
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. In Fiscal Year (FY) 2012, the sub-program focused on system engineering for transportation applications while continuing R&D efforts in materials-based storage including metal hydrides, chemical hydrogen storage materials, and hydrogen sorbents. Additionally, work was directed at reducing the cost of compressed gas storage systems (i.e., physical storage) as a near-term commercialization pathway. The storage portfolio, including Basic Energy Sciences, currently includes projects involving 22 universities, 11 companies, and 13 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 commercially viable hydrogen storage technologies for transportation and early market fuel cell applications including stationary power, backup power, portable power, and material handling equipment.

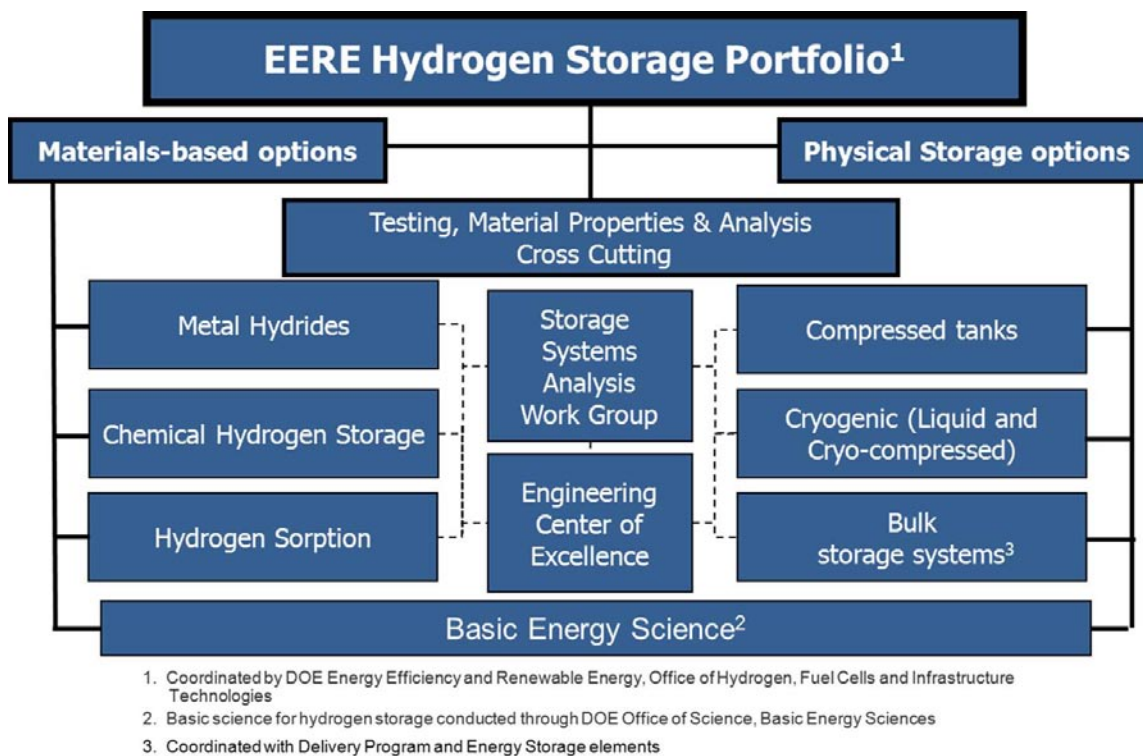
OBJECTIVES¹

The objective for the storage sub-program regarding light-duty vehicles is to store sufficient hydrogen onboard the vehicle 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. By 2017, the sub-program aims to develop and verify onboard automotive hydrogen storage systems achieving 1.8 kWh/kg system (5.5 wt%), 1.3 kWh/L system (0.040 kg hydrogen/L) and \$12/kWh (\$400/kg H₂). These targets will allow some hydrogen-fueled vehicle platforms to meet customer performance expectations, while the ultimate targets of 2.5 kWh/kg system (7.5 wt%), 2.3 kWh/L system (0.070 kg hydrogen/L), and \$8/kWh (\$266/kg H₂) 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.

The storage sub-program also aims to develop hydrogen storage for early market fuel cell applications including stationary and backup power, portable power, and material handling equipment. This effort is focused on developing technologies that provide enough hydrogen to enable efficient operation of fuel cells to meet customer-driven performance metrics in a safe, convenient, and cost-effective manner. These metrics include capacity (i.e., run-time), durability, and operability. The storage sub-program is currently working to finalize the technical and cost targets for these applications.

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 can be found in the *Multi-Year Research, Development, and Demonstration Plan (MYRD&D Plan)* www.hydrogenandfuelcells.energy.gov/mypp. These targets are based on the requirements of the application—not the current status of the technologies—and

¹ Note: Targets and milestones were recently revised; therefore, individual project progress reports may reference prior targets. Some targets are still currently under revision, with updates to be published in FY 2013.



in the transportation case, they account for differences in vehicle architecture between conventional vehicles and fuel cell vehicles.

FY 2012 STATUS AND PROGRESS

The hydrogen storage sub-program continues to pursue hydrogen storage materials discovery, including metal hydrides, chemical hydrogen storage, and sorbents, in addition to advanced tank development and total systems engineering to meet DOE onboard storage targets. The sub-program is also initiating efforts for early market fuel cell applications and has developed targets for material handling and portable power applications which can be found in the *MYRD&D Plan*. While there are several targets the sub-program is working towards, for transportation applications, system gravimetric and volumetric capacity, system cost, durability, and charging/discharging rates are important criteria to judge progress. System cost, in particular, is one of the most important barriers to commercialization of hydrogen fuel cell vehicles. On a routine basis the program assesses technical progress by evaluating the variable-volume manufacturing costs of compressed gas storage as shown in Figure 1. The 2012 high-volume (i.e., 500,000 units) manufacturing cost is \$15/kWh while the carbon fiber composite overwrap layer continues to contribute the majority of the costs. The sub-program also has system capacity projections made for the various onboard hydrogen storage technologies under development. The current projected storage system gravimetric and volumetric capacities are shown relative to the 2017 targets in Figures 2 and 3. 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 onboard storage technologies during the given year. The point within the bars is the average (mean) capacity for the technologies analyzed within the given year.

In FY 2012, the hydrogen storage sub-program started four new projects covering chemical hydrogen storage, sorbents, and advanced tank design. The University of Oregon, in collaboration with Pacific Northwest National Laboratory (PNNL), the University of Alabama, and Protonex, will develop and analyze a new class

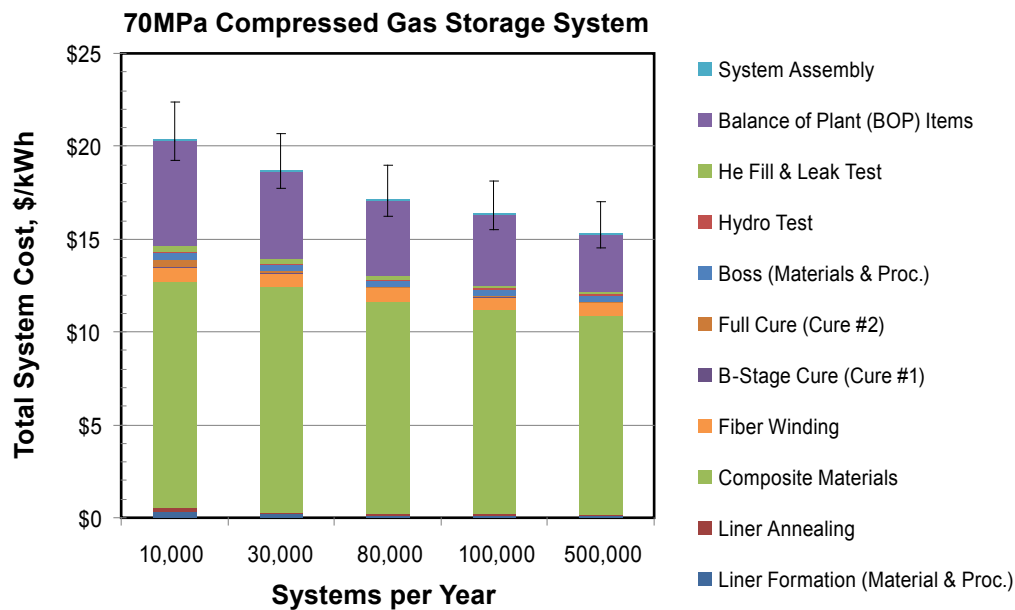
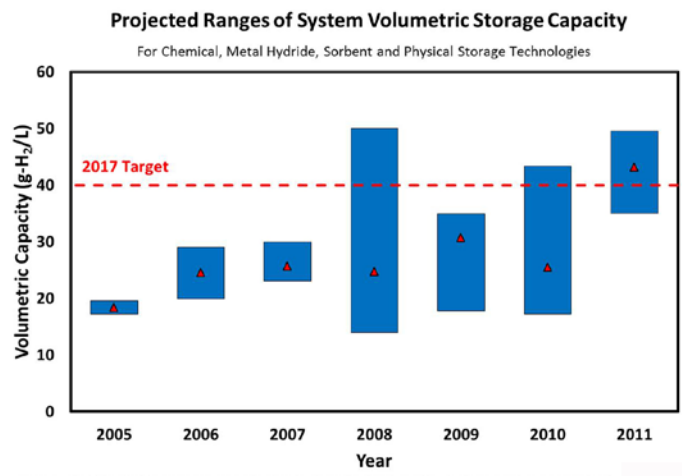
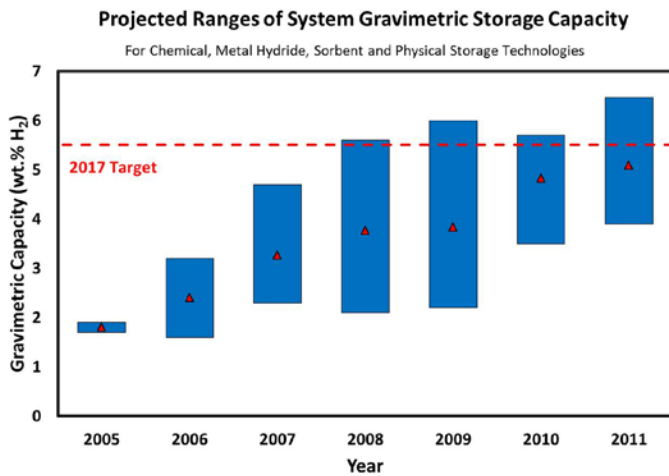


FIGURE 1. Projected cost, at various annual manufacturing capacities and in 2007\$, of compressed hydrogen storage systems, sized to deliver 5.6 kg of hydrogen to the vehicle fuel cell powerplant using two 700 bar, Type IV tanks. Cost analysis performed by Strategic Analysis, Inc. in 2012.



FIGURES 2 and 3. Status of projected hydrogen storage system gravimetric and volumetric capacities versus 2017 onboard 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 technologies and 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.)

of boron- and nitrogen-containing carbon heterocycle compounds (CBN), capable of high hydrogen capacities. The CBN materials to be synthesized are liquid phase and high capacity, and will include potentially reversible combinations which couple endothermic and exothermic hydrogen release to potentially enable onboard recharging with hydrogen. HRL Laboratories will explore ambient temperature hydrogen sorption in nanoconfined liquids. Solvent liquids within porous scaffolds have been shown to have greatly enhanced gas solubilities over that of bulk liquids. HRL will leverage this observed phenomenon and its experience with nano-scaffolds to develop materials that meet the DOE’s hydrogen storage targets. Lawrence Berkeley National laboratory, in collaboration with the National Institute of Standards and Technology and General Motors, will

develop coordination polymer (metal organic framework) compounds with high gravimetric and volumetric capacity and high isosteric adsorption enthalpies. The focus of this work will center on the synthesis of high valent metal coordinatively unsaturated cation structures with high micropore volume. PNNL, in collaboration with Toray, Lincoln Composites, AOC, and Ford Motor Company, will produce and test enhanced materials and manufacturing methods to reduce the cost of high-pressure storage tanks. As carbon fiber accounts for nearly 75% of overall tanks costs, the team will develop and implement design approaches that will reduce the carbon fiber content consistent with structural design criteria.

Materials Development

In FY 2012 the sub-program continued efforts in developing and improving hydrogen storage materials with potential to meet the 2017 onboard storage targets. In the area of chemical hydrogen storage materials, much of the focus was on developing liquid phase, such as slurries or solutions, in keeping with the findings of the Hydrogen Storage Engineering Center of Excellence. For hydrogen sorbents, efforts were focused on increasing the isosteric heat of adsorption to increase the adsorb capacity at higher temperatures. For metal hydrides, efforts emphasized reducing the desorption temperatures and improving kinetics. Also in FY 2012, the Hydrogen Storage sub-program launched a comprehensive hydrogen storage materials database (<http://hydrogenmaterialssearch.govtools.us/>) to collect and disseminate materials data and accelerate advanced hydrogen storage materials research and development.

Metal Hydrides

- Demonstrated the first example of the reversible, solid-state dehydrogenation of a borohydride at temperatures below 250°C (200°C dehydrogenation; 100°C, 50 atm re-hydrogenation). (University of Hawaii)
- Demonstrated a carbon-Ni catalyst that significantly enhanced the hydrogen desorption kinetics of complex hydrides. (Northwestern University)

Chemical Hydrogen Storage Materials

- Synthesized an additive hexylamineborane ($\text{H}_3\text{C}(\text{CH}_2)_6\text{NH}_2\text{BH}_3$, hexyl-AB) that has 3-4 wt% usable H_2 and maintains fluid phase at room temperature. Also demonstrated that 20 wt% AB in hexyl-AB (6 wt% H_2) transforms from a slurry to liquid upon dehydrogenation at 140°C. (Los Alamos National Laboratory/ University of Ottawa)
- Developed ammonia borane silicon oil slurry (45 wt% AB, 7 wt% H_2) that remains a liquid-slurry before and after dehydrogenation. (PNNL)
- Optimized dehydrogenation/trimerization reaction of the six-member ring CBN material with cheap and relatively environmentally benign catalyst FeCl_2 . (University of Oregon).
- Improved synthesis of the CBN-heterocyclic materials reducing processing steps by 50% and increased overall yield by five fold to 51% from commercially available starting materials. (University of Oregon)

Hydrogen Sorption Materials

- Synthesized a boron substituted templated carbon and with the use of a Ru-based catalyst, noted a 15 wt% improvement in hydrogen uptake over baseline materials. Moreover, the kinetics for the weak chemisorption effect were improved by a factor of 25 over that of similar materials with 95% of the adsorption process taking place within 10 minutes. (National Renewable Energy Laboratory, NREL)
- Initiated a startup by leveraging work within the H_2 storage sub-program that won DOE's National Clean Energy Business Plan Competition. NuMat Technologies employs rapid computational discovery, efficient synthesis technology and supercritical activation to design sorbents that will obviate the high pressures presently required for gas storage. (Northwestern University)

- Completed and established measurement, qualification, and characterization facilities as an outgrowth of its lead role of the Hydrogen Sorption Center of Excellence. Assisted materials-research groups to characterize and qualify samples for hydrogen-storage properties, and validated H₂ excess uptake in a metal organic framework (MOF) material synthesized by Northwestern University (NU-100). The validated excess capacity of ~8 wt% at 50 bar and 77 K for the NU-100 MOF is amongst the highest confirmed to date. (NREL)
- Continued efforts to incorporate boron into carbon utilizing X-ray photoelectron spectroscopy and Fourier transform infrared spectroscopic techniques to confirm the existence of B-C bonds in a material that has double the isosteric enthalpy of adsorption vs. unmodified material. The result of this modification is a 30% improvement in hydrogen wt% uptake when normalized to surface area. (University of Missouri)

Engineering

In FY 2012, the Hydrogen Storage Engineering Center of Excellence (HSECoE) completed hydrogen storage system level models for cryo-sorbents and liquid-phase off-board regenerable chemical hydrogen storage material systems. The HSECoE successfully transitioned from Phase 1 into Phase 2 and began conducting thorough tradeoff analyses comparing various novel system designs and candidate storage materials. Based on these results, the center chose MOF-5 as the base material for the cryo-sorbent system and ammonia borane (AB) for the chemical hydrogen storage system. In addition, the HSECoE began component level testing and model validation as the center moves towards final prototype design, construction, and testing in Phase 3.

- Based on the integrated Hydrogen Storage SIMulator vehicle model, the HSECoE:
 - Terminated work on metal hydride systems due to low probability of these materials meeting the required properties in the 2017 timeframe.
 - Identified ideal onboard reversible metal hydride material properties. (HSECoE)
- Completed down-select of adsorbent materials with selection of MOF-5. (HSECoE)
- Completed down-select of chemical hydrogen materials with selection of exothermic materials (AB). (HSECoE)
- Performed a failure modes and effects analysis for both adsorbent and chemical hydrogen material systems identifying potential failure modes not previously considered including adsorbent bed packing and impurity effects and chemical hydrogen material settling/flocculation and balance of plant (BOP) compatibility issues. (HSECoE)
- HSECoE identified primary technical barriers limiting advancement of materials-based hydrogen storage systems as:
 - Metal hydrides (heat transfer design, media compaction, media thermal conductivity, lowered mass of BOP components).
 - Chemical hydrogen materials (media slurry agent/solvent with 50 wt% capacity, media kinetics, novel impurity trapping).
 - Adsorbents (Type-4 vessels at cryogenic temperatures, media thermal conductivity improvement, flow through cooling, media compaction, minimized tank outgassing, potential low pressure Type-1 tank).
- Developed an advanced composite pressure vessel for cryo-sorbents with 11% lower weight, 4% greater internal volume, and 10% lower cost than the baseline vessel established in Phase I. (Lincoln)
- Performed vehicle-level tradeoff analyses to better understand the impact of key engineering designs, for example, the tradeoffs between mass, onboard hydrogen storage capacity, and vehicle range. (NREL)
- Developed and validated advanced vessel thermal isolation design capable of limiting parasitic heat load on a full tank to <2 W, a 38% improvement over the current state of art, resulting in increased dormancy

(“hold”) times for the idle vehicle over the entire operating range, -40°C to 60°C. (Jet Propulsion Laboratory)

- Completed a demonstration of a flow through cooling system and validated detailed models for super activated carbon. (Savannah River National Laboratory)

Advanced Physical Storage

In FY 2012, the sub-program continued to emphasize its efforts on reducing the cost of compressed hydrogen gas storage tanks by initiating new efforts on low-cost, high-strength carbon fiber. 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 fuel cell electric vehicles, 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. In addition to the new effort initiated with PNNL mentioned above, the Hydrogen Storage sub-program supported efforts at Oak Ridge National Laboratory (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 investigated the use of low-cost textile-grade fibers made from PAN blended with a methyl acrylate comonomer (PAN-MA) as lower cost precursors and continued development of melt-spinnable PAN precursors and processing techniques to replace the current more costly wet processing methods. A broad-based topic on “development of fibers, resins and/or composite additives” to reduce the cost of high-pressure hydrogen storage cylinders was included in the FY 2012 Small Business Innovation Research (SBIR) release 3 solicitation through which two new awards are anticipated. Additionally the project by Applied Nanotech, Inc. developing lightweight, high-strength carbon nanotube reinforced composite overwraps for tanks was selected to continue as a Phase II SBIR award.

In December 2012, DOE participated in a workshop to identify strategies and R&D needs for lowering the cost of high-strength carbon fiber and carbon fiber composite systems (<http://www.compositesworld.com/news/2011-carbon-fiber-workshop-reviews-low-cost-carbon-fiber-in-energy>). The input garnered from this activity will aid in identifying key challenges, priorities, and needs for carbon fiber composites and in development of future solicitations for R&D in these areas.

- Demonstrated carbonized fiber from low-cost textile-grade PAN-MA met the 2012 milestone of at least 300 KSI strength and 30 MSI modulus and identified areas for further refinement and improvement of properties. (ORNL)
- 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. (ORNL)

Testing & Analysis

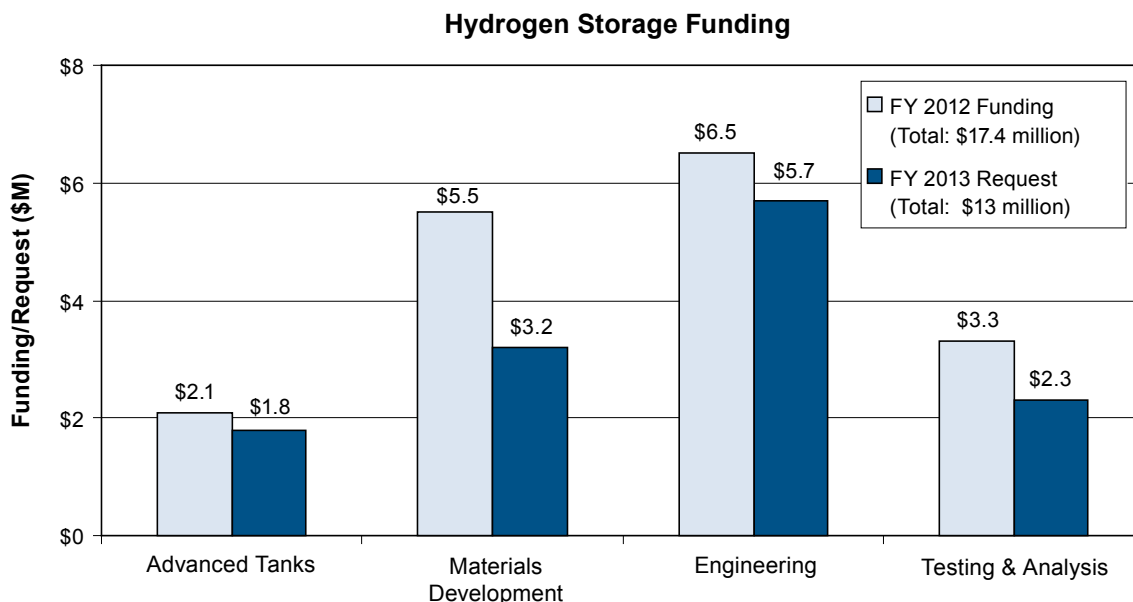
In FY 2012, the Hydrogen Storage sub-program continued carrying out assessments of hydrogen storage technologies to meet hydrogen fuel cell applications. A new effort was initiated with Strategic Analysis Inc. (SA) to develop cost models and carry out cost analyses of hydrogen storage technologies. Two national laboratories (Argonne National Laboratory [ANL] and NREL) will contribute as partners with SA.

- Completed an assessment of the technology and manufacturing readiness levels of hydrogen storage technologies to meet the requirements of identified early market hydrogen fuel cell applications. (PNNL)
- Updated the onboard analyses of the MOF-5 system (powder and pellets) with adiabatic para LH₂ refueling. Determined the intrinsic capacities, thermodynamics, dormancy, H₂ refueling dynamics, and discharge dynamics with the potential benefits of para-to-ortho conversion in the onboard storage tank. (ANL)

- Developed a model of the onboard hydrogen discharge reactor for the single-component liquid CBN hydrogen storage material and surmised that a more rapid or dispersed catalyst is needed to meet the required conversion in <10 s at 150°C. (ANL)
- Developed design to achieve 20% reduction in carbon fiber requirement. (ANL)
- Developed design to reduce or eliminate pre-cooling in fast fill of 700-bar compressed hydrogen storage tanks. (ANL)
- Developed and updated cost analysis model for the compressed hydrogen storage system. (SA)
- Conducted preliminary cost analyses for the 700 bar system with capacity of 5.6 kg of useable hydrogen, at varying manufacturing volumes using input from vehicle manufacturers to validate the cost model. (SA)
- Initiated analysis of using “wet-wind” versus using “pre-preg” in the composite cylinder manufacturing process. Determined that the following areas of the analysis require further work and scrutiny before the cost model can be finalized for further analyses: 1) carbon fiber composite mass requirement, 2) pre-preg fiber cost and comparison with wet-winding, 3) average winding speed, 4) BOP cost (particularly at low manufacturing rates), 5) complete assembly analysis, and 6) sensitivity studies: 350 bar and multiple vessels analyses. (SA)
- Updated and completed sections (Introduction, Kinetics, Capacity, Thermodynamics and Cycle-life) of the Best-Practices Document on the Characterization of Hydrogen Storage Materials were posted on the DOE website. Two additional sections on engineering related properties (Thermal and Mechanical Properties) are estimated to be 85 and 15% complete respectively. (H2 Technology Consulting through NREL)

BUDGET

\$13 million from the President’s FY 2013 budget request is planned for hydrogen storage—compared with \$17.4 million from the FY 2012 congressional appropriation. In FY 2013, 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 2013 PLANS

The technology portfolio for Hydrogen Storage emphasizes materials R&D to meet system targets for onboard 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 2013, goals and objectives for hydrogen storage for early market applications will be released. The increased emphasis on developing lower-cost physical storage technologies will continue to be expanded. Specifically, the sub-program will use the SBIR program and 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 analysis will continue through the HSECoE, ANL, and SA. Coordination with basic science efforts, including theory, characterization, and novel concepts, will continue during FY 2013. 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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