IV.0 Hydrogen Storage Sub-Program Overview

INTRODUCTION

The Hydrogen Storage sub-program supports early-stage research and development (R&D) of materials and technologies for compact, lightweight, and inexpensive storage of hydrogen for automotive, portable, and material handling equipment applications. The Hydrogen Storage sub-program strategy is to follow two parallel paths: a near-term focus on R&D to improve the performance and lower the cost of high-pressure (700 bar) compressed hydrogen storage systems currently being used for commercial introduction of hydrogen fuel cell electric vehicles (FCEVs) and a long-term focus on developing advanced cold/cryo-compressed and materials-based hydrogen storage system technologies that have potential to meet all of the onboard hydrogen storage targets.

In Fiscal Year (FY) 2017, the first round of five early-stage R&D seedling projects under the Hydrogen Materials–Advanced Research Consortium (HyMARC) began activities aimed at discovering hydrogen storage materials with increased capacity, more favorable thermodynamics, and lower cost with the potential to meet DOE targets. Another new project was also launched, focused on an advanced cryogenic hydrogen storage insulation system to enable hydrogen to be stored at higher densities and/or lower pressures when compared to traditional high-pressure approaches. The sub-program continued supporting existing material R&D efforts for metal hydrides and sorbents, ensuring their alignment and collaboration with HyMARC's core and support functions. Late in FY 2017 the sub-program also announced selection of (1) a second round of four new seedling projects to work under HyMARC to develop advanced hydrogen storage materials and (2) three new projects focused on developing novel carbon fiber precursors with potential to significantly lower the cost of high-strength carbon fiber and high-pressure hydrogen storage systems. A major programmatic effort during FY 2017 was the revision of the DOE onboard hydrogen storage targets for light-duty FCEVs, which were last updated in 2009 and originally set in 2003. The revised targets take into account the recent advancements made in commercial fuel cell vehicles.

GOAL

The sub-program's goal is to advance early-stage, innovative hydrogen storage technologies in transportation and other niche areas, such as portable power and material handling equipment.

OBJECTIVES

The Hydrogen Storage sub-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. The revised 2020, 2025, and ultimate targets for light-duty vehicles allow for a progression of improved performance to be competitive with conventional and other advanced powertrains across the breadth of light-duty vehicle platforms while also meeting packaging, cost, safety, and performance requirements.

2020

- 1.5 kWh/kg system (4.5 wt%)
- 1.0 kWh/L system (0.030 kg H_2/L)
- $10/kWh ($333/kg stored hydrogen capacity)

2025

- 1.8 kWh/kg system (5.5 wt%)
- 1.3 kWh/L system (0.040 kg H_2/L)
- $9/kWh ($300/kg stored hydrogen capacity)

Ultimate

- 2.2 kWh/kg system (6.5 wt%)
- 1.7 kWh/L system (0.050 kg H_2/L)
- $8/kWh ($266/kg stored hydrogen capacity)

In addition to these high-level targets, a comprehensive set of revised targets is available on the Hydrogen Storage website at https://energy.gov/node/1315186 and a target explanation document explaining the assumptions and inputs used to develop the revised targets for light-duty vehicles is available at https://energy.gov/node/826801.

Although some commercial FCEVs are able to meet the 300-mile driving range deemed as the minimum entry point into the market, this driving range is not currently achievable across the full range of vehicle models without compromising space, performance, or cost. The high cost of high-pressure hydrogen storage systems plus the fact that the bulk of incumbent vehicles are able to provide customers with greater than 400-mile driving range make it clear that current hydrogen storage system technology must be improved in order to provide customers with the expected driving range across all vehicle platforms at a reasonable cost.

In addition to the targets for onboard hydrogen storage systems for light-duty vehicles, the sub-program also has comprehensive sets of hydrogen storage performance targets for portable power and material handling equipment applications. These targets can be found in the Hydrogen Storage section of the Multi-Year Research, Development, and Demonstration Plan at https://energy.gov/sites/prod/files/2015/05/f22/fcto_myrdd_storage.pdf.

FY 2017 TECHNOLOGY STATUS AND ACCOMPLISHMENTS

Given that 700 bar hydrogen storage system cost remains a key barrier to the commercialization of current FCEVs, the sub-program continued addressing approaches to reduce the cost of high-pressure hydrogen storage systems. The current projected high-volume cost status for 700 bar compressed hydrogen storage systems is $15/kWh, which reflects technology advancements supported by the Hydrogen Storage sub-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.

During FY 2017 the sub-program placed a greater focus on ensuring that early-stage R&D efforts on innovative hydrogen storage materials were closely aligned with and coordinated through the HyMARC's core and support teams. The Hydrogen Storage sub-program worked to make HyMARC's full set of capabilities and expertise known and available to other hydrogen materials R&D efforts within the sub-program's portfolio, ensuring opportunities for collaboration were identified and that impact would be maximized moving forward. Figure 1 shows a screenshot of HyMARC's website and serves as an example of the HyMARC capabilities being disseminated to the hydrogen

Taming reactive nanoparticles

Graphene oxide encapsulation creates air-stable metal hydride nanoparticles

The Hydrogen Materials—Advanced Research Consortium (HyMARC), composed of Sandia National Laboratories, Lawrence Livermore National Laboratory, and Lawrence Berkeley National Laboratory, has been formed with the objective of addressing the scientific gaps blocking the advancement of solid-state hydrogen storage materials.

FIGURE 1. Homepage of HyMARC website

storage community. The HyMARC lab teams are routinely providing their results to the research community through publications in high-impact, peer-reviewed science journals.

Near-Term Focus: High-Pressure Storage

The Hydrogen Storage sub-program's near-term strategy continued to focus on innovative approaches for high-pressure compressed hydrogen storage systems and remained consistent with FCEV industry trends in 2017. Automotive companies are now in their third 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. This year, a third FCEV model was released to the commercial market in California. Like the previous two FCEV models released in FY 2015 and FY 2016, this one is equipped with a 700 bar compressed hydrogen system onboard.

In FY 2017, projects spanning the sub-program's high-pressure storage portfolio made progress in the areas of alternative manufacturing processes, alternative fiber and resin, and conformable tank designs. For example, 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 the Center of Transportation and the Environment and partners on conformable tank design moved the project a step closer to the development of conformable 700 bar hydrogen storage systems without use of carbon fiber composites. Finally, Sandia National Laboratories (SNL) has identified alloys for use in the balance of plant with the potential to reduce material cost and weight by over 50% compared to 316L stainless steel that has been traditionally used for balance of plant.

Three projects were selected in 2017 to develop low-cost, high-strength carbon fiber precursor materials to address the high cost of 700 bar onboard hydrogen storage systems. System cost projections indicated that high-strength carbon fiber will contribute at least 62% of the total system cost when manufactured in high annual volumes, with the precursor material contributing about half of the carbon fiber cost. The three selected projects are:

- University of Kentucky will develop hollow polyacrylonitrile (PAN) fibers using a low-cost PAN supply for conversion into high-strength carbon fiber. The project will also look to optimize the solution spinning process, especially the wash bath configuration and solvent recovery.
- The Pennsylvania State University will develop novel polyolefin precursor fibers for conversion into high-strength carbon fiber. The polyolefin fibers will not require sulfonation for conversion into carbon fiber and will provide higher mass yield of carbon fiber, reducing the mass of precursor required.
- Oak Ridge National Laboratory will investigate use of ionic liquid materials as plasticizers for reducing the melt temperature of PAN, allowing for lower-cost melt spinning of PAN precursor fibers. The ionic liquid plasticizers are also expected to facilitate the conversion into carbon fiber.

Specific accomplishment include:

- **Alternative manufacturing processes:** Materia, Inc., demonstrated improved vacuum infused composite tank processing, which reduced fabrication time from 2 h to 0.5 h for high-quality 7.5 L prototype vessels. They also achieved equivalent burst strength (1,833 bar [26,586 psi]) in static testing of small prototype vessels (Type III, 7.5 L).
- **Alternative material qualification:** SNL quantified fatigue performance for low-Ni austenitic stainless steel (21Cr-6Ni-9Mn) with nominally the same fatigue performance as the tested strain-hardened 316L stainless steel allowing potential cost saving for balance of plant components.
- **Conformable tank development:** The Center of Transportation and the Environment completed initial testing with baseline compressed natural gas vessels, including initial permeability performance measurements of the storage vessel resin, and proved test system workability.

Long-Term Focus: Cold/Cryo-Compressed and Materials-Based Storage

As shown in Figure 2, in addition to system cost challenges, compressed hydrogen storage systems are unable to meet the Program's 2020 targets for energy density. The density of hydrogen gas poses a theoretical limitation that prevents ambient compressed hydrogen systems from being able to meet the energy density targets. Given these limitations and as a longer-term strategy, the Hydrogen Storage sub-program continues to pursue less mature cold/cryo-compressed and materials-based hydrogen storage technologies that have the potential to satisfy all onboard hydrogen storage targets, including energy density.

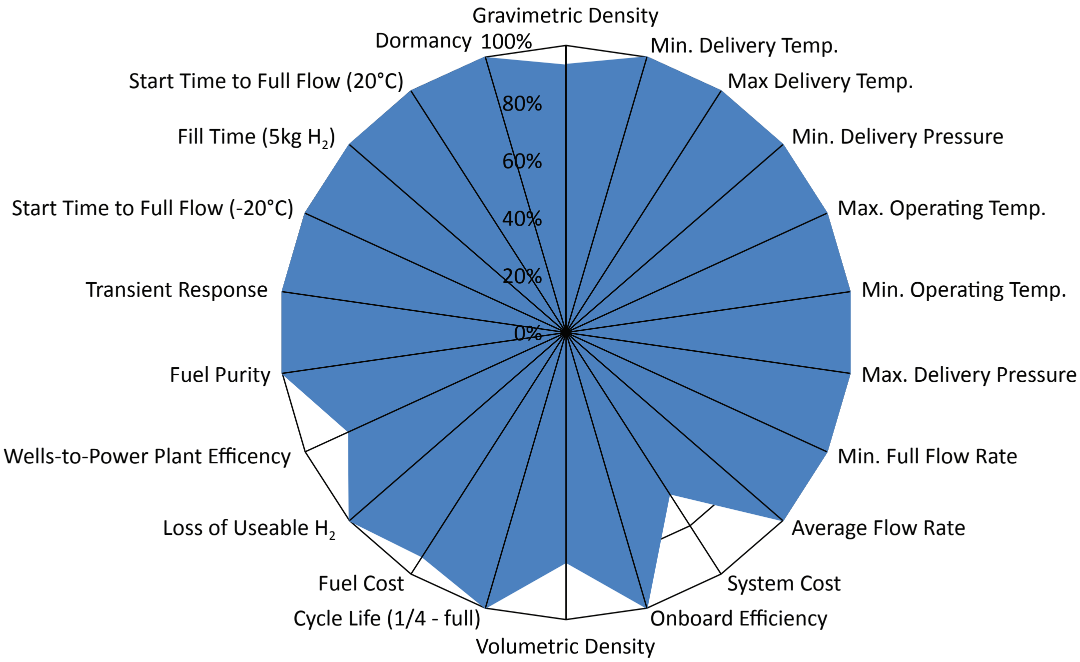

FIGURE 2. Current projected performance of a state-of-the-art 700 bar compressed hydrogen storage system with 5.6 kg usable hydrogen storage compared with the 2020 onboard automotive targets

In the area of cold-temperature operation, the sub-program selected a new project in FY 2016, led by Vencore Services and Solutions, focusing on improved thermal insulation systems for cold and cryogenic automotive tank applications, specifically to improve system dormancy (i.e., the length of time cold/cryogenic hydrogen can be stored before having to vent due to pressure build-up from warming of the hydrogen).

FY 2017 marked the second full year of efforts within HyMARC. The core team of national laboratory partners (SNL–lead, Lawrence Livermore National Laboratory, and Lawrence Berkeley National Laboratory [LBNL]) made a great deal of progress as they continue to address scientific gaps impeding the advancement of solid-state storage materials. For example, an experimental investigation involving several advanced characterization techniques showed that titanium is not present on the surface during hydrogen desorption from Ti-doped $NaAlH_4$, supporting the "zipper" mechanism and invalidating several other published mechanisms. This study demonstrates the power of bringing together these laboratory capabilities under the umbrella of HyMARC, as it utilized low energy ion scattering and X-ray adsorption spectroscopy at SNL, and scanning transmission X-ray microscopy as part of the Advanced Light Source at LBNL.

HyMARC researchers also continued to develop extensive theoretical modeling capabilities to complement these experimental tools. Modeling work at Lawrence Livermore National Laboratory on $Mg(BH_4)_2$, a promising material with over 14 wt% theoretical capacity and favorable thermodynamics, and its absorption/desorption reaction pathways continues to assist other HyMARC core efforts at SNL, HyMARC-supported efforts at Pacific Northwest National Laboratory (PNNL), and the seedling project at the University of Hawaii. In the past year, the researchers improved free energy predictions of hydrides by considering explicit thermal effects, with results tested and successfully validated on the Mg-B-H system. They also predicted stability trends of B_xH_y intermediates beyond the bulk crystalline limit to understand reaction pathways under non-equilibrium reaction conditions.

FY 2017 also marked the second full year of HyMARC's support team (also known as the Hydrogen Storage Characterization and Optimization Research Effort or HySCORE). This team, comprised of national laboratory partners (National Renewable Energy Laboratory [NREL], PNNL, LBNL) along with the U.S. Department of Commerce's National Institute for Standards and Technology Center for Neutron Research, is a subset of the overall HyMARC team and provides independent material measurement validation as well as support for the entire HyMARC consortium and seedling projects. Their function is especially focused on advanced characterization methodologies and validation of hydrogen storage concepts and mechanisms. Over the past year, NREL completed their round robin study on the hydrogen adsorption measurements of two different carbon samples, promoting improved best practices of collecting and reporting volumetric capacity data. The study included measurements by thirteen laboratories spanning industrial, national laboratory, and academic institutions, both domestic and international. In addition, new advanced characterization techniques have been brought online for use by HyMARC partners, including variable temperature thermal conductivity measurement at NREL, diffuse reflectance infrared spectroscopy at LBNL, and variable pressure nuclear magnetic resonance at PNNL.

Four additional seedling projects were selected in FY 2017 as the second round of individual projects to collaborate with the HyMARC consortium. These projects will develop specific hydrogen storage materials with potential to meet the performance requirements for onboard FCEV hydrogen storage. The four new awards selected in FY 2017 are:

- University of Michigan will apply machine learning techniques to design and experimentally demonstrate new metal-organic frameworks (MOFs) having high usable volumetric capacities, as well as control material crystal morphology and crystallite size distribution to increase packing densities.
- NREL will synthesize and characterize a series of partially fluorinated covalent organic frameworks that are intended to exhibit improved long-range ordering and assist in tuning hydrogen binding enthalpy.
- NREL will demonstrate that atomic layer deposition processes are compatible with metal borohydrides such that nanoparticles can be encapsulated with layers to promote rapid hydrogen discharging at lower temperatures and pressures through both protective and catalytic means.
- University of California, Berkeley will utilize post-synthetic modifications to introduce a large number of open metal sites into metal-organic frameworks while retaining a favorable pore environment to achieve improved hydrogen storage properties at ambient conditions.

The existing project at the University of Michigan, with subcontractor Ford, made significant progress in FY 2017 on computational-directed MOF synthesis. They used screening methods to examine a database of nearly a half-million real and hypothetical MOF structures and identified over 2,000 materials projected to surpass the usable gravimetric and volumetric capacities of MOF-5 by over 15%. Several materials were subsequently investigated experimentally. By using the Hydrogen Adsorbent System Model developed previously through the Hydrogen Storage Engineering Center of Excellence, it was demonstrated that both IRMOF-20 and DUT-23(Co) can outperform MOF-5 on a system-level basis.

Specific accomplishments include:

- **Insulation for cryogenic tanks:** Vencore down-selected the concept technologies for an integrated advanced insulation system for vehicle applications.
- **Metal hydride dehydrogenation mechanism elucidation:** An experimental investigation using several HyMARC capabilities at SNL and LBNL demonstrated that titanium is not present on the surface during hydrogen desorption from Ti-doped $NaAlH_4$, supporting the zipper mechanism and invalidating several published mechanisms.
- **Computational method development:** Lawrence Livermore National Laboratory continued progress on several types of modeling techniques, including detailed studies on surface and interface chemistry of hydrides, enabling the development of multiscale simulations to investigate the thermodynamics and kinetics of hydrogen storage in metal hydrides.
- **Round robin testing:** NREL completed the multi-laboratory round robin study on volumetric uptake in sorbents, including national laboratory, university, industrial, and international partners, and analyzed the results to identify sources of error in volumetric uptake measurements. These results are being prepared for dissemination to the hydrogen storage community.
- **Characterization method development:** LBNL commissioned and set up the diffuse reflectance infrared spectroscopy instrument with a sample cell to enable in situ gas loading capabilities to investigate hydrogen binding in sorbent materials.
- **Enhanced kinetics and cycling via “nanoencapsulation”:** Argonne National Laboratory successfully cycled sodium borohydride–graphene composite material six times with measured hydrogen capacity between 7.4 wt% and 9 wt% and improved kinetics when compared to the bulk phase material alone.

- **Material development:** For the first time, the University of Hawaii demonstrated the hydrogenation of a MgB_2 material to $Mg(BH_4)_2$ at 300°C and 700 bar.
- **High-throughput computational screening:** The University of Michigan identified multiple materials with high usable volumetric capacities by computational screening of MOF structure databases. Several MOFs were synthesized and their hydrogen adsorption properties were analyzed, experimentally confirming the predicted values.

Engineering

In FY 2017, NREL, in collaboration with Savannah River National Laboratory and PNNL, continued efforts to maintain and improve the usability and interface of the various models developed through the Hydrogen Storage Engineering Center of Excellence. The models are publicly available and continue to be a valuable tool for the hydrogen storage research community. Additionally, Savannah River National Laboratory continued leveraging the system models and system engineering expertise from the Hydrogen Storage Engineering Center of Excellence to design a materials-based storage system for use on a U.S. Navy unmanned underwater vehicle and provided a bench-scale prototype for evaluation. Preliminary analyses indicate a fuel cell system with alane (AlH_3) hydrogen storage can provide two to three times the energy storage of battery systems.

Specific accomplishments include:

- **System models development:** PNNL, NREL, and Savannah River National Laboratory completed a stand-alone isotherm data fitting routine to convert raw excess adsorption hydrogen data into its Dubinin-Astakhov parameters.
- **System models development:** NREL, Savannah River National Laboratory, and PNNL completed the executable stand-alone system design tools for both adsorbent and chemical hydrogen systems.
- **System development:** Savannah River National Laboratory refined engineering analysis to screen for the most attractive solid-state hydrogen storage material to meet Navy requirements for unmanned underwater vehicle 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.

Testing & Analysis

In FY 2017, the Hydrogen Storage sub-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 2017. Analyses were performed to investigate strategies to improve carbon fiber utilization as a means of reducing cost. A focus in FY 2017 was to model performance attributes of cryo-compressed hydrogen storage systems for heavy-duty flight applications, specifically in comparison to compressed hydrogen for bus applications.

In addition, models were developed and used to analyze the onboard and off-board performance of physical and material-based automotive hydrogen storage systems. Independent systems analyses were conducted for DOE to gauge the performance of hydrogen storage systems. Interface issues and opportunities and data needs for technology development were also identified, and reverse engineering to define material properties needed to meet system-level targets was performed.

Specific accomplishments include:

- **Onboard performance of cryo-compressed systems:** Demonstrated that 2-mm stainless steel liner is preferable to aluminum liner in cryo-compressed hydrogen storage systems for buses. Showed that compared to the baseline 350-bar cryo-compressed hydrogen storage tanks currently in use, 500-bar cryo-compressed hydrogen storage tanks can achieve 66% improvement in gravimetric capacity, 132% increase in volumetric capacity, and 36% saving in carbon fiber composite. Also determined >7-day loss-free dormancy with 95% full 500-bar cryo-compressed hydrogen storage tanks.
- **Preliminary cryo-compressed hydrogen storage system cost:** Analysis showed that (1) balance of system is nearly half the total cost, (2) automated insulation wrapping is predicted to lead to insulation costs of ~\$1.20/kWh at high volume, and (3) vacuum-degassing time uncertainty could lead to significant costs.

- **Preliminary savings for light-duty storage using cold compressed hydrogen:** Preliminary analysis suggests ~$2.50/kWh system savings are possible at 500 bar and 200 K.
- **Analysis of MOF-74 suggesting <$10/kg is achievable using liquid assisted grinding:** System-level cost with new MOF costs will be estimated in future work.
- **3,600 psi Type 4 compressed natural gas analysis:** The Institute for Advanced Composites Manufacturing Innovation, supported through the Office of Energy Efficiency and Renewable Energy's Advanced Manufacturing Office, provided specifications for two compressed natural gas vessels, one for potential use in light-duty vehicles and one for potential use in heavy-duty trucks. These specifications will be used to help validate the composite overwrapped pressure vessel cost models developed for compressed natural gas systems and to help establish a baseline for the Institute for Advanced Composites Manufacturing Innovation compressed gas storage efforts.

BUDGET

The FY 2017 budget request allocated $15.6 million to the Hydrogen Storage sub-program. This is consistent with the FY 2016 congressional appropriation of $15.6 million. In FY 2017, the Hydrogen Storage sub-program funds supported innovative 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. FY 2017 funds supported a variety of early-phase R&D efforts on advanced hydrogen storage materials and allowed for their coordination through the HyMARC efforts to ensure impact was maximized and resources were effectively utilized.

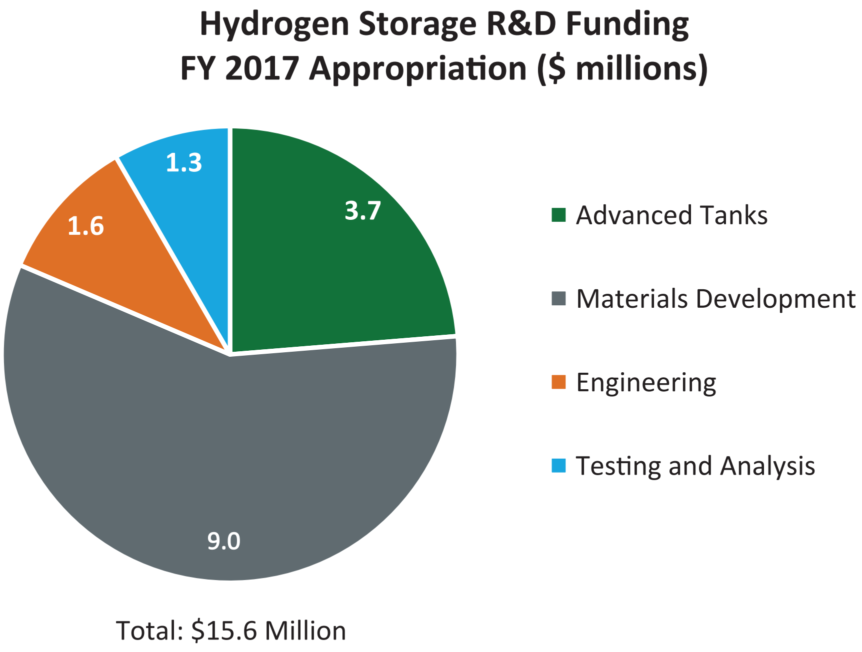

FIGURE 3. FY 2017 Appropriations

UPCOMING ACTIVITIES AND PLANS

The technology portfolio for the Hydrogen Storage sub-program will continue with a two-pronged approach focused on reducing the cost of high-pressure storage systems in the near term and increasing the capacity and overall performance of cold/cryo-compressed and material-based hydrogen storage systems for the long term to meet the Hydrogen Storage sub-program's revised 2020, 2025, and ultimate goals. The sub-program will continue early-stage R&D efforts to develop lower-cost high-pressure hydrogen storage systems in the near term with specific focus on low-cost precursors for high-strength carbon fiber. The sub-program will also coordinate with the Vehicle Technologies and Advanced Manufacturing Offices within the Office of Energy Efficiency and Renewable Energy on related carbon fiber composite activities. Specifically, the sub-program will continue to coordinate with and leverage efforts through the Institute for Advanced Composites Manufacturing Innovation, which is led by the Advanced Manufacturing Office, to develop approaches for manufacturing low-cost compressed gas storage systems. The sub-program will also continue to utilize the capabilities established through the HyMARC lab teams for early-stage R&D of materials and technologies to meet system targets for onboard automotive and non-automotive applications in the longer term. The sub-program's R&D activities will continue to be supported and informed by system performance and cost analysis efforts performed by Argonne National Laboratory and Strategic Analysis, Inc.

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, DC 20585-0121
Phone: (202) 586-9995
Email: Ned.Stetson@ee.doe.gov