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 DOE 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) 2016 Objectives

- Perform ABAQUS analysis of Type-IV tanks that incorporate the design features similar to the Toyota Mirai compressed hydrogen storage tanks.
- Determine the potential and attributes of high pressure metal hydrides that can improve the performance of high-pressure hydrogen storage tanks. Analyze the performance metrics for a 350 bar hybrid tank storage system.

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 on-board hydrogen storage systems.

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

FY 2016 Accomplishments

- Conducted ABAQUS simulations to determine the amount of carbon fiber (CF) for 700 bar Type-IV tanks that have similar design features as the Toyota Mirai storage tanks. The analysis predicts that these design features could reduce the amount of CF by 4–7% for tanks with length-to-diameter (L/D) ratio of 2.8–3.0, but there is no impact for tanks with L/D ~1.7. The CF composite weight reduction is ~20% if the tank is wound with the higher strength T720 carbon fiber.
- Established new 2015 status performance metrics for 700 bar compressed hydrogen storage tanks: 1.40 kWh/kg gravimetric capacity, 0.81 kWh/L volumetric capacity, 97 kg T700 CF composite.
- Conducted reverse engineering analysis 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. The analysis shows that a hybrid hydrogen storage system with a 350 bar Type-IV tank has the same volumetric and gravimetric capacities as a compressed hydrogen (cH_2) storage system with a 700 bar Type-IV tank. The required amount of carbon fiber in such a hybrid system is 51 kg compared to 97 kg in a 700 bar Type-IV cH_2 tank, and 62 kg in a 350 bar Type-IV cH_2 tank.

INTRODUCTION

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

APPROACH

The approach is to develop thermodynamic, kinetic, and engineering models of the various hydrogen storage systems being developed under DOE sponsorship. These models are then used to identify significant component and performance issues, and to assist DOE and its contractors in evaluating alternative system configurations and design and operating parameters. Performance criteria are established that may be used, for example, in developing storage system cost models. Data is refined and validated as the models become available from the various developers. The team works with the Hydrogen Storage Systems Analysis Working Group to coordinate research activities with other analysis projects to assure consistency and to avoid duplication. An important aspect of this 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

The team conducted ABAQUS analysis of the hydrogen storage tanks deployed on the Toyota Mirai. The Toyota Mirai storage tanks have three distinct features [1] that differ from conventional tanks: (1) the liner has a sharp transition from the dome to the cylinder, (2) hoop winding is concentrated in the inner portion of the overwrap with high angle helical winding eliminated, and (3) the boss has a smaller opening diameter and longer flange. The general winding sequence [2] consists of one helical layer over the entire liner, followed by concentrated hoop winding over the cylinder and finally helical/hoop winding over the tank as typically encountered in conventional tanks. Furthermore, the team considers an alternative winding scheme in which glass fiber is used for the first helical layer to take advantage of its high failure strain (3.5% compared to <2% for carbon fiber).

The team analyzed two tanks that have the same volume (~60 L) and length-to-diameter ratio (L/D = 2.8) as the Mirai front tank. The first tank is a conventional tank and the second incorporates the Mirai tank design features. Both tanks are wrapped with T700 carbon fiber. The conventional tank requires 43.0 kg carbon fiber composite (CF), while the tank with the Mirai design features requires 39.9 kg, a 7.2% reduction. The 3.1 kg reduction in CF comprises of 1.9 kg reduction in the cylinder section and 1.2 kg in the domes.

The team also analyzed two tanks that have the same volume (~62 L) as the Mirai rear tank, which has an L/D ratio of 1.7. The results show practically no difference (~0.3 kg) in the required amount of CF between a conventional tank and one that incorporates the Mirai design features. The reduction in the amount of CF wrapped over the domes (1.94 kg) is offset by a larger increase in the amount of CF wrapped through the cylinder section (2.24 kg). In terms of hoop/helical windings, there is a small reduction in hoop windings, which is offset by a small increase in helical windings. The distribution of CF in the cylinder section and the domes are shown in Table 1 for the front and rear tanks.

The team applied the Mirai design features and fiber winding scheme in constructing a finite element analysis (FEA) model for a full-sized tank that has a L/D ratio of 3.0 and holds 5.6 kg of usable hydrogen. The team considered four choices of composite materials: (1) T700 CF with epoxy, (2) T700 CF with vinyl ester low cost resin, (3) T700 CF with low cost resin and alternate sizing, and (4) T720 CF with epoxy. For each of the T700 CF composites, two tanks were analyzed, one with the conventional design and another that incorporates the Mirai design features. First, two tanks differing only in the boss configuration were analyzed to determine the impact of the boss on the amount of helical

TABLE 1. ABAQUS Results for 2.3-kg H_2 Front (L/D = 2.8) and Rear (L/D = 1.7) Tanks

	Front Tank (60 L), L/D = 2.8			Rear Tank (62 L), L/D = 1.7		
	Conventional	Mirai Design	Difference	Conventional	Mirai Design	Difference
Cylinder	34.6	32.7	-1.9	29.5	31.8	2.3
Dome	8.4	7.2	-1.2	15.3	13.4	-1.9
Total	43	39.9	-3.1	44.9	45.2	0.3

winding: one approximated the Mirai boss and another used a more typical boss that has a larger opening diameter and shorter flange. The results in stress distributions and amount of helical winding are practically unchanged. It should be noted that the Mirai boss simulated in the FEA model is derived from the drawing published in Reference 1. Details of the boss configuration and dimensions are not available.

The analysis results, presented in Figure 1, show that the T700 CF composite weight in the tanks that incorporated the Mirai design is 4.1–6.3% lower than that for comparable conventional tanks. In reference to the 2015 baseline tank which requires 97 kg carbon fiber composite [3], changing the liner design and winding method reduced the amount of composite to 92.3 kg (4.8% reduction). If glass fiber is used for the first helical layer, the amount of carbon fiber composite is further reduced to 90.8 kg, but 2.7 kg glass fiber is added to the tank. The tank wound with T720 CF composite weighs substantially less, because T720 CF has higher tensile strength, therefore less material is needed for reinforcement. The effect of L/D is illustrated in Figure 2. It compares the percentage reduction in CF composite weight relative to a conventional tank for tanks that hold 2.3 kg H_2 and 5.6 kg H_2. The tanks are reinforced with T700 CF/epoxy or T700 CF with low cost resin and alternate sizing. The integration of the Mirai tank design features could reduce the CF composite weight by 5–7% for tanks with L/D ~2.8–3.0, but has little or no impact for tanks with L/D ~1.7 due to geometric effect given constant volume.

Hydrogen Storage in High Pressure Metal Hydrides

The team developed a model for high pressure metal hydrides (HPMH) and used it to determine a map of desirable material properties to augment the performance of cH_2 systems. For the purpose of this study, HPMH is defined as a metal hydride that is unstable at room temperature and pressure, but can be formed at elevated hydrogen pressures. As a first application, a hybrid concept is considered in which hydrogen is stored as compressed gas at 350 bar in a Type-IV tank, which also contains HPMH to improve its overall volumetric capacity. The following is a list of some desirable material properties that HPMH should have for this hybrid storage concept.

- The equilibrium pressure at 80°C should be less than 200 bar so that the tank can be refueled at 350 bar (P_c) without exposing the liner to temperatures above the allowable limit for HDPE used in Type-IV tanks. The team has included a $\Delta P = P_c - P_{eq}(80°C)$ of 150 bar to accommodate for reasonable charge kinetics.
- The equilibrium pressure should be above the minimum delivery pressure (P_d = 5 bar) at all allowable operating and ambient temperatures. The requirement that the fuel cell is able to start at -40°C requires that $P_{eq}(-40°C)$ should be higher than 5 bar. Without this requirement, a buffer tank would be needed to supply hydrogen to the fuel cell until the tank pressure reaches 5 bar.
- The hybrid storage system has 100% on-board efficiency (i.e., all the stored hydrogen is available to the fuel cell) if HPMH can be discharged using the stack coolant as the heat source. In the fuel cell systems of current interest, the steady-state coolant temperatures may vary between 60°C and 90°C. The team requires that the HPMH should discharge at the lowest coolant temperature and, for reasonable discharge kinetics, $\Delta P = P_{eq}(60°C) - P_d$ be higher than 50 bar.

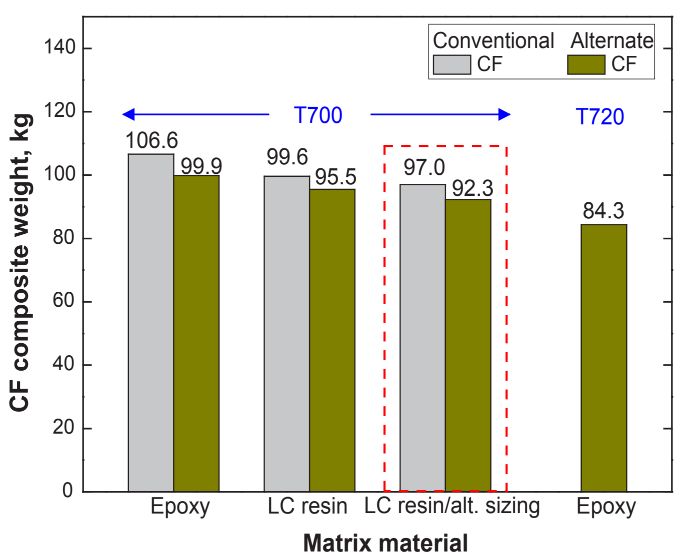

FIGURE 1. Composite weight in conventional tanks and tanks with Toyota Mirai design features

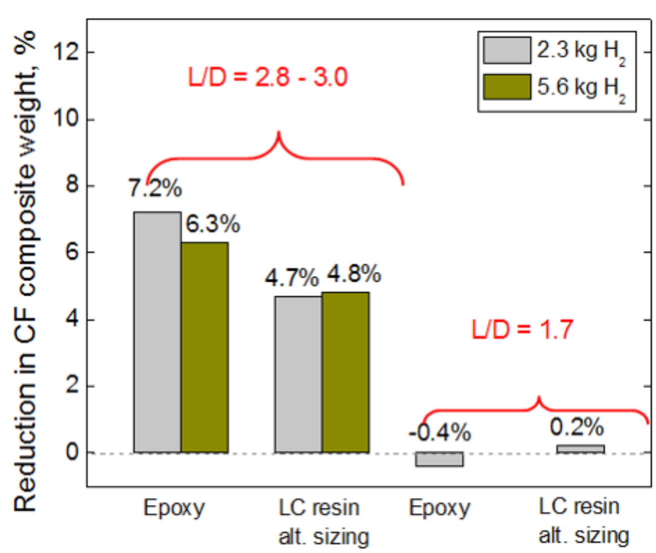

FIGURE 2. Effect of length-to-diameter ratio on carbon fiber savings

Figure 3 presents a ΔH vs. ΔS thermodynamic acceptability map of HPMH materials that meet the above requirements and for which the van't Hoff equation for plateau pressure is applicable. The boundary AB in Figure 1 is determined from the third requirement to discharge HPMH using the stack coolant at 60°C as heat source. The boundary BC is determined from the second requirement to maintain the tank pressure above 5 atm at all operating temperatures including -40°C. The boundary CD is determined from the first requirement to maintain reasonable ΔP while refueling the tank to 350 atm at 80°C

The team developed a dynamic model for refueling of a hybrid tank containing HPMH and incorporated the dynamic refueling model in the system analysis code. The combined code was used to conduct an initial study to determine HPMH properties, such that a hybrid hydrogen storage system with a 350 bar Type-IV tank (see Figure 4) has the same volumetric and gravimetric capacities as a cH_2 storage system with a 700 bar Type-IV tank, while also satisfying all other system targets. As shown in Table 2, the required amount of CF in such a hybrid system is much smaller than the CF needed in a 700 bar Type-IV cH_2 tank and is even smaller than the CF needed in a 350 bar Type-IV cH_2 tank.

Table 3 summarizes the initial results for HPMH material properties needed to satisfy the listed constraints. The results indicate that the material needs to have 6.9 wt% intrinsic hydrogen capacity with 10% minimum and 93% maximum state-of-charge (SOC) for the system to reach 4.3 wt% gravimetric capacity. The HPMH needs to be compacted to 292 kg/m^3 bulk density for 24.6 g/L volumetric capacity. The model includes an allowance of 10 wt% expanded natural graphite (ENG) for the medium to reach 5 W/m.K bed conductivity. The hybrid system can satisfy the 1.6 g/s full flow target even at the minimum SOC, if the HPMH discharge kinetics is such that SOC decreases isothermally in 6.2 min (τ_d) from 93% to 10% at 5 bar backpressure and 60°C. Similarly, the hybrid system can satisfy the 1.5 kg/min refueling rate target if the HPMH charge kinetics is such that SOC increases isothermally in 3.7 min (τ_c) from 10% to 93% at 350 bar backpressure and 60°C.

Only 45% of the 5.6 kg recoverable hydrogen in the hybrid system is stored in HPMH; the remaining 55% is stored in the voids and pores as compressed gas. According to our model, the charge kinetics is fast enough to reach 90% SOC during the refueling time, but hydrogen absorption continues even after the coolant flow is stopped. Future studies will evaluate the possibility of taking credit for the continuing hydrogen absorption after the refueling event.

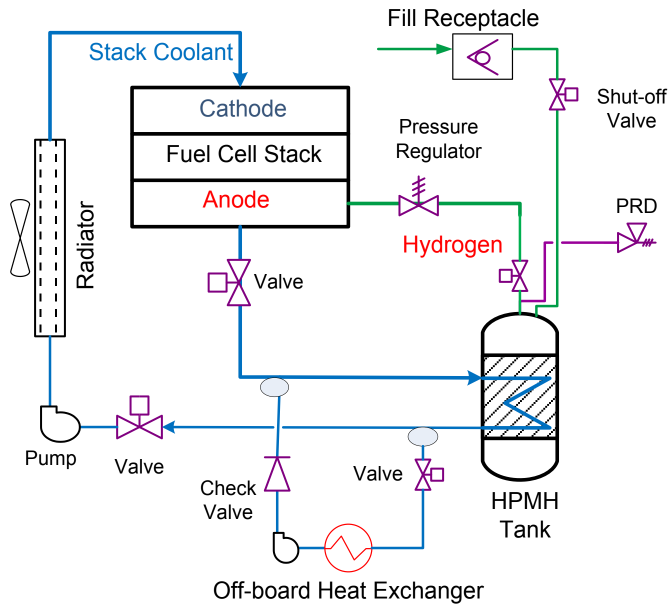

FIGURE 4. Hybrid system with 350-bar Type-IV tank filled with high pressure metal hydrides

TABLE 2. Performance of Hybrid Storage Concept Relative to Compressed Hydrogen Systems, All Systems with 5.6 kg Recoverable Hydrogen Capacity

Storage System	Compressed H_2		Hybrid
Storage Pressure	700 bar	350 bar	350 bar
Volumetric Capacity	24.4 g/L	17.7 g/L	24.6 g/L
Gravimetric Capacity	4.2 wt%	5.4 wt%	4.3 wt%
Carbon Fiber	97 kg	62 kg	51 kg

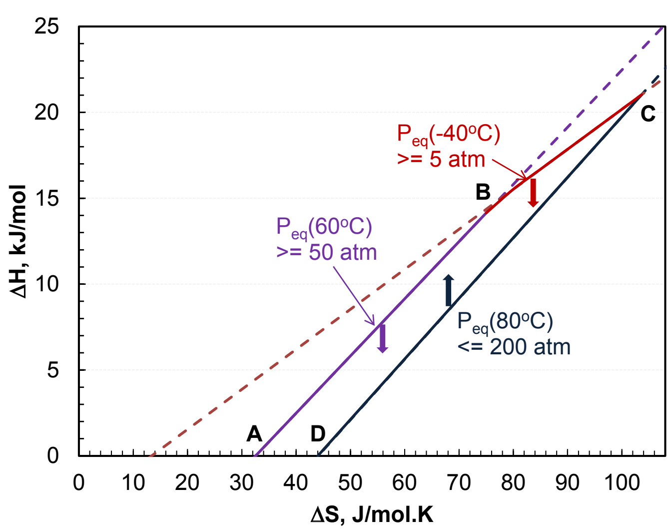

FIGURE 3. Thermodynamic acceptability map of high pressure metal hydrides. Boundary AB is determined from HPMH discharge temperature, BC from minimum operating pressure, and CD from refueling kinetics.

TABLE 3. Desired HPMH Physical, Transport, and Kinetic Properties

Variables	Related Variables	Reference Values	Constraints
HPMH Intrinsic Capacity		5.8% H capacity	4.3 wt% gravimetric
Fill Ratio	Bulk Density Thermal Conductivity	80.6% bed porosity 292 kg/m^3 HPMH bulk density 5 W/m.K bed conductivity	24.6 g/L volumetric
Desorption Kinetics	X_{min} = 10%	τ_d = 6.2 min	1.6 g/s min full flow
Sorption Kinetics	X_{max} = 93%	τ_c = 6.7 min	X_{min} to X_{max} in 3.7 min
HX Tube Spacing	Number of Tubes	r_2/r_1 = 4.5, 58 U tubes	1.5 kg/min refueling
Refueling Pressure	Storage Pressure	410 atm	350 bar pressure 25% overpressure limit
Mass of HPMH	Mass of Expanded Natural Graphite	46.5 kg HPMH 4.7 kg ENG ΔH = 14.8 kJ/mol DS = 77.2 J/mol.K E_A = 45 kJ/mol	5.6 kg usable H_2 3.4 kg as cH_2 2.5 kg H_2 in HPMH

CONCLUSIONS AND FUTURE DIRECTIONS

- The team estimates 4–7% (varying with tank capacity) reduction in the amount of T700 composite for a tank that incorporates the Mirai tank design features and with L/D ~2.8–3.0, but no reduction for L/D ~1.7. Replacing carbon fiber with glass fiber for the first helical layer could further reduce the carbon fiber amount by an additional 2–5%. The team estimates ~20% reduction in composite weight for a full-sized tank (5.6 kg H_2), with Mirai tank features, the majority of the reduction is due to switching to higher strength T720.
- The ABAQUS FEA results show practically no difference in the required amount of helical winding for using a boss with smaller diameter opening and longer flange.
- The team estimates that a hybrid system that stores hydrogen as compressed gas at 350 bar and also contains HPMH matches the gravimetric and volumetric capacities of a 700 bar cH_2 system. The required amount of CF in such a hybrid system is 47% less than the CF needed in a 700 bar Type-IV cH_2 tank and is even smaller than the CF needed in a 350 bar Type-IV cH_2 tank.
- The team estimates that 45% of the 5.6 kg recoverable hydrogen in the hybrid system is stored is in HPMH; the remaining 55% is in the voids and pores as compressed gas. According to the model, the charge kinetics is fast enough to reach 90% SOC during the refueling time, but hydrogen absorption continues even after the coolant flow is stopped.
- In FY 2017, the team will conduct ABAQUS simulations to determine potential CF savings in alternate tank concepts, such as an elliptical tank and assess the manufacturability of alternate concepts. The team will investigate the feasibility of packaging alternate tank configurations onboard light-duty vehicles to achieve optimal volumetric capacity.
- In FY 2017, the team will conduct fatigue and autofrettage analysis to determine the fatigue life of liner in Type-III tanks storing hydrogen at ambient and cryogenic temperatures. Additionally, the team will conduct MultiMech analysis to investigate the effect of void content in resin on the degradation of composite performance in pressure vessels.
- In FY 2017, the team will analyze the cryocompressed hydrogen storage option for captured fleets (e.g. busses, waste trucks) where dormancy is less of an issue. The team will utilize recent Lawrence Livermore National Laboratory data for cryotanks and the Linde liquid hydrogen pump in the system model.
- In FY 2017, the team will update the sorption model to analyze the performance of the best-of-class metal organic frameworks (e.g., M_2(m-dobdc), M = Mg, Mn, Fe, Co, Ni series of frameworks), developed at Lawrence Berkeley National Laboratory, in a representative on-board storage system under realistic operating conditions.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. R.K. Ahluwalia, J.K. Peng, and T.Q. Hua, "Sorbent Material Properties for On-board Hydrogen Storage for Automotive Fuel Cell Systems," International Journal of Hydrogen Energy. 40 (2015) 6373–6390.

2. R.K. Ahluwalia and T.Q. Hua, "Pressurized Systems," Chapter 15 in Data, Facts and Figures on Fuel Cells, Detlef Stolten and Remzi and Nancy Garland (Editors), Wiley-VCH, 2016, 143–148.

3. R.K. Ahluwalia and T.Q. Hua, "Onboard Safety," Chapter 18 in Fuel Cells Data, Facts and Figures, Detlef Stolten and Remzi Samsun and Nancy Garland (Editors), Wiley-VCH, 2016, 177–182.

4. R.K. Ahluwalia, J.K. Peng, and T.Q. Hua, "Implementing Hydrogen Storage Based on Metal Hydrides," Chapter 32 in Hydrogen Science and Engineering, Materials, Processes, Systems and Technology, Vol 2, Detlef Stolten and Bernd Emonts (Editors), Wiley-VCH, 2016, 791–808.

5. H.S. Roh, T.Q. Hua, and R.K. Ahluwalia "Modeling of Type IV Hydrogen Storage Tanks and the Toyota Mirai Storage Tank Design," Storage System Analysis Working Group Meeting, November 16, 2015.

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, March 17, 2016.

REFERENCES

1. Yamashita, A., Kondo, M., Goto, S., and Ogami, N., "Development of High-Pressure Hydrogen Storage System for the Toyota "Mirai"," SAE Technical Paper 2015-01-1169, 2015, doi:10.4271/2015-01-1169.

2. Hirokazu Otsubo and Shiro Nishibu, U.S. Patent US20130299505A1, November 2013.

3. DOE Hydrogen and Fuel Cells Program Record, Record # 15013, September 30, 2015.