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 low-pressure hydrogen storage system technologies.

In Fiscal Year (FY) 2015, the sub-program continued to focus on the development of lower cost precursors for high strength carbon fibers as well as alternative fiber and resins to lower the cost of composites used in high-pressure compressed hydrogen systems for ambient and sub-ambient conditions. The sub-program also continued efforts on materials-based system engineering for transportation applications and advanced material R&D efforts, including for metal hydrides 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 for the applications. For light-duty vehicles, this means providing a driving range of more than 300 mi (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 mi 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 (MYRDD) Plan.

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 H_2/L)
- \$10/kWh (\$333/kg stored hydrogen capacity)

To achieve widespread 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 H₂/L)
- \$8/kWh (\$266/kg stored hydrogen capacity)

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

FY 2015 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.

In the near term, automotive companies plan to commercialize FCEVs that use 700 bar compressed hydrogen storage systems onboard, with system cost being one of the most important challenges to commercialization. In fact, FCEVs have started to be offered this year in California by two automotive original equipment manufacturers (OEMs) for lease or commercial sale with 700 bar compressed hydrogen systems onboard the vehicle.

In FY 2015, the sub-program, working with automotive OEMs through the United States Driving Research and Innovation for Vehicle efficiency and Energy sustainability (U.S. DRIVE) Partnership, adjusted the onboard automotive hydrogen storage system cost targets to reflect advancement of technologies. In FY 2014, the cost target was \$12/kWh of usable stored hydrogen to be reached by 2017. This target has now been changed to \$10/kWh of usable stored hydrogen to be reached by 2020. The ultimate full fleet cost target remains unchanged at \$8/kWh of usable stored hydrogen.

In FY 2015, Strategic Analysis Inc. (SA) updated the cost projections for 700 bar compressed hydrogen storage systems. The updated analysis projects a system cost \$14.69/kWh, an overall cost reduction of approximately \$2/kWh from the baseline cost of \$16.76/kWh established in FY 2013. The analysis reflects recent technology advancements to reduce cost of carbon fiber precursor and resin and technology advancements through balance of plant (BOP) components integration. The analysis also includes changes in the tank design to better reflect commercially manufactured pressure vessels that result in increased projected costs. Specific changes to the 700 bar pressure vessel system cost include use of a low cost carbon fiber precursor based on high volume textile fiber processes developed by Oak Ridge National Laboratory (ORNL); BOP component revisions to reduce the number of fittings; and use of a low cost, low density resin identified by Pacific Northwest National Laboratory (PNNL). The analysis this year also explicitly accounted for cost increases associated with manufacturing design changes suggested by industry, including the removal of pre-woven endcaps and increased composite layer thickness to account for a more robust assessment of manufacturing variations. The relative cost impact of each component change is presented in Figure 1. The overall performance of the revised 700 bar compressed systems compared to the onboard storage targets is shown in Figure 2.

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 advanced hydrogen storage materials development. A major effort in materials-based system development the last several years has been through the Hydrogen Storage Engineering Center of Excellence (HSECoE).

The HSECoE is completing its Phase III activities in 2015, focusing on evaluation of two hydrogen adsorbent system designs that differ in heat exchanger concept, and completing the validation and posting of their complete system models for use by the research community. Updated spider charts, shown in Figures 3a–c, have been prepared for all three material types, indicating the current projected status of full scale systems compared against the DOE 2020 targets. The two prototype hydrogen adsorption systems have been built and are undergoing evaluation, primarily at Savannah River National Laboratory (SRNL), Oregon State University (OSU), and Université du Québec à Trois-Rivières (UQTR). One prototype (hexcell) uses a flow-through concept where excess hydrogen removes the heat of adsorption as it passes through the adsorbent that is packed within an aluminum hexagonal honeycomb structure. The second prototype uses a modular adsorption tank insert (MATI) microchannel heat exchanger that is cooled by flowing liquid nitrogen through it.

In the MATI concept, the adsorbent is compacted into densified pucks that are sandwiched between the MATI cooling plates, whereas, in the hexcell design, the adsorbent is packed as a powder within the hexagonal honeycomb structure. The effectiveness of the two heat exchange concepts will be evaluated, the performance compared with the modeled predictions, and the results used to improve and validate the system models. While the prototype testing focuses on removing/supplying the heat of hydrogen adsorption/desorption, PNNL and Hexagon Lincoln carried out efforts to evaluate the effectiveness of using liquid nitrogen to directly cool the vessel walls for fast fill capabilities. In their concept, the vessel includes an annular space around the outer surface of the pressure vessel containing the sorbent through which liquid nitrogen could flow.



PAN MA - polyacrylonitrile with methyl acrylate

FIGURE 1. Revised projected costs for 700 bar compressed hydrogen storage systems for light-duty vehicles at 500,000 systems per year production, comparing approximate cost impacts of multiple simultaneous changes in carbon fiber pressure vessel systems between 2013 and 2015



FIGURE 2. Spider chart comparing current projected performance of a state-of-the-art 700 bar compressed hydrogen storage system with 5.6 kg usable hydrogen storage with the 2020 onboard automotive targets

Results from sub-scale testing projected for a full scale vessel indicated that it could be cooled to the targeted temperature of 80 K in less than 3.5 min, meeting the fast fill requirements. National Renewable Energy Laboratory (NREL), working with the HSECoE partners, has posted framework models for all three material (metal hydride, chemical hydrogen, and sorbent) system types on the HSECoE.org website for use by the research community. One

improvement to these models in 2015 was the addition of a graphical user interface (GUI), making them more user friendly. The site also contains the metal hydride acceptability envelope and finite element models and the tank volume/cost estimator model.



FIGURE 3. Projected status of full scale, 5.6 kg usable hydrogen systems versus the DOE 2020 onboard light-duty vehicle targets: (a) metal hydride system with NaAIH₄, (R&D terminated at end of Phase I); (b) chemical hydrogen storage system (50 wt% alane slurry) (R&D terminated at end of Phase II); (c) sorbent system with metal organic framework (MOF)-5 and flow-through hexcell heat exchanger design (status at end of Phase II, prototype testing continuing in Phase III)

Testing & Analysis

In FY 2015, 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 2015, with detailed analyses to determine updated cost projections for the 700 bar system. Additionally, analyses were performed to reverse engineer chemical hydrogen storage material system performance to identify material property and well-to-tank (WTT) efficiency requirements to meet DOE system-level performance targets.

Specific accomplishments include the following.

• Updated analyses for the 700 bar compressed hydrogen storage system, resulting in a projected overall cost reduction of approximately \$2/kWh (12%) from the 2013 baseline cost of \$16.76/kWh (SA)

- Completed a Design for Manufacturing Assembly[®] analysis of two sorbent-based onboard hydrogen storage systems, the MATI and hexcell concepts as designed by the HSECoE (SA)
- Formulated system models and performed reverse engineering to determine material properties of chemical hydrogen storage materials needed to meet system targets, including WTT efficiency targets (Argonne National Laboratory [ANL])
- Conducted onboard cold gas (195 K and 400 bar) hydrogen storage system and related off-board WTT efficiency analyses; the results projected a ~30% increase in gravimetric capacity and a 13% decrease in off-board WTT efficiency over the baseline condition

Advanced Physical Storage

In FY 2015, 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, alternative fiber and resin, cold temperature operation, 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. The carbon fiber composite used as overwraps can contribute as much as 75% or more to the overall cost of advanced Type IV tanks. The Hydrogen Storage sub-program supported efforts at ORNL to reduce the cost of polyacrylonitrile-based (PAN) fibers used as precursors to produce high strength carbon fibers. The ORNL efforts focused on advanced precursor materials and processing since precursors have been shown to contribute approximately 50% of the total cost of high strength carbon fibers. The team continued to investigate the development of melt-spinnable PAN precursors and processing techniques to replace the current more costly solution spinning methods. Additionally, a team led by PNNL focused on reducing the cost of a Type IV tank system by developing novel alternative resins and resin matrix modifications, modifying the carbon fiber surface to improve composite translational efficiency, developing methods for alternative fiber placement, and identifying enhanced operating conditions that demonstrate routes to increase carbon fiber usage efficiency.

In FY 2015, one new sub-program award was made.

• Center for Transportation and the Environment will work to develop advanced conformable 700 bar hydrogen storage systems that employ an over-braided, coiled pressure vessel that has the potential to surpass DOE system targets for specific energy (3.7 kWh/kg) and cost (<\$10/kWh).

Specific accomplishments include the following.

- Developed alternative low cost and low density resin with equivalent or better performance than the currently used epoxy resin, resulting in a projected reduction in storage system cost (by SA) of \$0.59/kWh compared to DOE's 2013 baseline (PNNL)
- Evaluated a graded construction approach utilizing thick wall effect and, evaluating various low cost fibers, identified Panex 35[™] as a potential candidate fiber for the outer wrappings of the pressure vessels (Composite Technology Development)
- Produced a thick composite panel with less than 1% void volume through use of vacuum infusion of a low viscosity resin into dry-wound fiber forms (Materia)
- Initiated pilot scale production development of an ultra-high strength glass fiber (≥5,500 MPa) and evaluation of its performance in composites as a low cost alternative to carbon fiber in Type III and IV tanks (PPG Industries Inc.)
- Established a baseline for strain-hardened Type 316L stainless steel as a first step in an effort to identify alternative metal alloys that can be used as substitutes for materials of construction in balance of plant components for hydrogen applications, leading to lower costs and lower mass (Sandia National Laboratories)
- Initiated preliminary testing of the liquid hydrogen cryo-pump installation with 875 bar capability and installation of test facilities for extended cycle testing of high pressure cryo-compressed hydrogen storage systems (Lawrence Livermore National Laboratory [LLNL])

Advanced Materials Development

In FY 2015, the sub-program continued efforts in developing and improving hydrogen storage materials with potential to meet the 2020 onboard storage targets. In the area of metal hydrides, efforts emphasized material

discovery coupled with reducing desorption temperatures and improving kinetics. 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, as well as on improving standard measurement practices for hydrogen capacity. Also in FY 2015, the Hydrogen Storage sub-program continued efforts to collect and disseminate materials data on advanced hydrogen storage materials that comprise the hydrogen storage materials database (http://hydrogenmaterialssearch.govtools.us/).

Four new awardees were selected in FY 2015.

- California Institute of Technology will develop high surface area adsorbents using graphene or exfoliated graphite to prepare materials with high volumetric capacity and gravimetric capacity of 11 wt% or higher.
- Texas A&M University will develop MOF sorbents with capacities that exceed the conventional storage limit per unit surface area of 1 wt% excess per 500 cc/g (the Chahine Rule) and improve system performance through enhanced thermal conductivity of sorbents/carbon composites.
- University of Michigan will investigate best-in-class sorbents that can simultaneously achieve higher volumetric and gravimetric density, identified through a computational survey of materials reported in the Cambridge Structural Database.
- Ames Laboratory will investigate silicon borohydrides and graphene composites as a way to develop low cost, reversible, high performance hydrogen storage materials; computational modeling will guide the experimental work in development of these materials.

Specific accomplishments include the following.

- Developed recommended volumetric capacity definitions and measurement protocols for hydrogen sorbent analyses to help the research community better report and understand its volumetric capacity material results and initiated dissemination of the protocols to the research community (NREL)
- Completed a comprehensive evaluation of the top performing MOFs for hydrogen storage, including Ni₂(m-dobdc), Co₂(m-dobdc), Ni₂(dobdc), Co₂(dobdc), and MOF-5. High-pressure isotherms were measured at 100°C, 75°C, 50°C, 25°C, 0°C, -25°C, -40°C, -50°C, and -75°C in order to determine the optimal temperature process to maximize total volumetric hydrogen usable capacity (Lawrence Berkeley National Laboratory [LBNL])
- Used high pressure neutron diffraction to determine the binding profile of hydrogen within MOF-5 at high pressures (up to 100 bar) and moderate temperature (77 K); this technique allows for the understanding of the density profile of hydrogen in the pores of MOFs and is currently being expanded for use with other MOF materials (LBNL)
- Developed a reverse pulsing technique to significantly reduce dendrite formation during electrochemical generation of alane and optimized the crystallization process for pure a-alane production (SRNL)
- Demonstrated formation of polymerized BH_x from $B_{10}H_{14}$ and hydrogen evolution from a reaction between BH_x and LiH (HRL Laboratories)
- Established initial modeling framework to predict phase fractions, accounting for (1) thermodynamics of interfaces, surfaces, and bulk; (2) elastic effects and mechanical stress/strain; and (3) phase nucleation/evolution and non-equilibrium (de)hydrogenation; completed initial calculations of thermodynamic parameters for bulk and surface MgB₂-Mg(BH₄)₂ (LLNL)

Engineering

In FY 2015, the HSECoE constructed two 2-L hexcell and MATI prototype sorbent systems and initiated evaluation of each. The MATI system was constructed and modeled by OSU, and evaluations are being carried out by SRNL. The hexcell system was constructed and is being evaluated by UQTR, with SRNL modeling the system. PNNL and Hexagon Lincoln carried out testing to evaluate the use of liquid nitrogen to quickly cool the vessel walls for fast refilling of the sorbent systems. Several HSECoE partners, such as NREL, United Technologies Research Center (UTRC), PNNL, OSU, and SRNL, were involved in continued efforts in developing and validating the complete system models integrated into a framework with vehicle and fuel cell level models. In FY 2015, significant efforts were also devoted to developing a GUI to make the models more user friendly. The models are posted on the models page of the HSECoE website (http://hsecoe.org/models.html), publically available for use by the hydrogen storage R&D community.

Specific accomplishments include the following.

- Completed assembly of a cryo-sorbent prototype test station (SRNL)
- Completed assembly and initiated evaluation testing of two sub-scale sorbent prototype systems (SRNL, OSU, UQTR)
- Evaluated alternative concepts for thermal conductivity enhancements (Ford, OSU)
- Evaluated use of liquid nitrogen to rapidly cool vessel walls to enable fast fill of hydrogen cryo-sorbent systems (PNNL, Hexagon Lincoln)
- Designed, built, and demonstrated an apparatus for and performed thermal conductivity measurements of hydrogen sorbent materials at hydrogen pressures up to 100 bar at liquid nitrogen temperatures; quantified the isotropic and anisotropic thermal conductivities for MOF-5 at elevated hydrogen pressures (LANL)
- Updated and posted HSECoE system models, including for 700 bar compressed storage systems, metal hydride systems, two chemical hydrogen storage systems, and adsorbent systems; completed sub-model validation, GUI improvements, and model parametrization (NREL, UTRC, PNNL, SRNL)

BUDGET

Of the FY 2016 budget request, \$15.6 million is planned for hydrogen storage, consistent with \$15.6 million from the FY 2015 congressional appropriation (Figure 4). In FY 2016, 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-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 applications.



FIGURE 4. Hydrogen 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 and the relative merit and applicability of projects competitively selected through planned funding opportunity announcements.

FY 2016 PLANS

The technology portfolio for the Hydrogen Storage sub-program emphasizes materials R&D to meet system targets for onboard automotive and non-automotive applications. The emphasis on developing lower cost physical storage technologies will continue and be coordinated with related activities through the Vehicle Technologies Office and Advanced Manufacturing Office (AMO) of the DOE Energy Efficiency and Renewable Energy Office. Specifically, the sub-program will coordinate with and leverage efforts through the recently established AMO-led Institute for Advanced Composite Manufacturing Innovation to develop approaches to low cost compressed gas storage systems manufacturing. System analysis will continue through efforts at ANL and SA. A new major thrust is planned for FY 2016 and includes a coordinated effort on development of advanced hydrogen storage materials with the requisite properties needed to enable a complete system to meet all of the onboard storage targets. The effort will involve a core national lab team that will carry out coordinated basic and applied research to further understanding of the interaction of hydrogen with storage materials; develop computational material design tools for developing materials with target properties; and work with individual research projects, competitively selected through future funding opportunity announcements, to design materials possessing characteristics needed to meet performance requirements.

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