IV.0 Hydrogen Storage Sub-Program Overview

The Hydrogen Storage sub-program supports research and development (R&D) of materials and technologies for compact, lightweight, and inexpensive storage of hydrogen. In Fiscal Year (FY) 2011, the sub-program continued to focus on R&D of low-pressure, materials-based technologies and engineered systems applicable to both stationary and transportation applications. Materials projects are focused in three main areas: metal hydrides, chemical hydrogen storage materials, and hydrogen sorbents. Additionally, increased efforts were directed at reducing the cost of compressed gas storage systems (i.e., physical storage) as a near-term commercialization pathway. The storage portfolio currently comprises projects involving 39 universities, 13 companies, and 14 federal laboratories and involves work in hydrogen storage materials discovery; materials-based system engineering; advanced high-pressure tank R&D; and system performance and costs analyses.

Goal

The sub-program's goal is to develop and demonstrate viable hydrogen storage technologies for transportation and early market fuel cell applications such as stationary power, backup power, and material handling equipment.

Objectives[1]

For light-duty vehicles, the key objective is 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. Although automakers have made progress in demonstrating some vehicles able to travel more than 300 miles on a single fill, using high-pressure tanks, this driving range must be achievable across different vehicle models without compromising space, performance, or cost. The sub-program's 2017 intermediate targets for transportation applications will allow some hydrogen-fueled vehicle platforms to meet customer performance expectations, while the ultimate targets are intended to facilitate the introduction of hydrogen-fueled propulsion systems across the majority of vehicle classes and models. Advanced storage materials and concepts will be needed to meet the 2017 and ultimate targets.

In pursuit of high level goals and targets for hydrogen storage, there are many requirements for achieving technical success, including improvements in volume, weight, cost, durability, cycle life, and transient performance. The full set of detailed hydrogen storage targets for light-duty vehicles can be found at: http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_on-board_hydro_storage.pdf. These targets are based on the requirements of the application—not the current status of the technologies—and they account for differences in vehicle architecture between conventional vehicles and fuel cell vehicles.

FY 2011 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 (Figure 1). There are two principal classes of on-board storage systems: "on-board reversible" systems that can be refueled onboard the vehicle from a hydrogen supply at the fueling station and "regenerable off-board" systems involving materials that are not easily and quickly "refilled" or regenerated with hydrogen while onboard the vehicle. On-board reversible systems 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 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 the vehicle.

The current projected storage system gravimetric and volumetric capacities are shown relative to the 2017 targets in Figures 2 and 3. On a routine basis the sub-program has system capacity projections made for the

[1] Note: Targets and milestones are under revision; therefore, individual progress reports may reference prior targets.

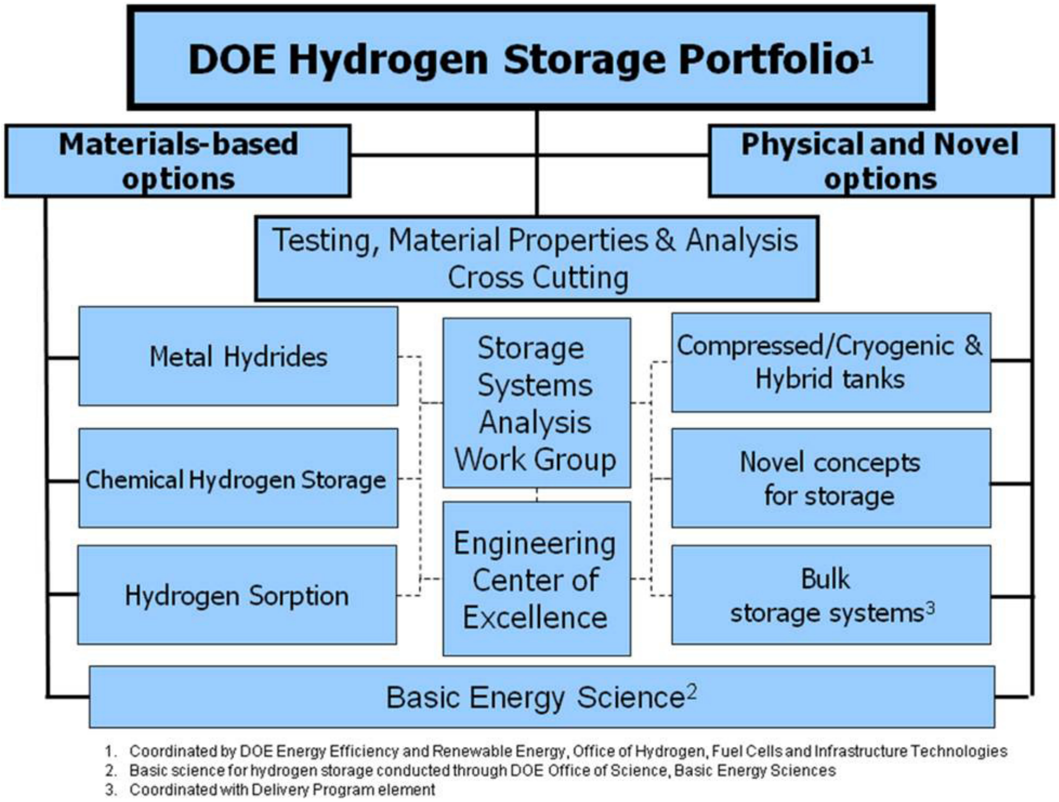
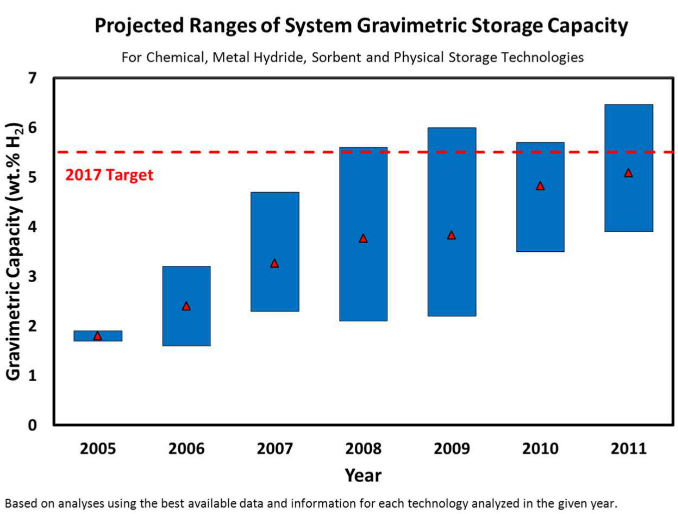
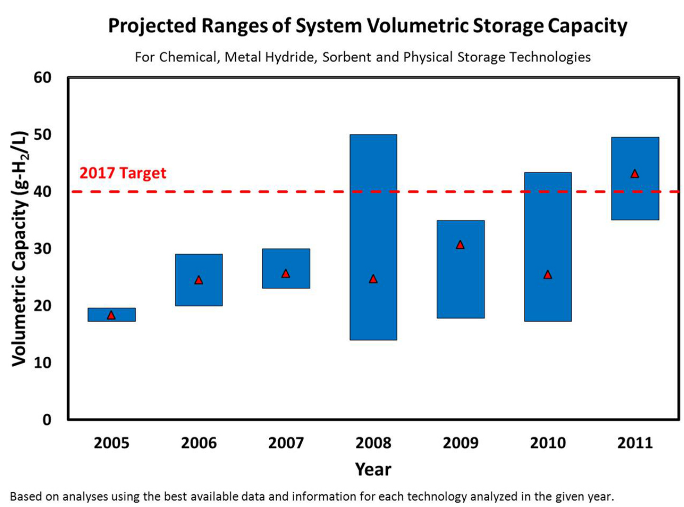


FIGURE 1. Structure of the DOE Hydrogen Storage Activities





FIGURES 2 AND 3. Status of projected hydrogen storage system gravimetric and volumetric capacities versus 2017 on-board system targets. Note that all systems were sized to provide 5.6 kg of useable hydrogen and that the plotted data points are the average value for all systems analyzed during each year while the bars correspond to the range of maximum and minimum values obtained for the year. Also note that systems with predicted capacities exceeding the gravimetric targets do not necessarily meet all other targets.

various on-board hydrogen storage technologies under development. Analytical models use the best available data for the technologies to project the gravimetric and volumetric capacities of complete storage systems that meet the required operational specifications. The capacity projections are periodically revised as new and more complete data become available and when improvements to system models are developed. Confidence in the accuracy of the projection improves with the maturity of the technology; for instance, there is higher confidence in projections for relatively mature compressed gas systems than for much less mature complex hydride systems. The range bars shown in Figures 2 and 3 represent the ranges of volumetric and gravimetric capacity projections conducted for all the on-board storage technologies during the given year. The point within the bars is the average (mean) capacity for the technologies analyzed within the given year.

FY 2011 Accomplishments

Hydrogen Storage Materials

In FY 2011, the sub-program's materials-discovery projects developed a number of new materials and improved the performance of other materials. Key accomplishments in FY 2011 include: characterization of high surface area sorbents with specific surface areas greater than 6,000 m^2 per gram and excess hydrogen sorption capacities exceeding 8% by weight at 77 K; demonstration of cycling of $Mg(BH_4)_2$ at hydrogen capacities greater than 12% by weight under high temperature and pressure conditions; demonstration of alane slurry with 60% capacity by weight and with kinetics exceeding non-slurried alane; and determination that thermal stability of ionic liquids is dominated by choice of cation.

- Metal Hydrides
  - Brookhaven National Laboratory demonstrated 6 wt% hydrogen capacity from a slurry of alane, with desorption kinetics projected to meet the DOE targets at temperatures of ~100°C.
  - Demonstrated reversibility of greater than 12 wt% for $Mg(BH_4)_2$ under high pressure and temperature (950 bar and 400°C) conditions (University of Hawaii).
  - Demonstrated 2.5 wt% reversibility between $Mg(BH_4)_2$ and the triborane ($Mg(B_3H_8)_2$) under moderate pressure and temperature (100 bar and 200°C) conditions (University of Hawaii).
  - Demonstrated that nano-confined $NaAlH_4$ undergoes a single step desorption to NaH, Al, and H_2–i.e., it does not decompose through the Na_3AlH_6 phase as does bulk $NaAlH_4$, with a measured $\Delta H°=47$ kJ mol^{-1} and $E_a = 47\text{-}53$ kJ mol^{-1}(Sandia National Laboratories).
- Chemical Hydrogen Storage Materials
  - Partially identified cation/anion selection rules for ionic liquid performance (thermal degradation) resulting in desirable liquid fuel range, and identified ionic liquids with good thermal stability (Los Alamos National Laboratory/University of Pennsylvania).
  - Experimentally determined the energetic landscape of several favorable carbon-boron-nitrogen (CBN) materials and provided a direct comparison with results from the high-level computationally predicted values (University of Oregon).
  - Synthesized the parent six-membered fully charged fuel and partially charged parent BN-indole material system for the CBN materials (University of Oregon).
  - Formulated N-H, N-tBu, and N-Me materials as liquids at around 80°C (University of Oregon).
- Hydrogen Sorption Materials
  - A highly stable porous polymer network (PPN-4) was synthesized and independently validated at Southwest Research Institute® with a Brunauer-Emmett-Teller (BET) surface area of 6,460 m^2/g and 8.3 wt% excess hydrogen adsorption capacity at 77 K and 55 bar (Texas A&M University).
  - Demonstrated spectroscopic evidence that appears to support the spillover effect, through observation of C-H bonds via both diffuse reflectance infrared Fourier transform spectroscopy measurements where Pt-C showed a unique stretch that was tentatively assigned to spillover hydrogen atoms and neutron scattering that revealed apparent hydrogen wagging modes which correlated to those energies predicted by theory (National Renewable Energy Laboratory).
  - Manufactured boron-substituted carbon by deposition and thermolysis of B10H14, resulting in a high-surface-area (BET surface area greater than 2,100 m2/g), high-boron-containing (8.6 wt% boron) material that achieved a ~30% increase in hydrogen excess absorption relative to the carbon precursor (on a per-surface-area unit basis) due to the increase in the average binding energy provided by the substituted boron.

System Engineering

In FY 2011, the Hydrogen Storage Engineering Center of Excellence (HSECoE) completed a baseline assessment of storage system models for reversible metal hydrides, cryo-sorbents, and both solid- and liquid-phase off-board regenerable chemical hydrogen storage material systems. The HSECoE assessed these models against the full set of DOE on-board storage targets. The Hydrogen Storage Simulator, which couples the onboard storage system model with fuel cell power plant and vehicle performance models, was run through various drive cycles to vary the hydrogen demand required from the storage system. The comparison of storage system performance against the DOE storage targets was factored into the decision to continue cryo-sorbent and liquid-phase chemical hydrogen storage material systems into Phase II of the HSECoE. Work on solid-phase chemical hydrogen storage will not be continued, due to the difficulties involved in moving solid material onto and off the vehicle rapidly enough to meet the refueling-time target. In addition, the HSECoE will not continue work on reversible metal-hydride storage materials, because these materials require elevated temperatures for charging and discharging and/or have high sorption enthalpies. While there are complex hydride materials that could allow a system to meet the system gravimetric target, the additional hydrogen that is required to be consumed to provide the sorption temperatures and energy means that the systems cannot meet DOE performance targets for onboard vehicle use.

- Conducted a status assessment of complete, engineered, materials-based hydrogen storage systems to meet the DOE 2010 and 2017 on-board hydrogen storage targets. The assessments were used as a basis for go/no-go decisions for continuing or not continuing engineering development of systems into Phase II of the HSECoE for the material classes. A decision was made to continue development of sorbent and fluid-phase chemical hydrogen storage systems and not to continue development reversible metal hydride and solid-phase chemical hydrogen storage material systems in Phase II of the HSECoE.
- Completed a unified model utilizing the MATLAB®/SimuLink environment that incorporates the performance demands and requirements of a vehicle powered by a fuel cell and those of a fuel cell with the hydrogen storage system, including thermal management (HSECoE).
- Demonstrated that expanded natural graphite, when added at levels as low as 5% weight fraction, effectively improves the thermal conductivity of compacted metal hydrides and simplifies heat-exchanger design (United Technologies Research Center).
- Obtained a 4X improvement in excess volumetric capacity with only ~15% reduction in gravimetric capacity for compacted MOF-5 versus powder MOF-5 (Ford).
- Validated kinetic models for ammonia borane by pressure composition isotherm measurements and larger-scale testing (Pacific Northwest National Laboratory).
- Demonstrated ability to scrub borazine and diborane from hydrogen released from ammonia borane to meet fuel cell quality specifications (Los Alamos National Laboratory).

Compressed and Cryogenic Tanks

In FY 2011, the sub-program increased its efforts on reducing the cost of compressed hydrogen gas storage tanks by initiating new efforts on low-cost, high-strength carbon fiber. Inexpensive storage vessels for compressed hydrogen gas are considered the most likely near-term hydrogen storage solution for the initial commercialization of fuel cell electric vehicles, as well as for other early market applications. Carbon fiber composites can currently contribute as much as 75% or more to the overall cost of tanks. A topic on "reducing the cost of high-pressure hydrogen storage tanks" was included in the FY 2011 Small Business Innovation Research solicitation, and two projects were selected–a project by Quantum Fuel Systems Technologies Worldwide, Inc., addressing advanced high-pressure tank manufacturing techniques and a project by Applied Nanotech, Inc., addressing alternative glass fibers and lightweight, high-strength carbon nanotube reinforced composites for tanks. Additionally the Hydrogen Storage sub-program supported an effort (co-funded with the DOE Vehicles Technology Program) at Oak Ridge National Laboratory to investigate the use of low-cost textile-grade fibers made from polyacrylic nitrile with methyl acrylate comonomer as precursors for high-strength carbon fiber production.

In February 2011, DOE held two workshops to identify strategies and R&D needs for lowering the cost of high-pressure hydrogen storage systems and to identify R&D needs and technical pathways for continued development of cryogenic storage, including both cryo-sorbent and cryo-compressed systems. The input garnered from these activities will aid in identifying key challenges, priorities, and needs for both compressed and cryogenic hydrogen storage systems and in development of future solicitations for R&D in these areas.

- Demonstrated the ability to melt-spin PAN precursor fibers with the target denier (for fibers 10 to 20 microns in diameter) with a one-step spinning/drawing process (Oak Ridge National Laboratory).

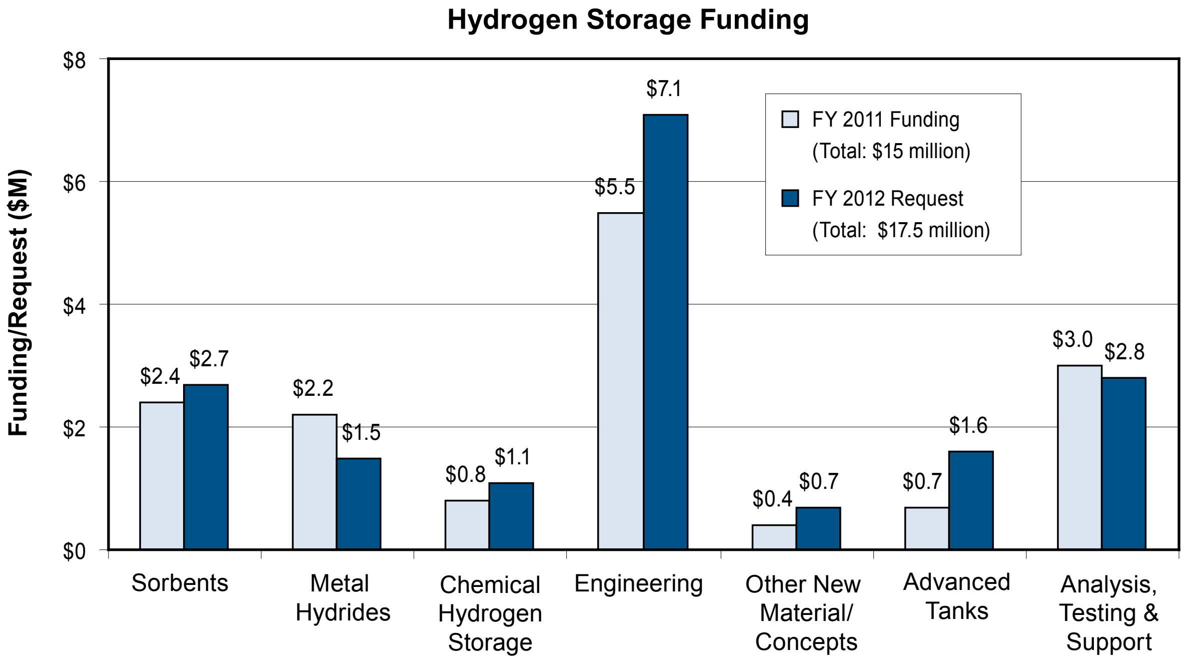
Testing, Materials Properties, and Analysis Cross-Cutting

In FY 2011, the Hydrogen Storage sub-program enlisted the National Renewable Energy Laboratory (NREL), Sandia National Laboratories (SNL), and the Pacific Northwest National Laboratory (PNNL) to carry out hydrogen storage needs assessments for non-automotive, early market applications. NREL and SNL were asked to identify the key early market applications for fuel cells where hydrogen storage presents a critical barrier for commercialization. They were also asked to determine the hydrogen storage needs for those applications and to perform gap analyses between the needs and current technologies. PNNL was asked to perform technology readiness level and manufacturing readiness level assessments of the applications and of hydrogen storage technologies these applications will require. These laboratories have gathered input (through workshops, interviews, and other activities) from stakeholders including end-users, integrators, and technology developers. The results from these assessments will be used by the sub-program to develop hydrogen storage targets, R&D plans, and future funding opportunity announcement topics for key early market applications.

- Performed system-level analysis of four hydrogen storage approaches (AX-21 and MOF-5 sorption, AB in ionic liquids, and alane), addressing capacity, charge/discharge rates, greenhouse gas emissions, safety, and cost, in addition to analysis of off-board regeneration (Argonne National Laboratory).
- Conducted and updated independent cost assessments of hydrogen storage systems using: MOF-177 sorption ($16/kWh), AX-21 sorption ($18/kWh), liquid hydrogen carriers ($16/kWh), and 350-bar ($15/kWh) and 700-bar ($19/kWh) high-pressure tanks. All of these analyses were conducted assuming systems with capacities of 5.6 kg of useable hydrogen. Also completed preliminary on-board cost assessments for 350 and 700 bar compressed single-tank systems at different manufacturing volumes–costs for the 350-bar system ranged from $15–$29 per kWh, and costs for the 700-bar system ranged from $19–$36 per kWh (TIAX, LLC).
- Three sections (Introduction, Capacity, and Kinetics) of the Best-Practices Document on the Characterization of Hydrogen Storage Materials were completed with two more sections (Thermodynamics and Cycle-Life Properties) 95% complete.
- Performed independent capacity validation of three storage materials:1) polyether ether ether ketone-derived carbon provided by State University of New York, 2) microporous carbon provided by the National Renewable Energy Laboratory, and 3) porous polymer network provided by Texas A&M University (Southwest Research Institute®).

Budget

The President's FY 2012 budget request includes $17.5 million for hydrogen storage–compared with the FY 2011 congressional appropriation of $15 million. In FY 2012, the Hydrogen Storage sub-program will continue to focus on materials discovery, system engineering for materials-based storage technologies, R&D to lower the cost of high-pressure storage systems, and systems analysis. The sub-program will also initiate activities focused on hydrogen storage for early market applications.



FY 2012 Plans

The technology portfolio for Hydrogen Storage emphasizes materials R&D to meet system targets for on-board and early market applications. While a focus on light-duty vehicle applications will continue, increased emphasis will be placed on new materials and novel concepts to meet performance requirements for early market applications. In FY 2012, goals and objectives for hydrogen storage for early market applications will be developed. The increased emphasis on developing lower-cost physical storage technologies will be strengthened. Specifically, the sub-program will use the Small Business Innovation Research program and coordinate with other efforts (e.g., DOE Vehicle Technologies Program, Defense Advanced Research Projects Agency, etc.) on development of approaches to produce low-cost carbon fiber for composite cylinders. System engineering and analysis will continue through the HSECoE and Argonne National Laboratory. Coordination with basic science efforts, including theory, characterization, and novel concepts, will continue during FY 2012. The sub-program will also coordinate with the National Science Foundation and Advanced Research Projects Agency–Energy through activities such as workshops and joint meetings.

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