IV.A.1 System Analysis of Physical and Materials-Based Hydrogen Storage

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Start Date: October 1, 2004
Projected End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Model various developmental hydrogen storage systems.
- Provide results to the Hydrogen Storage Engineering Center of Excellence for assessment of performance targets and goals.
- Develop models to "reverse-engineer" particular approaches.
- Identify interface issues, opportunities, and data needs for technology development.

Fiscal Year (FY) 2014 Objectives

- Perform impact damage analysis for Type 4 hydrogen storage tanks.
- Determine potential reduction in carbon fiber (CF) requirement with advanced resins.
- Determined gravimetric and volumetric capacities, and CF requirement with cold hydrogen storage.
- Establish sorbent properties needed to satisfy onboard and off-board storage system targets.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) System Weight and Volume

(B) System Cost

(C) Efficiency

(E) Charging/Discharging Rates

(J) Thermal Management

(K) System Life-Cycle Assessments

Technical Targets

This project is conducting system level analyses to address the DOE 2017 technical targets for onboard hydrogen storage systems:

- System gravimetric capacity: 1.8 kWh/kg
- System volumetric capacity: 1.3 kWh/L
- Minimum H_2 delivery pressure: 5 bar
- Refueling rate: 1.5 kg/min
- Minimum full flow rate of H_2: 0.02 g/s/kW

FY 2014 Accomplishments

- Conducted ABAQUS/Explicit analysis of impact damage in a fiber composite plate and validated the damage model with experimental data. Simulated horizontal and 45^{o} drop tests of Type 4 tanks per SAE International (SAE) J2579 protocol. Determined the damage volume in Type 4 tanks with and without advanced resins and with and without foam protection in the dome.
- Performed MultiMech analysis to determine the mechanical properties of nanocomposite resins and CF composites with advanced resins. Calibrated and validated MultiMech model against experimental data.
- Analyzed cold gas storage option that achieved ~50% reduction in CF and ~30% increase in gravimetric capacity (if a Type 4 tank can be used) compared to ambient 700-bar tanks. Identified off-board issues related to cryogenic cooling and insulated Type 3 vessels for trailer tubes and cascade refueling.
- Formulated models and performed reverse engineering to determine thermodynamic properties of sorbent materials needed to meet onboard system and off-board well-to-engine efficiency targets.

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INTRODUCTION

Several different approaches are being pursued to develop onboard hydrogen storage systems with the goal of meeting the DOE targets for light-duty vehicle applications. Each approach has unique characteristics, such as the thermal energy and temperature of charge and discharge, kinetics of the physical and chemical process steps involved, and requirements for the materials and energy interfaces between the storage system and the fuel supply system, on the one hand, and the fuel user on the other. Other storage system design and operating parameters influence the projected system costs as well. We are developing models to understand the characteristics of storage systems based on the various approaches, and to evaluate their potential to meet the DOE targets for onboard applications, including the off-board targets for energy efficiency.

APPROACH

Our approach is to develop thermodynamic, kinetic, and engineering models of the various hydrogen storage systems being developed under DOE sponsorship. We then use these models to identify significant component and performance issues, and to assist DOE and its contractors in evaluating alternative system configurations and design and operating parameters. We establish performance criteria that may be used, for example, in developing storage system cost models. We refine and validate the models as data become available from the various developers. We work with the Hydrogen Storage Systems Analysis Working Group to coordinate our research activities with other analysis projects to assure consistency and to avoid duplication. An important aspect of our work is to develop overall systems models that include the interfaces between hydrogen production and delivery, hydrogen storage, and the fuel cell.

RESULTS

Physical Storage

We developed a model to investigate impact energy absorption and damage of the composite overwrap in Type 4 tanks. We used this model to determine the minimum CF requirement for a Type 4 tank to pass the drop tests. We used ABAQUS/Explicit to model the transient dynamic response of the composite layer by layer. We simulated the drop tests for a full-sized Type 4 tank as defined in SAE J2579 [1], including horizontal drop impacting the cylinder, and 45° drop impacting the dome. In both cases, the center of mass is located at 1.8 m above ground. The tank was modeled with conventional 90° hoop winding and 15° helical winding. It was wound with sufficient CF composite to meet the 2.25 safety factor for 70 MPa nominal storage pressure. The impact analysis included three damage criteria: (1) matrix cracking, (2) layer delamination, and (3) fiber breakage. For horizontal drop, results from our analysis indicated that the matrix on the surface cracked but there was no internal damage to the matrix or the fiber. There was no delamination. Surface matrix cracking can be prevented with a thin layer of glass fiber over the CF composite overwrap. For 45° drop, our model predicted matrix damages through the composite thickness near the impact area. The calculated damage volume was 73 cm^3. There was no fiber breakage.

We investigated the effect of matrix dominant properties on impact resistance by varying each of the three properties (transverse tensile, transverse compressive, and shear strengths) independently of the other two. Simulation results show that the impact damage resistance is highly correlated to the shear strength with only small effects of the transverse tensile and compressive strengths. We simulated the 45° drop test for a full-sized Type 4 tank using advanced resins in the composite to determine the tank performance relative to one with neat resins. The advanced resins selected for this analysis is similar to the Applied Nanotech resins that include 1 wt% carbon nanotubes and 0.25 wt% SiO_2 which show ~20% improvement in tensile, compressive, and shear strengths over neat resins [2]. Figure 1a shows the reduction in the damage volume for 10 to 30% enhancement in the matrix dominant properties. We predicted a 35% reduction in damage volume with 30% enhancement in transverse tensile, transverse compressive, and shear strengths. We also investigated the effect of placing a foam "cap" over the CF composite overwrapped pressure vessel and then applying a thin layer of glass fiber overwrap over it all. Figure 1b shows that 1 cm of polyurethane foam can reduce the damage volume by 50%. A 2.5-cm foam can completely prevent damage to the dome in the 45° drop test. While foam is significantly more effective in protecting the dome from impact damage, advanced resins can provide protection in areas without foam such as near the boss and in the cylinder section.

We analyzed the off-board and onboard performance of the cold hydrogen storage option. We evaluated one scenario for hydrogen production (central steam methane

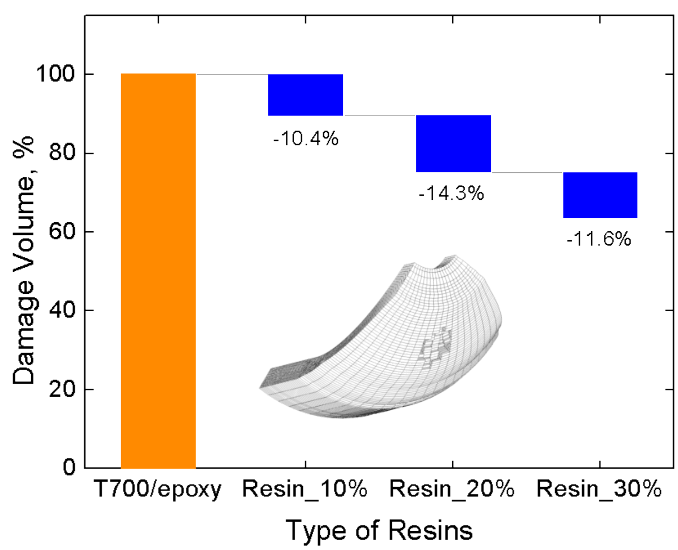

FIGURE 1a. Damage Volume Reduction with Enhancement in Matrix Dominant Properties

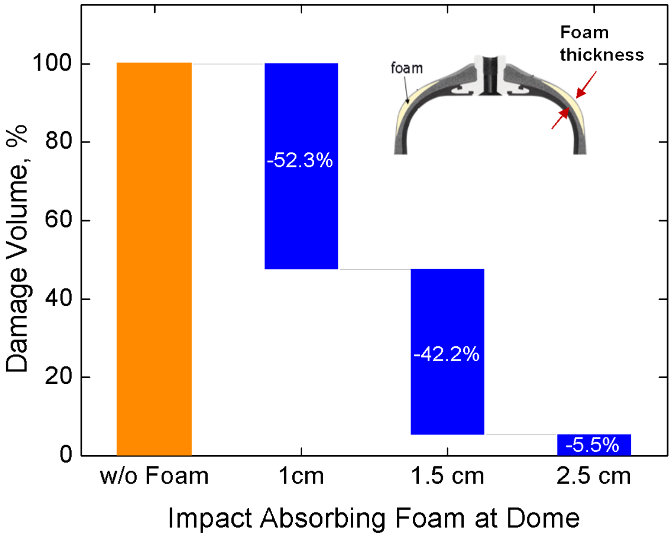

FIGURE 1b. Damage Volume in Dome With and Without Foam "Cap"

reformation), refrigeration (liquid nitrogen cooling at the city gate), and delivery (transmitted via pipeline to the city gate, insulated Type 3 tube trailers for trucking of compressed cold hydrogen to the refueling station). At the forecourt, the cold hydrogen is stored in Type 1 tube banks and dispensed using a cascade refueling system. For this scenario, we estimate a well-to-tank (WTT) efficiency of 47.4%, which is 13% lower than 54.2% WTT efficiency of the baseline ambient temperature 700-bar compressed hydrogen storage option.

The onboard storage system is adapted from the cryo-compressed system configuration [3] except that we analyzed the options of storing hydrogen in both Type 3 and Type 4 insulated tanks. The composite pressure vessel consists of T700S CF composite (2,550 MPa tensile strength) wound on an Al 6061-T6 alloy liner (Type 3), or high-density polyethylene (HDPE) liner (Type 4) and it is thermally insulated with multi-layer vacuum super insulation encased in a 3-mm-thick Al alloy vacuum shell. For Type 3 tanks, we conducted fatigue analyses to estimate the required metal liner thickness to meet the target life of 5,500 pressure cycles (SAE J2579 requirement). The thickness of the insulation was determined so as to limit the heat transfer rate from the ambient to 5 W.

Figure 2a shows the dependence of the operating temperatures on the storage pressure. It includes the temperature of the refueled cold gas, initially at 90 K and 340 bar in the tube trailer, compressed to 135% of the storage pressure in one stage with 65% isentropic efficiency. It also includes the tank temperatures prior to refueling and after discharging of 5.6 kg hydrogen, allowing for a 50 W-d heat gain from the ambient and the pressure/volume work. At 400 bar, the storage temperatures are above the HDPE

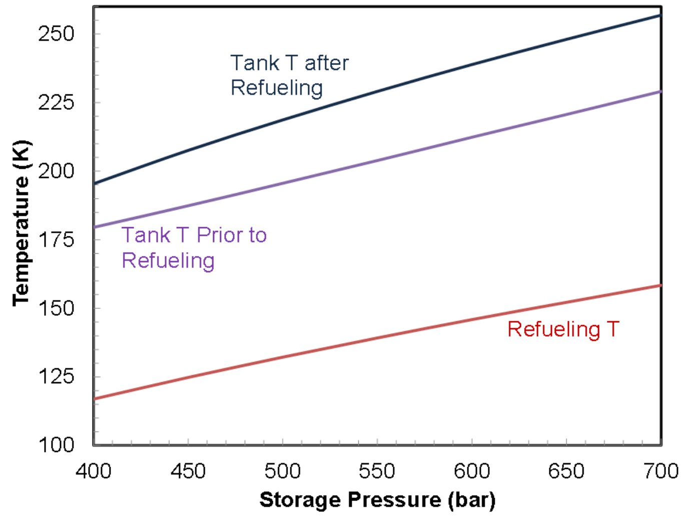

FIGURE 2a. Operating Temperatures as a Function of Storage Pressures

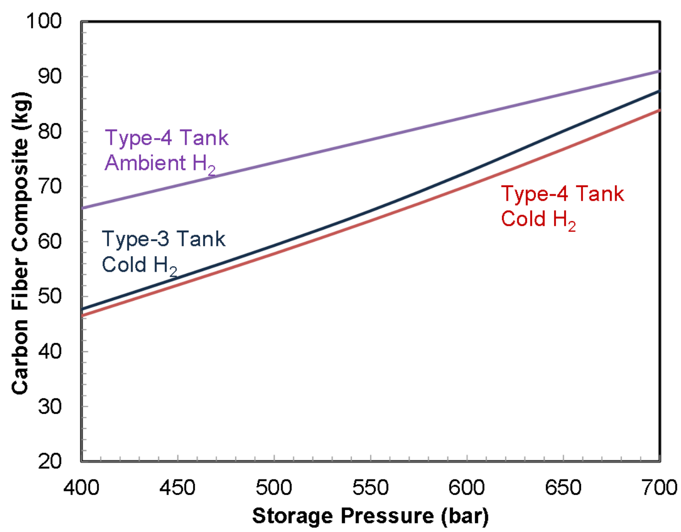

FIGURE 2b. CF Composite Requirements for Ambient and Cold Hydrogen Storage Options

glass transition temperature but below the ductile to fragile transition temperature.

Figure 2b indicates that nearly 50% reduction in CF composite (from 91 kg in baseline 700-bar Type 4 tank) is possible if cold gas (fixed 90 K nominal tube trailer temperature) is stored at 400 bar. There is only a small difference in CF composite requirements for Type 3 and Type 4 tanks storing cold gas. The projected CF usage is based on fiber strengths that are independent of storage temperature and translation efficiencies that only depend on storage pressure.

Figure 3a indicates that the volumetric capacity of the cold gas option with fixed 90 K tube trailer temperature

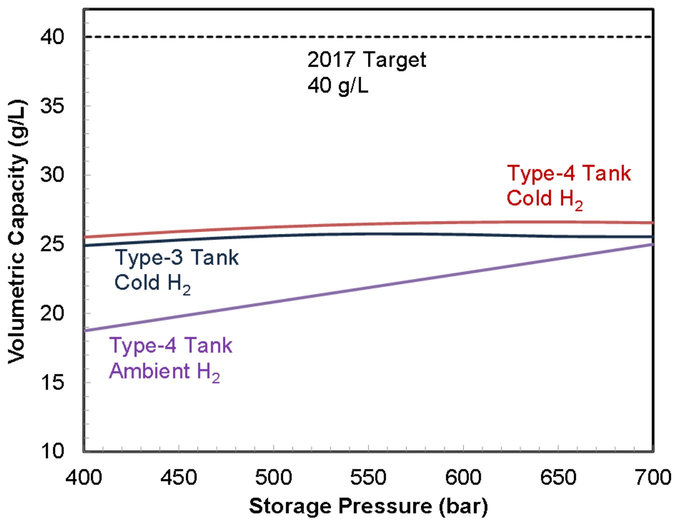

FIGURE 3a. Volumetric Capacity for Ambient and Cold Hydrogen Storage Options

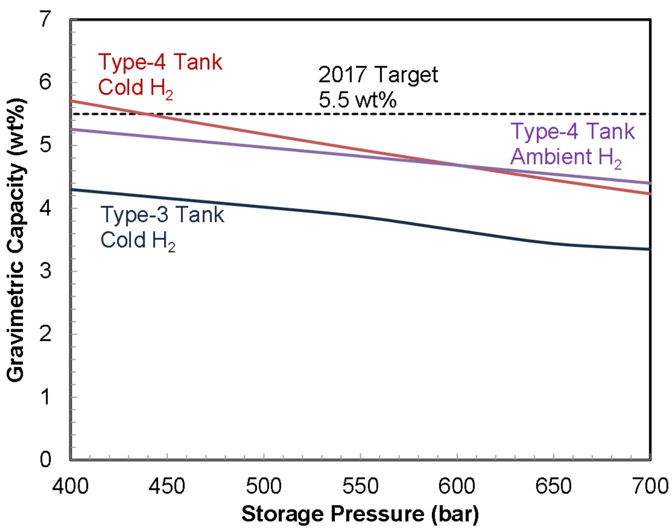

FIGURE 3b. Gravimetric Capacity for Ambient and Cold Hydrogen Storage Options

is nearly the same for Type 3 and Type 4 tanks, is nearly independent of the storage pressure, and is marginally (2-6%) higher than the volumetric capacity (25 g/L) of the baseline ambient temperature 700-bar compressed hydrogen system. Figure 3b suggests that it may be possible to meet the 5.5 wt% 2017 gravimetric capacity target with cold hydrogen storage in Type 4 tanks at storage pressures below 450 bar.

In summary, compared to the baseline 700-bar compressed hydrogen option, cold hydrogen storage (90 K nominal tube trailer temperature) at 400 bar in insulated Type 4 tanks has the potential of achieving 30% increase in gravimetric capacity (without sacrificing the volumetric capacity) and 50% saving in CF composite. The penalty is that the required cooling with liquid nitrogen incurs a 13% decrease in WTT efficiency.

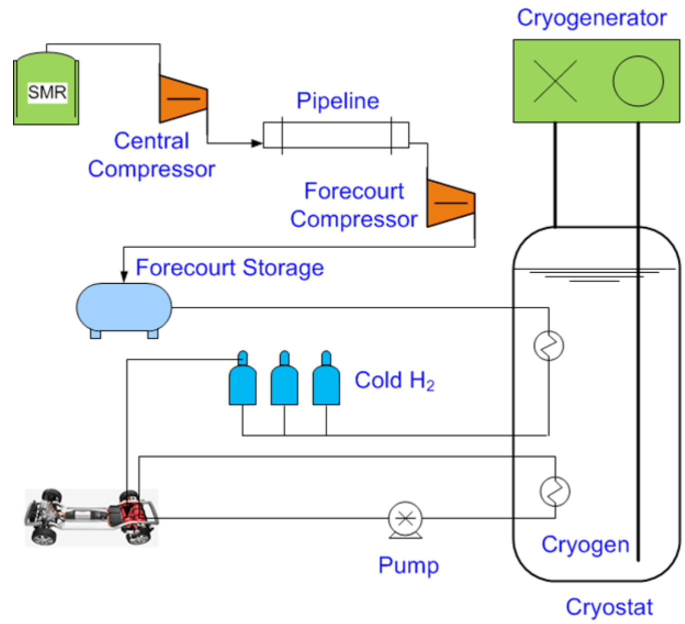

FIGURE 4a. Hydrogen Production, Delivery and Forecourt Scenario

Hydrogen Storage in Sorbents

We conducted a “reverse engineering” analysis to determine the minimal material requirements for a sorbent storage system to meet the DOE 2017 performance targets. We first conducted a literature search to develop an empirical correlation for coefficient of performance of cryogenic systems as a function of the refrigeration temperature and plant size. We used this correlation to formulate a simple model that determines the allowable cooling duty for specified coolant temperature and target WTT efficiency for a hydrogen production, delivery, and forecourt scenario outlined in Figure 4a.

Figure 4b shows the reference onboard system used in the reverse engineering analysis. A model was developed to determine the performance of this system in terms of the sorbent sorption properties and the operating conditions. The system model uses a single-Langmuir equation to describe the adsorption isotherms, a model for thermodynamic of adsorption, a correlation for bed thermal conductivity as function of additive weight fraction and fill factor, transient heat transfer module for refueling and discharge, and a containment module for liner thickness and CF requirement.

Table 1 summarizes the results of the reverse engineering analysis. The main conclusion is that a promising sorbent should have >120 g-H_2/kg excess sorption capacity at 150 K or higher temperature and 100 bar, when compacted to 420 kg/m^3 bulk density, and mixed with 10-20% expanded

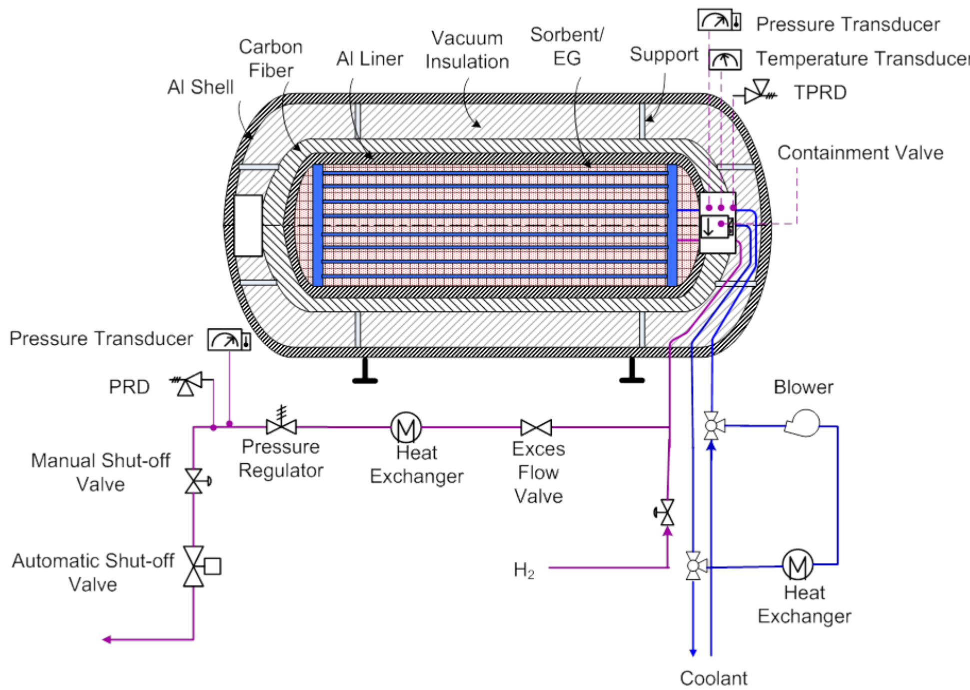

FIGURE 4b. Schematic of Onboard System for Hydrogen Storage in Sorbents

natural graphite or other conductivity enhancement materials to reach 1 W/m·K bed thermal conductivity. A material with ΔH^o of 5 kJ/mol will need to have a minimum excess capacity of 190 g-H_2/kg-sorbent at 77 K for the system to meet the 5.5 wt% gravimetric capacity target. The off-board coolant temperature needs to be above 135 K to reach the study target of >55% WTT efficiency. Adsorbents with ΔH° >7.5 kJ/mol are especially appealing as they may lead to higher storage temperatures, lower storage pressures, and 60% WTT efficiency.

CONCLUSIONS AND FUTURE DIRECTIONS

- We estimate that the damage volume in the dome for a Type 4 tank holding 5.6 kg usable hydrogen is 73 cm^3 when it is dropped at 45° from a height of 1.8 m. The damage volume can be reduced with advanced resins in the composite, or by placing a foam “cap” over the CF composite overwrapped pressure vessel. A 2.5-cm foam “cap” can completely prevent damage to the dome in the 45° drop test.

TABLE 1. Reference Values for Meeting Onboard Targets

Independent Variables	Related Variables	Reference Values	Constraints
Material Properties			
Excess Uptake at 77 K	DH^o = 5 kJ/mol	190 g-H_2/kg-sorbent	5.5 wt% gravimetric capacity
Fill Ratio	Bulk Density	67% bed porosity	40 g/L volumetric capacity
		420 kg/m^3 sorbent bulk density	
	Thermal Conductivity	1 W/m.K bed conductivity	
Operating Temperatures			
Off-board Coolant	WTT Efficiency	135 K	>55% WTT efficiency
Storage Temperature		155 K	
Temperature Swing	Usable H_2	60 K	95% usable H_2
System Variables			
Mass of Sorbent	Mass of Expanded	42 kg sorbent	5.6 kg usable H_2
	Graphite	8.4 kg ENG	
HX Tube Spacing	Number of HX Tubes	r_2/r_1 = 3.4	1.5 kg/min refueling rate
		112 U tubes	

HX – heat exchanger

- We project that cold hydrogen storage at 400 bar and 180-195 K can achieve ~50% reduction in CF and ~30% increase in gravimetric capacity (if Type 4 tanks can be used at these service temperatures) compared to ambient 700-bar tanks. The WTT efficiency, however, would be 13% lower to 47.4% because of the liquid nitrogen needed to cool the hydrogen to 90 K at the city gate.
- We suggest that a sorbent needs to have ΔH° >5 kJ/mol and an excess uptake >190 g-H_2/kg at 77 K for the storage system to meet the 5.5 wt% gravimetric capacity target at 150 K and >55% WTT efficiency. The sorbent material should be capable of being compacted to >420 kg/m^3 bulk density for >40 g/L system volumetric capacity. The sorbent compact should also have thermal conductivity >1 W/m.K, when mixed with up to 10-20 wt% conductivity enhancement additives, for 1.5 kg-H_2/min refueling rate.
- In FY 2015, we will continue to run ABAQUS simulations to analyze hydrogen storage in near term, Type 4 700-bar CF-wound pressure vessels. We will simulate local dome winding as an alternate to the endcap concept and investigate helical angle tailoring in the cylinder section to optimize CF performance.
- In FY 2015, we will perform independent analyses to determine the optimal storage pressures and temperatures for physical storage with respect to cost and driving range. We will conduct the analysis for both onboard Type 3 and Type 4 CF wound storage tanks. We will work with the Analysis and Delivery Team personnel to include results for off-board cost and energy consumption.
- In FY 2015, we will analyze the data obtained by the Hydrogen Storage Engineering Center of Excellence for alane slurries of up to 60 wt% loadings. We will use the data to improve, calibrate, and validate the models for dehydrogenation kinetics, component size and volume, and storage system. We will conduct onboard system analysis to evaluate the viability of chemical hydrogen storage and identify the technology gaps for meeting the DOE 2017 performance targets.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. H.S. Roh, T.Q. Hua, and R.K. Ahluwalia, “ Optimization of Carbon Fiber Usage in Type-4 Hydrogen Storage Tanks for Fuel Cell Automobiles,” International Journal of Hydrogen Energy, 38 (2013) 12795-12802,

2. J.K. Peng and R.K. Ahluwalia, “Enhanced Dormancy due to Para-to-Ortho Hydrogen Conversion in Insulated Cryogenic Pressure Vessels for Automotive Applications,” International Journal of Hydrogen Energy, 38 (2013) 13664-1367.

3. R.K. Ahluwalia, J.K. Peng, and T.Q. Hua, “Bounding Material Properties for Automotive Storage of Hydrogen in Metal Hydrides for Low-Temperature Fuel Cells,” Accepted for publication in International Journal of Hydrogen Energy.

4. R.K. Ahluwalia and T.Q. Hua, “Onboard Safety,” Data, Facts and Figures on Fuel Cells, Detlef Stolten and Remzi Samsun (Editors), Wiley-VCH, to be published in 2014,

5. R.K. Ahluwalia and T.Q. Hua, “Pressurized System,” Data, Facts and Figures on Fuel Cells, Detlef Stolten and Remzi Samsun (Editors), Wiley-VCH, to be published in 2014.

6. R.K. Ahluwalia, T.Q. Hua, J.K. Peng, and H.S. Roh, “System Level Analysis of Hydrogen Storage Options,” Hydrogen Storage Tech Team Meeting, Southfield, MI, February 20, 2014.

7. H.S. Roh, T.Q. Hua, and R.K. Ahluwalia, “Effect of Resin Properties on Impact Damage Tolerance in Carbon Fiber Composite Tanks,” Storage System Analysis Working Group Meeting, Webinar, April 10 2014.

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1. SAE J2579, Technical Information Report for Fuel Systems in Fuel Cell and Other Hydrogen Vehicles. SAE International, 2013.

2. Dongsheng Mao, “Ultra Lightweight High Pressure Hydrogen Fuel Tanks Reinforced with Carbon Nanotube,” 2013 DOE Hydrogen Program review, Washington, DC, May 2013.

3. R.K. Ahluwalia, T.Q. Hua, J.K. Peng, D. Papadias, and R. Kumar, “System Level Analysis of Hydrogen Storage Options,” 2011 DOE Hydrogen Program review, Washington, DC, May 2011.