IV.0 Hydrogen Storage Program Overview

INTRODUCTION

The Hydrogen Storage 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 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) 2016, the program initiated efforts on conformable high-pressure storage tank design and continued to focus on the development of lower-cost precursors for high-strength carbon fiber and alternative fiber and resins to lower the cost of composites used in high-pressure compressed hydrogen systems for ambient and sub-ambient conditions. The program also continued advanced material R&D efforts for metal hydrides and sorbents and launched the Hydrogen Materials-Advanced Research Consortium (HyMARC), a collaborative, comprehensive, materials-based hydrogen storage R&D effort.

GOAL

The program's goal is to develop and demonstrate advanced hydrogen storage technologies to enable widespread commercialization of fuel cells in transportation applications as well as enable early markets such as portable power and material handling equipment applications.

OBJECTIVES

The Hydrogen Storage program's objective is to develop technologies that provide sufficient onboard hydrogen storage to allow fuel cell devices to meet the performance and run-time demanded for the applications. For light-duty vehicles this means providing a driving range of more than 300 miles (500 km) while meeting packaging, cost, safety, and performance requirements 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 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 Hydrogen Storage section of the *Multi-Year Research Development and Demonstration Plan* (MYRDD Plan).

By 2020, the 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 stored hydrogen capacity)

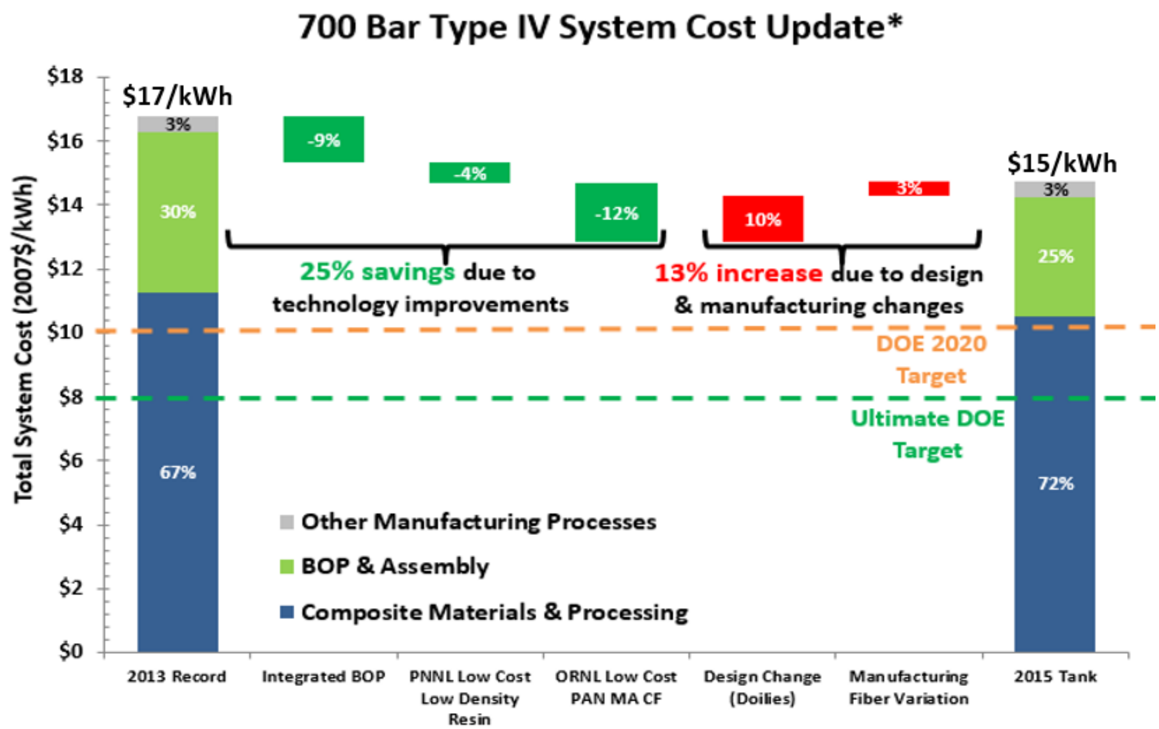
To achieve widespread commercialization of hydrogen FCEVs across the full range of light-duty vehicle platforms, the program has established the following Ultimate Full Fleet onboard hydrogen storage targets to meet the needs for full fleet adoption:

- 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 nearer-term and longer-term targets for onboard automotive, portable power, and MHE applications can be found in the MYRDD Plan. Targets are currently under revision based on recent progress and will be updated in FY 2017.

FY 2016 TECHNOLOGY STATUS AND ACCOMPLISHMENTS

Given that hydrogen storage system cost remains a key barrier in the commercialization of FCEVs, the program continued to focus on analysis to understand the costs associated with high-pressure hydrogen storage systems. The projected cost status for 700 bar compressed hydrogen storage systems remained at $15/kWh, which reflects technology advancements supported by the Hydrogen Storage program to reduce the cost of carbon fiber precursor and resin, balance of plant components integration, as well as changes in tank design to better reflect commercially manufactured pressure vessels. Figure 1 shows the 2013 and the 2015 breakdown of projected costs at high volume for 700 bar compressed hydrogen storage systems for light-duty vehicles.



*At 500k units/yr. Based on Program Record 15013

PNNL – Pacific Northwest National Laboratory; ORNL – Oak Ridge National Laboratory; PAN – polyacrylonitrile; MA – methyl acrylate; CF – carbon fiber; BOP – balance of plant

FIGURE 1. Revised projected costs for 700 bar compressed hydrogen storage systems for light-duty vehicles at 500,000 systems per year, comparing analyses between 2013 and 2015

The Hydrogen Storage program's near-term strategy focused on high-pressure compressed hydrogen storage systems and remained consistent with FCEV industry trends in 2016. Automotive companies are now in their second year of commercializing FCEVs that use 700 bar compressed hydrogen storage systems onboard, and system cost remains one of the most important challenges to widespread commercialization. Currently, there are two FCEV models that are available for lease or commercial sale in California, and both are equipped with 700 bar compressed hydrogen systems onboard.

In FY 2016, projects spanning the program's physical storage portfolio made progress in the areas of low-cost, high-strength carbon fiber precursors; alternative fiber and resin; cold-temperature operation; and conformable tank designs. For example, ORNL and partners have identified plasticizers effective in reducing the melt temperature of PAN/MA blends to the range of 145–175°C, significantly below the cross-linking temperature, to allow melt processing. Materia has demonstrated improved and optimized vacuum processing for the resin impregnation of dry fiber wound tanks and demonstrated equivalent burst strength to baseline conventional tanks. Additionally, work by Composite Technology Development Inc. (CTD) and partners on conformable tank design moved the project a step

closer to the development of conformable 700 bar hydrogen storage systems by selecting the resin for the prototype vessel permeability testing. In terms of cold-temperature operation, the program initiated a new project in FY 2016, led by Vencore Services and Solutions, focusing on thermal insulation for cold and cryogenic automotive tank applications.

In addition to system cost and as shown in Figure 2, current projected energy densities for compressed hydrogen storage systems are unable to meet the program's 2020 targets. Given these limitations and as a longer-term strategy, the Hydrogen Storage program continues to pursue less mature materials-based hydrogen storage technologies that have the potential to satisfy all onboard hydrogen storage targets, including those related to energy density. These technologies include cold compressed (sub-ambient temperatures as low as ~150–200 K) and cryo–compressed (temperatures <150 K) hydrogen and materials-based storage technologies. In FY 2016, Lawrence Livermore National Laboratory (LLNL) constructed and commissioned their cryogenic hydrogen test facility allowing for the safe testing of full-size cold/cryogenic hydrogen storage vessels using a hydrogen cryo-pump supplying high-pressure supercritical hydrogen.

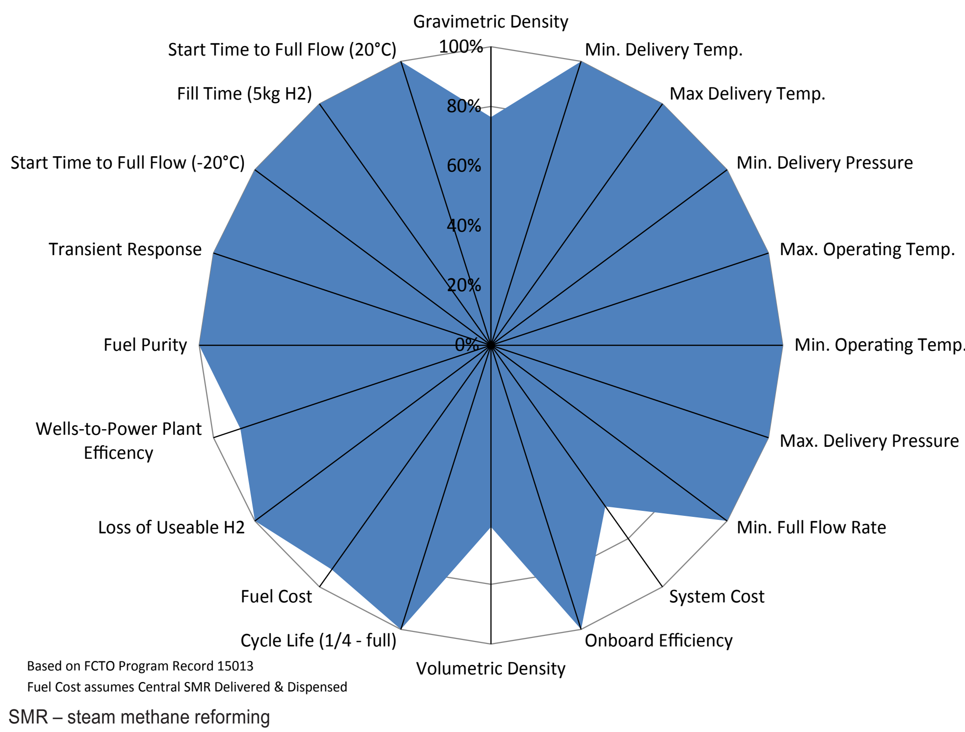


FIGURE 2. Current projected performance of a state-of-the-art 700 bar compressed hydrogen storage system with 5.6 kg usable hydrogen storage with the 2020 onboard automotive targets

In FY 2016, the materials-based storage efforts were focused to a greater extent on advanced hydrogen storage materials development and to a lesser extent on total systems engineering. A significant materials-based scientific breakthrough in the area of hydrogen adsorption within metal organic frameworks (MOFs) was achieved. A collaborative effort between University of California, Berkeley, Lawrence Berkeley National Laboratory (LBNL), and National Institute of Standards and Technology (NIST) demonstrated, for the first time, the binding of two hydrogen gas molecules to a single open metal site within an MOF, paving the way for a synthetic path to identifying materials with higher densities of adsorbed hydrogen and with the potential to meet the program's 2020 and ultimate density targets. Figure 3 shows a portion of the synthesized organic structure with multiple hydrogen molecules adsorbed at a single metal site.

A major FY 2016 effort initiated in the program's materials-based storage portfolio was the launch of HyMARC. Comprised of a core team of three national laboratories (Sandia National Laboratories [SNL]-lead, LLNL, and LBNL), the HyMARC team is addressing the scientific gaps impeding the advancement of solid-state storage materials. HyMARC's scientific activities will provide the foundational understanding of the interaction of hydrogen with

materials, such as the thermodynamic and kinetic properties of storage materials, including mass transport, surface chemistry, and processes at solid-solid interfaces, information which is critical in achieving all of the program's 2020 and ultimate targets. Five new individual projects were selected in 2016 to collaborate with the HyMARC national laboratory core team to develop specific hydrogen storage materials with the potential to meet the demanding performance requirements for onboard FCEV hydrogen storage. These projects will be led by University of Missouri–St. Louis, University of Hawaii–Manoa, The Pennsylvania State University, Liox Power Inc., and Argonne National Laboratory (ANL).

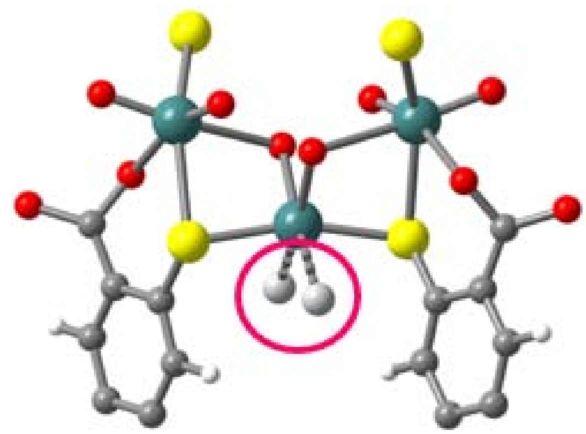


FIGURE 3. Crystal structure of Mn2(dsbdc) with two hydrogen molecules (gray spheres, circled) bound at the open metal site (Mn atoms shaded in green, S atoms in yellow, O atoms in red, and C atoms in gray) [Tomče Runčevski, et al., Chem. Commun., 2016, 52, 8251-8254, DOI: 10.1039/C6CC02494G]

In FY 2016, the program consolidated the core characterization and validation activities into the Hydrogen Storage Characterization Optimization Research Effort (HySCORE). The HySCORE team is led by researchers at National Renewable Energy Laboratory (NREL) and includes LBNL, PNNL, and NIST's Center for Neutron Research. This team provides a wide range of capabilities to support the program's materials-based storage development project portfolio, including HyMARC. These capabilities cover the validation of hydrogen capacity measurements, thermal conductivity measurements, infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy, advanced microscopy, neutron scattering, and diffraction measurements, among others. The expertise and resources of the HyMARC national laboratory core team and the HySCORE team are available to support the individual projects in the program's materials-based hydrogen storage portfolio to accelerate progress.

FY 2016 marked the last year of the Hydrogen Storage Engineering Center of Excellence (HSECoE), which covered the program's materials engineering efforts. The HSECoE completed the evaluation of the HexCell and the Modular Adsorption Tank Insert (MATI), two sorbent prototype systems designed to achieve higher hydrogen adsorption densities, and finalized the validation of the framework models for the metal hydride, chemical hydrogen, and sorbent systems. Other models that were finalized through the HSECoE include the metal hydride acceptability envelope and finite element models and the tank volume/cost estimator model. A major milestone achieved during FY 2016 was making these models and resources accessible through the HSECoE.org website for use by the materials-based hydrogen storage R&D community. In FY 2016, a subset of the HSECoE partners (NREL, PNNL, and Savannah River National Laboratory [SRNL]) made improvements to the performance of the modeling package and incorporated an improved graphical user interface that is better suited for the end users.

Testing and Analysis

In FY 2016, the Hydrogen Storage program continued carrying out technoeconomic assessments of hydrogen storage technologies. Technical analysis and cost modeling of Type IV pressure vessel systems remained a critical focus during FY 2016. Analyses were performed to investigate strategies to improving carbon fiber utilization as a means of reducing cost. Analyses were also conducted for the hydrogen storage tanks deployed on the Toyota Mirai.

Additionally, initial reverse engineering analyses were performed to map the desired material physical, transport, thermodynamic, and kinetic properties needed for the hybrid high-pressure metal hydride tank system to approach the near-term system performance targets.

Specific accomplishments include:

- **Impact of winding speed:** Analyzed faster carbon fiber winding speeds (enabled by use of pre-preg or dry fiber winding) showing potential system cost reductions up to 3% markup versus lower manufacturing variations and faster winding speed tradeoffs for carbon fiber pre-impregnated with resin (pre-preg). (Strategic Analysis, Inc. [SA])
- **Alternate design:** Analyzed winding pattern improvements and tank boss redesign (as published by Toyota) showing system cost reductions of $0.50/kWh. (SA)

- **Balance of plant:** Evaluated impact of changing integrated valve from 316 stainless steel to aluminum, which results in a cost reduction of $0.16/kWh. (SA)
- **Vehicle tank analysis:** Studied the Toyota Mirai tank design and conducted ABAQUS simulations and determined the amount of carbon fiber required for 700 bar Type IV tanks that have similar design features as the Toyota Mirai tanks. The analysis predicted the design features could reduce the amount of carbon fiber composite by 4 to 7 weight percent for tanks with length-to-diameter ratios of 2.8–3.0. The carbon fiber composite weight reduction can be as high as ~20% if the tank is wound with the higher-strength T720 carbon fiber. (ANL)
- **Hybrid system modeling:** Evaluated a hybrid system concept of incorporating hydrogen storage materials into a 350 bar high-pressure tank and identified key material characteristics required for the hybrid system to match or exceed the performance of a 700 bar compressed hydrogen storage system. Initial analyses indicate the need for a material with an enthalpy and corresponding entropy of absorption of -21 kJ/mol and -104 J/mol·K, respectively, or less with a gravimetric capacity of at least 5.8 wt%. (ANL)

Advanced Physical Storage

In FY 2016 the program continued to investigate varying approaches 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 conformable 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 program supported efforts at ORNL to reduce the cost of PAN-based 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 spinning methods, which tend to be a more costly solution. Additionally, a team led by PNNL focused on reducing the cost of a Type IV tank system by developing enhanced operating conditions that demonstrated routes to increase carbon fiber usage efficiency.

Specific accomplishments include:

- **Cold gas tank testing:** Completed cold gas burst tests, with average burst pressure for tanks precooled to 200 K at 714 bar exceeding the target room temperature burst of ~625 bar. (PNNL)
- **Melt-spun PAN development:** Selected processing conditions and water–plasticizer formulations and demonstrated melt spinning of PAN-MA precursor fiber with >100 filament tows and >10 m in length. (ORNL)
- **Alternative manufacturing processes:** Demonstrated improved vacuum infused composite tank processing with reduced fabrication time from 2 h to 0.5 h for high-quality 7.5 L prototype vessels. Also achieved equivalent burst strength (26,586 psi) in static testing of small prototype vessels (Type III, 7.5 L). (Materia)
- **Alternative material qualification:** Quantified fatigue performance for low-Ni austenitic stainless steel (21Cr-6Ni-9Mn) with nominally the same fatigue performance as the tested strain-hardened 316L, allowing potential cost saving for balance of plant components. (SNL)
- **High-strength glass development:** Successfully demonstrated a high-throughput, high-temperature melting unit run to make high-strength fiber glass cullet. (PPG Industries Inc.)
- **Conformable tank development:** Completed initial testing with baseline compressed natural gas vessels and proved test system workability. Also measured baseline permeability performance for a storage vessel resin with permeability value at about half of the expected value. (Center for Transportation and the Environment)
- **Alternative design:** Evaluated both coupons and prototype tanks fabricated with a graded construction (i.e., replacing outer layers of higher-strength carbon fiber with a lower-strength carbon fiber) to demonstrate it as a viable option for lower-cost tanks. (CTD)
- **Cryo-compressed:** Constructed and commissioned a cryogenic hydrogen test facility allowing for the safe testing of full-size cold/cryogenic hydrogen storage vessels using a hydrogen cryo-pump to supply high-pressure supercritical hydrogen. (LLNL)

Advanced Materials Development

In FY 2016 the program continued efforts in developing and improving hydrogen storage materials with potential to meet the 2020 onboard storage targets. Both the HyMARC and HySCORE teams were initiated, and the first round of individual projects was selected. Overall efforts on metal hydrides continued to emphasize material discovery coupled with reducing desorption temperatures and improving kinetics. For hydrogen sorbents, efforts were focused on increasing the isosteric heat of adsorption through inclusion of open metal centers or metal atom doping of carbons to increase the adsorbed capacity at higher temperatures, and improving standard measurement practices for hydrogen capacity.

Five new awards were selected in FY 2016 as the initial individual projects within HyMARC:

- **Argonne National Laboratory** will develop novel graphene-encapsulated complex hydride (hydride@graphene) composite materials which display high gravimetric capacities with improved thermodynamics, kinetics, and reversibility compared to the bulk metal hydrides.
- **The Pennsylvania State University** will synthesize boron-doped polymers containing high surface areas and exposed acidic binding sites for enhanced hydrogen adsorption enthalpies.
- **University of Hawaii** will develop new magnesium boride etherate compounds in an effort to find improved kinetic and thermodynamic pathways for the reversible hydrogenation of magnesium boride to magnesium borohydride.
- **University of Missouri-St. Louis** will develop functionalized porous carbons doped with nitrogen heteroatoms to kinetically stabilize alane and improve its reversibility.
- **Liox Power, Inc.** will investigate the inclusion of a thin solvent layer to improve sorption kinetics of hydrogen storage materials at moderate temperature and pressure conditions.

Specific accomplishments include:

- **Multiple H_2 adsorption:** Validated, for the first time, the adsorption of two hydrogen molecules bound to a single open metal site in a sorbent material, as confirmed by neutron powder diffraction. (LBNL, NIST)
- **Round-robin testing:** Initiated a multi-laboratory, round-robin study on volumetric uptake in sorbents, which includes national laboratories, universities, industry, and international participants, to identify sources of error in volumetric uptake measurements—the results of which will be disseminated to the adsorption community to improve data reliability. (NREL)
- **Characterization method development:** Developed new advanced NMR techniques which allowed the measurement of solid-state ^{1}H NMR spectra for hydrogen physisorbed to an open metal site in a MOF to gain insight into binding energies. (PNNL)
- **Computational method development:** Made significant progress using several types of computational techniques to move towards multiscale simulations that investigate thermodynamics and kinetics at interfaces and surfaces of storage materials. (LLNL)
- **Sample handling development:** Developed and implemented clean, air-free techniques for sample transfer for X-ray studies, and established X-ray adsorption spectroscopy as a tool for probing metal hydrides, including separate bulk- and surface-sensitive approaches. (SNL)
- **High-throughput computational screening:** Utilized computational screening of structure databases to discover MOFs that display improved hydrogen capacities over the baseline MOF-5 material, with IRMOF-20 experimentally demonstrated to have 27% higher usable gravimetric capacity at 100 bar. (University of Michigan)

Engineering

FY 2016 was the final year of the HSECoE. The effort for the year was focused in two areas: completing the evaluation of the two hydrogen sorbent prototypes and validating and posting the various models developed through the HSECoE. SRNL led the testing and evaluation of the sorbent prototypes, one with flow-through cooling using an aluminum honeycomb cell core heat exchanger (HexCell) and a second with a liquid N_2 cooled microchannel MATI heat exchanger. NREL will lead a continuing effort to maintain and improve the various models developed through

the HSECoE and available to the research community through a website. SRNL and PNNL will collaborate with NREL in this effort. SRNL also leveraged the system models and system engineering expertise from the HSECoE to design a materials-based storage system for use on a U.S. Navy unmanned underwater vehicle (UUV) and provided a bench-scale prototype for evaluation. Preliminary analyses indicate a fuel cell system with alane hydrogen storage can provide two to three times the energy storage of battery systems.

Specific accomplishments include:

- **Prototype testing:** Completed evaluation of the HexCell and MATI prototype hydrogen adsorbent systems and validation of the HexCell and MATI vehicle-level system models. (SRNL)
- **System models development:** Updated and integrated several HSECoE storage system models within the vehicle modeling framework and posted them on HSECoE's website portal. These included a 700 bar physical storage model, a metal hydride model, two cold hydrogen models, and two adsorbent system models. (NREL, SRNL, PNNL)
- **Model dissemination:** Completed documentation website updates for the posted models (including website text and downloadable user manual). (NREL, SRNL, PNNL)
- **System development:** Completed an engineering analysis to screen for the most attractive solid-state hydrogen storage material to meet Navy requirements for UUV application, performed testing to demonstrate alane storage and delivery performance against steady-state and transient operations, and prepared and delivered a bench-scale prototype system to the Naval Underwater Warfare Center for evaluation. (SRNL)

BUDGET

The FY 2017 budget request allocates $15.6 million to the Hydrogen Storage program. This is consistent with the FY 2016 congressional appropriation of $15.6 million. In FY 2017, the Hydrogen Storage program will continue to focus on nearer-term R&D to lower the cost of high-pressure storage systems through low-cost carbon fiber precursors, demonstrate alternative fibers and resins, and identify innovative approaches to tank design. Longer-term advanced materials R&D work will be coordinated through the newly established HyMARC and HySCORE efforts to ensure impact is maximized and resources are utilized effectively. The program will also continue to complete systems analyses. The program plans to initiate new activities in these areas for onboard automotive applications.

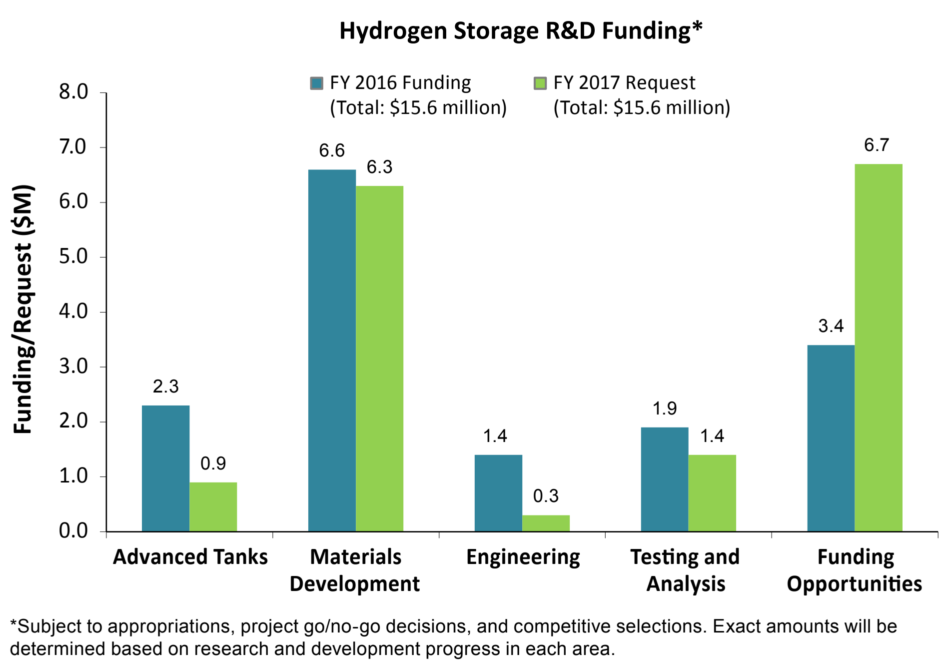


FIGURE 4. FY 2016 budget appropriations and FY 2017 budget request for the Hydrogen Storage program, indicating funds allocations per technology area

FY 2017 PLANS

The technology portfolio for the Hydrogen Storage 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 will be coordinated with related activities through the Vehicle Technologies Office and Advanced Manufacturing Office (AMO) within the Office of Energy Efficiency and Renewable Energy. Specifically, the program will continue to coordinate with and leverage efforts through the 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. With the newly established HyMARC and the consolidation of the characterization and validation efforts, the existing and future materials-based hydrogen storage R&D efforts and individual projects will be coordinated to maximize the use of capabilities and ensure collaboration across groups to enable results that are both impactful and relevant to the Hydrogen Storage program's 2020 and ultimate goals.

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