Introduction

Hydrogen Storage activities in Fiscal Year (FY) 2010 continued to focus on research and development (R&D) of low-pressure, materials-based technologies applicable to both stationary and transportation applications. For transportation, 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. Materials projects are focused in three main areas: metal hydrides, chemical hydrogen storage materials, and hydrogen sorbents.

FY 2010 saw continued close coordination between the Office of Science’s basic research activities and Energy Efficiency and Renewable Energy’s (EERE’s) applied R&D portfolio. Twenty-five fundamental studies on hydrogen storage materials are being supported by the Office of Science. Within EERE, several projects were completed this past year and no new projects have been initiated. In summary, the storage portfolio currently comprises projects involving 39 universities, 13 companies, and 14 federal laboratories (Figure 1).

Goal

The sub-program’s primary goal is to develop and demonstrate viable hydrogen storage technologies for transportation and stationary fuel cell applications.

Objectives

The sub-program’s ultimate targets for transportation applications are intended to facilitate the introduction of hydrogen-fueled propulsion systems across the majority of vehicle classes and models, whereas the 2010 and 2015 intermediate targets will allow some hydrogen-fueled vehicle platforms to meet customer performance expectations. In pursuit of high-level goals and targets for hydrogen storage, there are many requirements to achieve technical success, including improvements in volume, weight, cost, durability, cycle life, and transient performance. The full set of 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.

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 without compromising space, performance, or cost. Advanced storage materials and concepts are needed to meet 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 FY 2010, the sub-program began to address storage options for stationary, portable, and backup power systems—to aid in the deployment of fuel cells in these early markets. A “hydrogen storage for early markets” topic was included in the FY 2010 Small Business Innovation Research solicitation, and a new project (at Hawaii Hydrogen Carriers LLC) on the use of low-cost metal hydrides in forklift applications was selected.

In October 2009, DOE issued a request for information to gather input from stakeholders on the requirements for fuel storage subsystems for early market fuel cell applications. In November 2009, DOE held a workshop on fuel storage requirements for early market applications. The input garnered from these activities will aid in identifying key challenges, priorities, and needs for fuel storage in early market, non-automotive applications and in development of future solicitations for research proposals in these areas.
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 the vehicle.

The current projected storage system gravimetric and volumetric capacities are shown relative to the 2010 and 2015 targets in Figures 2 and 3. On a routine basis the sub-program has system capacity projections made for the 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 on-board hydrogen 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 for all the on-board storage technologies made during the given year. The point within the bars is the average capacity (mean) for the technologies analyzed within the given year.
FIGURES 2 and 3. 2010 status of projected hydrogen storage system gravimetric and volumetric capacities versus 2010 and 2015 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 meet other targets.
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FY 2010 Accomplishments

During FY 2010, a number of new materials were developed and the performance of earlier materials improved through the three material Centers of Excellence (CoEs) and independent projects. Formal down-select reports were published for the Metal Hydride Center of Excellence (MHCoE)\(^1\) and Chemical Hydrogen Storage Center of Excellence (CHSCoE)\(^2\) in FY 2009. Through FY 2010, approximately 81 distinct materials have been considered experimentally within the MHCoE, and work on about 75% of those has been discontinued, based on criteria developed by the MHCoE—including material reversible capacity, sorption thermodynamics, and kinetics. Through FY 2010, the CHSCoE has evaluated a total of approximately 130 materials and combinations of materials; research on 95% of those has been discontinued, due to issues related to storage capacities, release temperature, kinetics, and spent-fuel regeneration. The Hydrogen Sorption Center of Excellence (HSCoE) has investigated 210 hydrogen sorbent materials through FY 2010; R&D continues on about 20% and has been discontinued on about 80% of these sorbent materials.

In FY 2010, the HSCoE published the Materials Go/No-Go Recommendation Document.\(^3\) The report gives an overview of the research strategies that the center has pursued in developing hydrogen sorbents to meet the DOE technical targets and makes recommendations on which strategies and sorbent material classes DOE should or should not continue to pursue in the future. The objective of the HSCoE has been to develop hydrogen sorbent materials that can store hydrogen at close to ambient temperature and at moderate pressure with the potential to meet the DOE system performance targets. The center’s strategy has included developing high-surface-area sorbents with high binding energy to allow closer to ambient temperature adsorption and moderate pressure. The report categorizes the sorbent materials and sorption mechanisms into four classes: physisorbsents, substituted/heterogeneous materials, multiple dihydrogen adsorption, and weak chemisorption (spillover). For pure physisorption, the center recommends continued development only on materials exceeding 2,500 m\(^2\)/g with pore sizes between 0.7 and 1.2 nm. For substituted/ heterogeneous materials, they recommend continued development of materials with properly coordinated elements in high-surface-area structures (e.g., uncoordinated metal centers in a framework material). In the area of materials with multiple dihydrogen sorption sites, experimental work is needed to synthesize materials with appropriate structures to validate theoretical predictions. Finally, for weak chemisorption materials, further research is recommended to improve reproducibility of materials synthesis and measurements, hydrogen sorption kinetics, and catalyst integration.

CoE efforts will be completed by the end of FY 2010 as planned. During this last year, much of their efforts are devoted to optimizing key parameters for the promising storage systems as well as generating required data for use by the HSECoE and analysis efforts to develop complete system models for the more promising materials. To capture the research carried out by the three CoEs and independent projects, DOE is establishing a searchable materials database. The database will be populated with material compositions, synthesis methods, measured properties, spent fuel regeneration schemes, and references. Predicted materials and properties from theoretical computational modeling will also be included. The database is expected to be available on the DOE Web site by January 2011.

Three key material properties needed for system models are the materials’ capacity, thermodynamics (e.g., heat of ad/absorption and/or heat of reaction), and sorption kinetics under different temperature and pressure conditions. Significant R&D is needed to modify or “tune” the properties of high-hydrogen-capacity materials toward the required range of operating temperatures and pressures. The optimum scenario is to utilize the waste heat of the powerplant (i.e., fuel cell or internal combustion engine). For example, if hydrogen could be released at acceptable rates at less than 80°C,

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the waste heat of the fuel cell could be utilized for endothermic desorption—avoiding the need to burn hydrogen to generate the needed temperature.

A useful alternative to depictions of gravimetric and volumetric capacity is to show capacity as a function of temperature. Figure 4 shows the current status of materials development 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 temperature are defined by the dashed lines (greater than 5.5 wt% H₂ for the 2015 target 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 temperatures across which hydrogen is discharged (or charged). The values shown in Figure 4 have been updated for new candidates identified during FY 2010 and will be further modified by DOE as advancements are made in this rapidly progressing field.

This past year the HSECoE made significant strides in developing complete system models for the three material classes and identifying engineering and material property gaps and research needs. In order to determine the impact of storage system performance on vehicle performance, the HSECoE developed the Hydrogen Storage Simulator (HSSIM) as well as a fuel cell power plant model. Preliminary models for metal hydride, chemical hydrogen, and adsorbent systems were also completed. The various models were coupled through a MATLAB/COMSOL/Simulink environment so that effects of changes in one model on the other models could be determined. For the three material classes, parametric models were identified for thermal modeling. Thermal modeling of the material based systems is critical, due to the exothermic/endothermic nature of the hydrogen uptake and release reactions. The center was also able to develop acceptability criteria for the material classes for use in selecting materials with suitable properties in on-board automotive storage systems. To establish a baseline, a well-
characterized material from each class (NaAlH₄, NH₃BH₃ and AX-21) was selected for the initial system modeling to determine current system status versus the DOE performance targets for on-board hydrogen storage. Figure 5 shows a representative spider chart for a metal hydride system. The spider chart clearly indicates areas where there are knowledge gaps (i.e., zero values) as well as engineering and material property deficiencies. For example due to the material’s low gravimetric and volumetric capacities, the system is unable to meet the gravimetric and volumetric system targets. Also, due to the combination of the material’s intrinsic uptake kinetics and the system’s heat transfer properties, the modeled system is unable to meet the refill-time target. The models can therefore be very useful in identifying areas to focus engineering R&D and material properties requiring additional development.

**FIGURE 5.** Spider chart for a representative modeled metal hydride system against the DOE 2010 system performance targets, showing technical and/or knowledge gaps in gravimetric and volumetric densities and cycle life.

**Metal Hydrides**

- Five distinct pathways for forming alane (AlH₃) from hydrogen gas and aluminum powder under relatively mild conditions were developed (Brookhaven National Laboratory).
- An electrocatalytic additive that approximately doubled the rate of electrochemical production of alane was identified (Savannah River National Laboratory [SRNL]).
- An efficient, low-temperature and low-pressure route to rehydrogenate spent LiAlH₄ in dimethyl ether was developed (University of Hawaii, University of New Brunswick).
- Stable, reversible capacity greater than 10 wt% in LiNH₂ was demonstrated through the introduction of nitrogen into the hydrogen phase (University of Nevada, Reno).
- The first example of a “kinetically coupled” destabilized system (LiBH₄/Mg₂NiH₄) with favorable thermodynamics (ΔH=15 kJ/mol H₂ and ΔS=62 J/mol H₂) was discovered (HRL Laboratories).
- Additives to increase hydrogen release rates from Mg(BH₄)₂ and 2LiNH₂/MgH₂ were developed and demonstrated (Sandia National Laboratories [SNL]).
- Improved desorption kinetics through metal hydride incorporation into aerogels were demonstrated (United Technologies Research Center, HRL Laboratories, University of Hawaii).
- Partial reversibility of several metal borohydrides under mild conditions was demonstrated (University of Hawaii).
Chemical Hydrogen Storage Materials

- Demonstrated a new ammonia borane (AB) first-fill process with higher purity and yield and completed reactor scale up capable of providing 100-gram batches of high-purity AB to center partners (Pacific Northwest National Laboratory [PNNL]).
- Significant rate enhancements with reduced borazine formation and a high mat-wt% H2-release (up to 11.4%) were achieved with 20 wt% ionic-liquid/AB mixtures at 110°C (University of Pennsylvania).
- High release rates for liquid AB at temperatures as low as 70°C with non-platinum group metal catalysts were demonstrated (Los Alamos National Laboratory [LANL]).
- Impurities and their formation rates were quantified in hydrogen released from AB, which led to demonstration that impurity formation may be mitigated through proper choice of process conditions (LANL, PNNL).
- A one-pot AB spent-fuel regeneration cycle using hydrazine was developed with an overall yield through reduction steps exceeding 90% (LANL).
- The one-pot AB spent-fuel regeneration cycle was demonstrated to work for multiple spent-fuel forms, including spent-fuel from AB in ionic liquids (LANL).
- Costs analyses were performed that indicate the one-pot AB spent-fuel regeneration cycle substantially reduces process costs but may have higher raw material costs than a previous AB spent-fuel regeneration processes (Dow).
- Resource studies were carried out that indicates the U.S. boron supply is adequate to meet boron requirements for AB fuel for projected vehicle market penetration scenarios (US Borax).
- Demonstrated syntheses of endothermic/exothermic cyclo-carbon-boron-nitrogen compounds, pathways for regeneration of spent-fuel, first-fill syntheses, and measured thermodynamic parameters that have corroborated computational studies on these molecules (University of Oregon, University of Alabama).

Hydrogen Sorption Materials

- The HSCoE Materials Go/No-Go Recommendations Report was published with five specific recommendations for continued sorption materials R&D; the report provided tabulated data on 36 specific materials the center has investigated, and research on 26 of these has been discontinued (National Renewable Energy Laboratory [NREL]).
- Boron-substituted carbon materials were synthesized and demonstrated to have increased hydrogen binding energy as a function of coverage (isosteric heats of 9–11 kJ/mol) agreeing with theory predictions (The Pennsylvania State University, University of Missouri, Air Products and Chemicals, Inc., NREL).
- Polyetheretherketone material treated with CO\textsubscript{2} and steam at 900°C was demonstrated to have greater than 5 wt% excess hydrogen adsorption capacity with a binding energy of about 8 kJ/mol at 77 K and 20 bar (Duke University).
- An isoreticular framework material (PCN-68) was synthesized with a Brunauer-Emmett-Teller surface area of 5,109 m\textsuperscript{2}/g and 7.2 wt% excess hydrogen adsorption capacity at 77 K and 50 bar (Texas A&M University).
- Cs and Rb-intercalated graphite with narrow “slit-pore” geometries of 5.3 to 5.8 Å were shown to have nearly constant isosteric heats of adsorption (at low coverage) of 14 and 12 kJ/mole (Caltech).

System Engineering

- Completed programming of HSSIM, which will improve the speed of analyses and enhance the assessment of the tradeoffs involved in the use of different technologies (NREL, Ford, General Motors).
- Coupled vehicle, fuel cell power plant, and on-board storage system models through MATLAB/COMSOL/Simulink environment so that on-board system performance impacts on vehicle...
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performance can be readily determined (NREL, Ford, General Motors, United Technologies Research Center, PNNL, SRNL).

- Developed candidate material matrix and acceptability criteria for the three material classes (LANL, United Technologies Research Center, Ford, BASF, General Motors, PNNL, L'Université du Québec à Trois-Rivières, SRNL).
- Developed and demonstrated a novel acoustic fuel gauge sensor for use with hydrides (LANL).
- Developed preliminary complete system models with baseline materials for the three material classes for comparison against DOE performance targets (LANL, PNNL, Jet Propulsion Laboratory, Caltech, L'Université du Québec à Trois-Rivières, General Motors, United Technologies Research Center, SRNL).

Compressed and Cryogenic Tanks

- Demonstrated a third generation cryogenic vessel with verified zero evaporative losses for day dormancy of more than eight days. The conversion of para-H$_2$ to ortho-H$_2$ was shown to double the dormancy for a nearly full vessel (Lawrence Livermore National Laboratory).

Testing, Materials Properties, and Analysis Cross-Cutting

- Performed system-level analysis of six hydrogen storage technologies, addressing all aspects of on-board storage targets including capacity, charge/discharge rates, greenhouse-gas emissions, safety, and cost. Technologies analyzed or updated included 350-bar and 700-bar compressed hydrogen, cryo-compressed hydrogen, liquid hydrogen, MOF-177 sorption systems, activated carbon sorption systems, and AB in ionic liquids chemical systems (Argonne National Laboratory [ANL]).
- Conducted independent cost assessments of MOF-177 sorption ($12/kWh), liquid hydrogen ($8/kWh), cryo-compressed hydrogen ($12/kWh), and 350-bar ($13/kWh) and 700-bar ($20/kWh) compressed hydrogen systems, all with 5.6 kg of useable hydrogen (TIAI LLC).
- Evaluated four potential mitigation strategies for hazards associated with flammable hydrogen storage materials; several were found to be promising (SRNL).
- Found polymer matrices to be a potential hazard mitigation strategy for materials-based systems by demonstrating a 70% reduction of heat generation and formation of little to no oxidation products when flowing air through a reactive metal hydride bed encapsulated within polystyrene (SNL).

Budget

The President's FY 2011 budget request includes $40 million for hydrogen fuel R&D, of which $20 million is planned for hydrogen storage—compared with the FY 2010 congressional appropriation of $32 million for hydrogen storage. The reduction is primarily reflected in the completion of the three materials centers that are ending in FY 2010 in accordance with their five year plan. In FY 2011 the Hydrogen Storage sub-program will continue to focus on hydrogen storage materials discovery, new concepts, and systems analysis, as well as on continued system engineering R&D. The sub-program will also consider hydrogen storage requirements for early market applications and rebalance the portfolio to address near-term and longer-term R&D needs.
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**FY 2011 Plans**

The technology portfolio for Hydrogen Storage emphasizes materials R&D to meet system targets for on-board and early market applications. The three Materials CoEs are ending in FY 2010 according to their five-year plans. In FY 2011 detailed reports of the research efforts carried out within the CoEs over their five year lives will be published and the materials data made available through an on-line searchable database. This information will be accessible to researchers, the fuel cell industry, and the general public. With the end of the three Materials CoEs, research and development on advanced hydrogen storage materials with improved material volumetric capacity, hydrogen uptake and discharge kinetics, overall system efficiency, durability, and life cycle cost will continue through independent projects. 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 2011, understanding of the hydrogen storage needs and performance requirements for early market applications will be further developed. Additionally, increased emphasis will be placed on developing lower-cost physical storage technologies that have the potential to meet customer requirements for some vehicle platforms for near-term commercialization. Specifically, the sub-program will coordinate with other efforts (e.g., Vehicle Technologies, Defense Advanced Research Projects Agency, etc.) on development of approaches to produce low-cost carbon fiber for composite cylinders. System engineering and analyses will continue through the HSECoE and ANL. Coordination with basic science efforts, including theory, characterization, and novel concepts, will continue during FY 2011. Coordination with the National Science Foundation and Advanced Research Projects Agency–Energy will also be investigated through activities such as workshops and joint meetings.