H₂. This approach offers the advantage of higher gravimetric and volumetric densities than ambient compressed H₂ but requires an insulated container. Other than liquid H₂, this approach comes closest to meeting the DOE 2010 systems targets for weight and volume (see Figure 3). (Lawrence Livermore National Laboratory).

⁴ Novel Efficient Solid Storage for H₂ – an integrated project partly funded by the European Commission in the context of the 6th Framework Programme for Research and is coordinated by the European Research Laboratory of the National Research Center “Demokritos” and comprises a major European initiative in the field of Hydrogen Storage in Solids.

- Projected high-volume cost analyses have been made for 700 bar composite tank systems (ambient temperature). The result was on the order of \$27/kWh (~\$900/kg H₂), significantly higher than the \$4/kWh (\$133/kg) 2010 DOE targets. This clearly shows the need for new design and material approaches to lower the cost, as well as low-pressure materials technologies that constitute the primary bases of the three materials CoEs and HSECoE. (TIAX)

Testing, Materials Properties and Analysis Cross-Cutting

- A “Best Practices” document for hydrogen storage equilibrium and kinetics measurements has been completed in draft form.⁵ This document should be of considerable interest to the global hydrogen storage R&D community, especially to new researchers in the field. It communicates measurement techniques, potential issues and lessons learned. (K. Gross, H₂ Technology Consulting and P. Parilla, National Renewable Energy Laboratory)
- Three material chemical and environmental reactivity projects have made good progress to identify and quantify potential risks that may be associated with hydrogen storage materials and systems. These three projects are part of an international effort under the IPHE started in FY 2006. (Savannah River National Laboratory, Sandia National Laboratories, United Technologies Research Center)

FY 2009 Plans and Budget

The funding 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 requested EERE FY 2009 funding profile (subject to congressional appropriations), which includes the CoEs and independent projects, continues to address the NAS’ recommendations and the FreedomCAR and Fuel Partnership goals. The requested FY 2009 funding profile, shown in Figure 5, includes increased activities in all storage categories over FY 2008. It continues the materials CoEs and independent

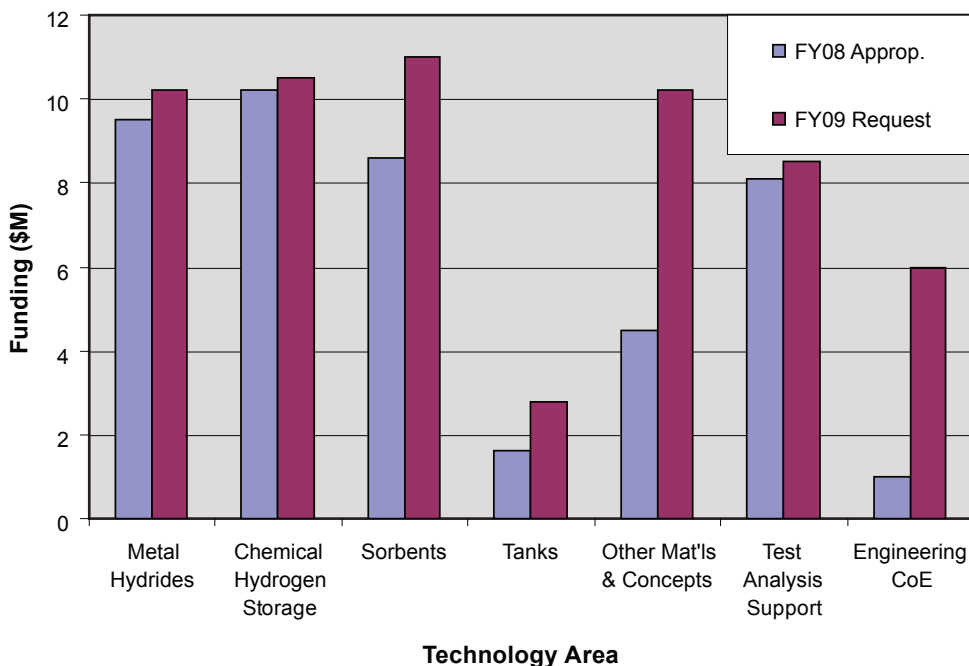
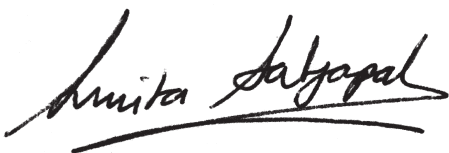


FIGURE 5. FY 2008 Funding and Planned FY 2009 Funding based on Budget Request

⁵ K.J. Gross, K.R. Carrington, Best Practices for the Characterization of Hydrogen Storage Materials, http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/bestpractices_h2_storage_materials.pdf

projects, with special emphasis on increased improvements towards all storage targets, new materials and new Hydrogen Storage Engineering CoE efforts. While most of the increased effort is on novel, potential breakthrough materials and on-board engineering system R&D, some additional funding is aimed at compressed hydrogen/cryogenic tanks with emphasis on cost reduction, novel conformable designs, and advanced tank concepts with potential to accelerate early market penetration.

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 also remain flexible to exploit new ideas and opportunities that will likely appear in FY 2009, using the annual solicitation process (subject to appropriation). The coordination with basic science, including theory, characterization and novel concepts, will continue to expand during FY 2009 via co-located contractors' meetings and jointly planned workshops.



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