IV.0 Hydrogen Storage Sub-Program Overview

INTRODUCTION

The Hydrogen Storage sub-program supports research and development (R&D) of materials and technologies for compact, lightweight, and inexpensive storage of hydrogen for automotive, portable, and material handling equipment (MHE) applications. The Hydrogen Storage sub-program has developed a dual strategy, with a near-term focus on improving performance and lowering the cost of high-pressure compressed hydrogen storage systems and a long-term focus on developing advanced cold/cryo-compressed and materials-based hydrogen storage system technologies.

In Fiscal Year (FY) 2014, the sub-program continued its focus on development of lower-cost precursors for high-strength carbon fibers to lower the cost of high-pressure compressed hydrogen systems, system engineering for transportation applications, and advanced material R&D efforts, including for metal hydrides, chemical hydrogen storage materials, and hydrogen sorbents.

GOAL

The sub-program's goal is to develop and demonstrate advanced hydrogen storage technologies to enable successful commercialization of fuel cell products in transportation, portable, and MHE applications.

OBJECTIVES

The Hydrogen Storage sub-program's objective is to develop technologies that provide sufficient onboard hydrogen storage to allow fuel cell devices to provide the performance and run-time demanded by the application. For lightduty vehicles this means providing 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 some fuel cell electric vehicles (FCEVs) have been demonstrated to travel more than 300 miles on a single fill using high-pressure tanks, this driving range must be achievable across the full range of vehicle models without compromising space, performance, or cost. The Hydrogen Storage sub-program has developed comprehensive sets of hydrogen storage performance targets for onboard automotive, portable power, and MHE applications. The targets can be found in the *Multi-Year Research*, *Development, and Demonstration* (MYRD&D) *Plan.*¹

By 2020, the sub-program aims to develop and verify onboard automotive hydrogen storage systems achieving the following targets that will allow some hydrogen-fueled vehicle platforms to meet customer performance expectations:

- 1.8 kWh/kg system (5.5 wt%)
- 1.3 kWh/L system (0.040 kg hydrogen/L)
- \$10/kWh (\$333/kg hydrogen storage capacity)

To achieve wide-spread commercialization of hydrogen FCEVs across the full range of light-duty vehicle platforms, the sub-program has established the following onboard hydrogen storage targets to ultimately meet the needs for full fleet adoption:

- 2.5 kWh/kg system (7.5 wt%)
- 2.3 kWh/L system (0.070 kg hydrogen/L)
- \$8/kWh (\$266/kg stored hydrogen capacity)

Tables that include the complete sets of near-term and longer-term targets for onboard automotive, portable power, and MHE applications can be found in the MYRD&D Plan.

FY 2014 TECHNOLOGY STATUS AND ACCOMPLISHMENTS

The status of the various storage technologies pursued is evaluated through techno-economic analyses within individual projects, but also through independent analyses carried out for the sub-program.

¹http://energy.gov/eere/fuelcells/fuel-cell-technologies-office-multi-year-research-development-and-demonstration-plan



FIGURE 1. Projected costs in 2007\$, at various annual manufacturing volumes, for (a) 350 bar and (b) 700 bar compressed hydrogen storage systems, sized to deliver 5.6 kg of hydrogen to the vehicle fuel cell powerplant. Cost analysis performed by Strategic Analysis Inc. in 2013.

In the near term, automotive companies plan to commercialize FCEVs that use compressed hydrogen systems onboard, with system cost being one of the most important challenges to commercialization. The sub-program, working with automotive original equipment manufacturers through the United States Driving Research and Innovation for Vehicle efficiency and Energy sustainability Partnership, established onboard automotive hydrogen storage system cost targets of \$10/kWh of usable stored hydrogen to be reached by 2020, and \$8/kWh of usable stored hydrogen as an Ultimate Full Fleet target. In 2013, Strategic Analysis Inc., working with Argonne National Laboratory (ANL) and the National Renewable Energy Laboratory (NREL), using a Design for Manufacturing and Assembly (DFMA[®]) methodology, completed a thorough cost analysis for baseline Type IV 350- and 700-bar compressed hydrogen storage systems, for both single- and multi-tank configurations. Figure 1 shows the projected variable volume manufacturing costs for 700-bar, Type IV onboard systems with a 5.6 kg hydrogen usable capacity, including component breakdown costs. While the cost for the carbon fiber composite must be reduced to meet the ultimate cost targets, at lower manufacturing volumes, the cost of the balance-of-plant (BOP) components was shown to be the largest cost contributor. Therefore, in 2014, the Strategic Analysis Inc. team was tasked with carrying out a detailed failure mode and effects analysis of the BOP to understand the major cost contributors. Figure 2 shows the projected cost breakdown for 700-bar system BOP at 500,000 units per year. The piping/fittings, integrated in-tank valve, and pressure regulator were found to be the largest three cost contributors. These results will be used to develop strategies to reduce BOP costs.



IR - infrared; TPRD - temperature/pressure relief device; PRV - pressure relief valve



As a longer-term strategy, the Hydrogen Storage sub-program continues to pursue less mature hydrogen storage technologies that have the potential to satisfy all onboard hydrogen storage targets. These technologies include cold (sub-ambient temperatures as low as ~150-200 K) and cryo-compressed (temperatures <150 K) hydrogen and materials-based storage technologies. The materials-based efforts include total systems engineering and hydrogen storage materials development, including adsorbents, metal hydrides, and chemical hydrogen storage materials. A major effort in this area the last several years has been through the Hydrogen Storage Engineering Center of Excellence (HSECoE). In 2014, the HSECoE transitioned into Phase III—sub-scale system prototype development and evaluation. The Phase II-III transition decisions included the phase-out of activities on chemical hydrogen storage materials systems and continuing with prototype evaluation of two sorbent systems with differing heat exchanger design—a flow-through system with a hexagonal honey-comb aluminum (hexcell) heat exchanger and a liquid-nitrogen-cooled design with the "Module Adsorption Tank Insert" (MATI) heat exchanger. Figure 3 shows the modeled systems performance at the end of Phase II for the hexcell sorbent and alane chemical systems, respectively. Neither system is projected to meet all of the DOE targets for onboard hydrogen storage with currently available materials. However, these efforts are able to help define the material properties that are needed for a complete system to meet the targets. While the chemical systems are projected to be able to meet most of the 2020 storage targets, the decision to discontinue work on these systems was partially based on the lack of any practical materials on the foreseeable horizon available at low initial cost and with low-cost, energy-efficient regeneration processes. Therefore, it was decided to not continue towards sub-scale system prototype evaluation until materials are available that are projected to be low-cost and are able to be efficiently regenerated.

Testing & Analysis

In FY 2014, the Hydrogen Storage sub-program continued carrying out techno-economic assessments of hydrogen storage technologies. Technical analysis and cost modeling of Type IV pressure vessel systems remained a critical focus during FY 2014, with detailed analyses to determine costs for BOP components and validation of the low-volume costs through comparisons with compressed natural gas (CNG) tank data. Additionally, analyses were performed to "reverse engineer" sorbent system performance to identify adsorbent material property requirements to meet DOE system-level performance targets.



FIGURE 3. (3a) Status of projected sorbent (hexcell) and chemical hydrogen storage (50 wt% alane slurry); (3b) system performance versus 2020 onboard system targets. Note that the systems were sized to provide 5.6 kg of usable hydrogen.

Specific accomplishments include:

- Completed a DFMA[®] analysis of high-pressure (>825 bar [>12 kpsi]) and low-pressure (<28 bar [<400 psi]) hydrogen fittings and for the integrated valve.
- Validated the hydrogen pressure vessel DFMA[®] cost model at a low production rate by using it to model a CNG pressure vessel, and obtained close agreement with CNG industry quotations for the same size tank at an annual production rate of 1,000 vessels per year.

- Formulated system models and performed reverse engineering to determine thermodynamic properties of sorbent materials needed to meet onboard system and off-board well-to-engine efficiency targets. (ANL)
- The "Recommended Best Practices for the Characterization of Storage Properties of Hydrogen Storage Materials" document was completed, which now contains the following sections: Introduction, Capacity, Kinetics, Thermodynamics, Cycle-Life, Thermal Properties, and Mechanical Properties measurements. (NREL)

Advanced Physical Storage

In FY 2014, the sub-program continued to reduce the cost of compressed hydrogen gas storage tanks with efforts focused on low-cost, high-strength carbon fiber precursors and advanced tank designs. Lightweight compressed gas storage vessels requiring a composite overwrap to contain hydrogen gas are considered the most likely near-term hydrogen storage solution for the initial commercialization of FCEVs, as well as for other early market applications. Carbon fiber composite overwraps can currently contribute as much as 75% or more to the overall cost of advanced Type IV tanks. The Hydrogen Storage sub-program supported efforts at the Oak Ridge National Laboratory (ORNL) to reduce the cost of polyacrylonitrile (PAN)-based fibers used as precursors to produce high-strength carbon fibers. ORNL efforts focused on advanced precursor materials and processing since precursors have been shown to contribute over 50% of the total cost of high-strength carbon fibers. The team investigated the use of low-cost textilegrade fibers made from PAN blended with a methyl acrylate comonomer (PAN-MA) as lower-cost precursors and continued to improve on the development of melt-spinnable PAN precursors and processing techniques to replace the current more costly wet processing methods. Additionally, a team led by the Pacific Northwest National Laboratory (PNNL) focused on reducing the cost of a Type IV tank system by developing novel alternative resins and resin matrix modification, modifying the carbon fiber surface to improve composite translational efficiency, developing methods for alternative fiber placement and enhanced operating conditions that demonstrated routes to increase carbon fiber usage efficiency.

One new Small Business Innovation Research Phase II award was made that focuses on a graded construction approach of using a lower-cost, lower-performance carbon fiber in the outer layers where fibers are exposed to lower stress due to the thick wall effect with 700-bar Type IV tanks. Three new sub-program awards were made:

- Materia Inc. will investigate use of a low-viscosity resin and a vacuum-assisted resin transfer molding process as alternatives to the traditional epoxy resin and wet-wind manufacturing process for Type IV tanks.
- PPG Industries Inc. will investigate the production scale-up of an ultra-high-strength glass fiber (≥5,500 MPa) and evaluate its performance in composites and a low-cost alternative to carbon fiber in Type III and IV tanks.
- Sandia National Laboratories (SNL) will screen alternative metal alloys for use in place of 316/316L stainless steel for materials of construction in balance of plant and other hydrogen applications, leading to lower costs and lower mass.

Specific accomplishments include:

- Increased tensile strength from 405 KSI to 649 KSI and tensile modulus from 33 MSI to 38 MSI for carbon fibers produced from PAN-MA precursor fibers manufactured on high-volume textile lines. (ORNL)
- Projected a 52% mass reduction and 30% cost reduction in compressed hydrogen storage systems with 5.6 kg hydrogen usable capacity, at 500 bar and cold (approximately 200 K) operating conditions, compared to baseline 700-bar ambient systems. (PNNL)
- Initiated preliminary testing of the liquid hydrogen cryo-pump installation, with 875-bar capability. (Lawrence Livermore National Laboratory, LLNL)
- Carried out initial testing of thermotropic liquid crystal polymers as potential load-bearing, thermally conducting liner materials as an alternative to high-density polyethylene liners and with potential to reduce carbon fiber composites in Type IV tanks. (Savannah River National Laboratory, SRNL)

Advanced Materials Development

In FY 2014, the sub-program continued efforts in developing and improving hydrogen storage materials with potential to meet the 2020 onboard storage targets in addition to the 2015 portable power and MHE targets. In the area of metal hydrides, efforts emphasized material discovery coupled with reducing desorption temperatures and improving kinetics. For chemical hydrogen storage materials, much of the focus was on developing reversible or

regenerable liquid-phase materials, and also increasing efficiency of regeneration routes for solid-phase materials. For hydrogen sorbents, efforts were focused on increasing the isosteric heat of adsorption, mainly through inclusion of open metal centers or boron doping, to increase the adsorbed capacity at higher temperatures and improving standard measurement practices for hydrogen capacity. Also in FY 2014, the Hydrogen Storage sub-program maintained efforts to collect and disseminate materials data on advanced hydrogen storage materials through the hydrogen storage materials database (http://hydrogenmaterialssearch.govtools.us/).

Three new awards were initiated in FY 2014:

- HRL Laboratories, with partners SNL and University of Missouri-St. Louis, will investigate two material systems, mixed metal borohydrides and lithiated boranes, with potential to offer high gravimetric capacity with fast kinetics at temperatures and pressures relevant to automotive applications.
- LLNL, with partners SNL, Georgia Tech, and University of Michigan, will use a combined multi-scale computational and experimental approach to develop and validate strategies to improve the performance of Mg(BH₄)₂, a material with potential for 14 wt% reversible hydrogen storage.
- Ardica Technologies, with partner SRI, will transition and scale up a version of the SRNL-developed electrochemical method of alane (AlH₃) production/regeneration from the laboratory to production to significantly lower the cost of alane compared to conventional solution synthesis methods.

Specific accomplishments include:

- Hydrogen desorption and decomposition pathways were studied for $2 \operatorname{LiBH}_4 + 5 \operatorname{Mg(BH}_4)_2$ using nuclear magnetic resonance; experimentally observed reaction products were consistent with theoretically predicted $\operatorname{B}_2\operatorname{H}_6$ anion. Using a combination of experiments and density functional theory, all but one reaction product was able to be assigned. (Northwestern University)
- Developed the M₂(4,6- dioxido benzene 1,3-dicarboxylate) (known as m-dobdc) (M = Mg, Mn, Fe, Co, Ni) series of metal organic frameworks via a new structural isomer that shows a significantly improved hydrogen binding enthalpy as compared to the regular M₂(dobdc) for the Mn, Fe, Co, and Ni analogues. The open metal coordination sites are shown to have a greater positive charge in M₂(m-dobdc) than in M₂(dobdc), leading to the experimentally determined higher isosteric heats of H₂ adsorption (~1.0 kJ/mol higher on average) and up to 40% increase in adsorption enthalpy. (Lawrence Berkeley National Laboratory, LBNL)
- Demonstrated a volumetric capacity for Ni₂(m-dobdc) at room temperature and 100 bar of 12.1 g/L, which is the highest demonstrated to date and 50% greater than H₂ gas. (LBNL)
- Developed recommended volumetric capacity definitions and measurement protocols to help the research community better report and understand their volumetric capacity material results. (NREL)

Engineering

In FY 2014, the HSECoE developed prototype designs and evaluation plans for each of the hexcell and MATI sorbent systems using a 2-L Type I (all metal) aluminum pressure vessel. The MATI system is being constructed and modeled by partner Oregon State University, with evaluations to be done by SRNL. The hexcell system will be constructed and evaluated by partner University of Quebec-Three Rivers, with SRNL modeling the system. Efforts this past year included designing, constructing, and modifying test apparatuses at University of Quebec-Three Rivers and SRNL for evaluating the larger prototype systems. Additionally, the HSECoE completed evaluation work on chemical hydrogen storage material systems, demonstrating use of up to a 60% mass-loaded alane slurry, and refined their validated system models. These results were used to "reverse engineer" the chemical hydrogen storage material property requirements for a system to meet the full set of onboard storage targets. The models are posted on the models page of the HSECoE website (http://hsecoe.org/models.html) and are publically available for use by the hydrogen storage R&D community.

Specific accomplishments include the following:

- Demonstrated hydrogen release through a flow-through auger reactor with up to 60% mass-loaded slurries of alane. (Los Alamos National Laboratory, LANL)
- Developed and validated a single chemical hydrogen storage system model that combines exothermic and endothermic materials. Preparing it for public release through the HSECoE model website page. (PNNL)

- Quantified chemical hydrogen storage material property requirements to be able to meet all onboard hydrogen storage targets and submitted as a manuscript to Journal of Power Sources. (LANL and PNNL)
- Demonstrated that use of a liquid-nitrogen-cooled wall tank concept could significantly reduce the amount of hydrogen needed to be used with flow-through sorbent systems. (PNNL, Hexagon Lincoln)
- Tested at pressure and validated a computational fluid dynamics model of a gas-liquid separator uniquely designed for use with chemical hydrogen storage systems capable of separating hydrogen from liquids up to a peak power level of 80 kW_e. (UTRC)
- Successfully completed design, cycle, and burst (ambient and cryogenic) testing of a 2-L, Type I aluminum threepiece pressure vessel for use in Phase III prototype sorbent system evaluations. (Hexagon Lincoln)
- Delivered over 9 kg of MOF-5 adsorbent to HSECoE partners for Phase III testing, with scaled-up batch material achieving performance within 10% of lab-scale batch material. (Ford)
- Demonstrated 20x improvement in MOF-5 thermal conductivity using an enhanced natural graphite layering approach compared to random loading. (Ford)
- Completed experimental verification of the fast-fill and discharge dynamics of a cryo-adsorbent bed, enabling validation of the transport models. (General Motors)
- Completed design and assembly of the MATI for 2-L prototype system testing. (Oregon State University)
- Completed design and commenced construction of two test stations for evaluating the hexcell and MATI 2-L sorbent system prototypes. (SRNL, University of Quebec-Three Rivers)
- Established the HSECoE model website page² and posted metal hydride acceptability envelope, metal hydride finite element model, hydrogen tank mass and cost estimator, and hydrogen vehicle simulation framework models for public availability. (NREL)

BUDGET

\$15.6 million from the FY 2015 budget request is planned for hydrogen storage—consistent with \$15.6 million from the FY 2014 congressional appropriation. In FY 2015, the Hydrogen Storage sub-program will continue to focus on nearer-term R&D to lower the cost of high-pressure storage systems and longer-term technology development including cold/cryo-compressed hydrogen and materials discovery and system engineering for materials-based storage technologies. The sub-program will also continue to carry out systems analyses. The sub-program plans to initiate new activities in these areas for onboard automotive and non-automotive applications.

² http://hsecoe.org/models.html

Storage R&D Funding*



* Subject to appropriations, project go/no-go decisions, and competitive selections. Exact amounts will be determined based on research and development progress in each area.

FY 2015 PLANS

The technology portfolio for Hydrogen Storage emphasizes materials R&D to meet system targets for onboard automotive and non-automotive 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 portable power and MHE applications. The emphasis on developing lower-cost physical storage technologies will continue and be coordinated with related activities through the Vehicle Technologies and Advanced Manufacturing Offices of Energy Efficiency and Renewable Energy. Specifically, the sub-program will coordinate with and leverage other efforts through the planned Advanced Manufacturing Office Advanced Composites Institute and Vehicle Technologies Office efforts on CNG storage to develop approaches to produce low-cost compressed gas storage systems. System engineering and analysis will continue through the HSECOE, ANL, and Strategic Analysis Inc. Coordination with basic science efforts, including theory, characterization, and novel concepts, will be pursued during FY 2015.

Ned Stetson Hydrogen Storage Program Manager Fuel Cell Technologies Office Office of Energy Efficiency and Renewable Energy U.S. Department of Energy 1000 Independence Ave., SW Washington, D.C. 20585-0121 Phone: (202) 586-9995 Email: Ned.Stetson@ee.doe.gov