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

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Project Start Date: October 1, 2004
Project 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) 2017 Objectives

- Perform ABAQUS[1] and fatigue analyses to determine carbon fiber (CF) and liner thicknesses in Type III cryo-compressed tanks for light-duty and commercial fuel cell vehicles.
- Conduct system analysis of cryo-compressed hydrogen (CcH_2) storage for fuel cell buses with emphasis on dormancy, durability, and capacity.
- Update reverse engineering analysis for hydrogen storage in sorbents.
- Update 700-bar compressed hydrogen (cH_2) storage system parameters.

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 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 2017 Accomplishments

- Conducted autofrettage and fatigue analyses to determine the metal liner thickness for cryo-compressed Type III tanks. Demonstrated that 2-mm stainless steel liner is preferable to aluminum liner for fuel cell buses.
- Performed system analysis for cryo-compressed hydrogen storage for fuel cell buses. Showed that compared to the baseline 350-bar cH_2 tanks currently in use, 500-bar CcH_2 can achieve 66% improvement in gravimetric capacity, 132% increase in volumetric capacity, and 36% savings in carbon fiber composite. Determined >7-d loss free dormancy with 95% full 500-bar CcH_2 tanks.
- Updated analysis for 700-bar cH_2 storage. Showed that reducing the ambient temperature to 15°C and tank empty pressure to 10 bar can save ~3% CF, and the alternate tank design can save ~5% CF.
- Updated reverse engineering analysis for hydrogen storage in sorbents. Improved the heat transfer module in system analysis code to account for temperature dependence of medium thermal conductivity, and thermal resistance models in MOF-5 (metal organic framework) with random and layered enhanced natural graphite.

[1] ABAQUS is a software package for finite element analysis and computer-aided engineering.

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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 pressure and temperature, the thermal energy and temperature of charge and discharge, and 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 onboard 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. An important aspect of this work is to develop overall system models that include the interfaces between hydrogen production and delivery, hydrogen storage, and the fuel cell.

RESULTS

Physical Storage – Cryo-Compressed Storage for Buses

We analyzed the cryo-compressed hydrogen storage option in buses with a particular focus on dormancy. The storage tank is a Type III tank; it consists of a stainless steel (SS) 316 or Al 6061-T6 alloy liner wrapped with T700 CF designed to withstand 225% of the nominal storage pressure with a minimum fatigue life of 15,000 cycles [1]. The storage system, shown schematically in Figure 1, consists of four tanks that hold 40 kg usable H_2. Each tank is surrounded by a vacuum gap (10^{-5} torr) filled with multi-layer vacuum superinsulation (MLVSI). A thin aluminium outer shell,

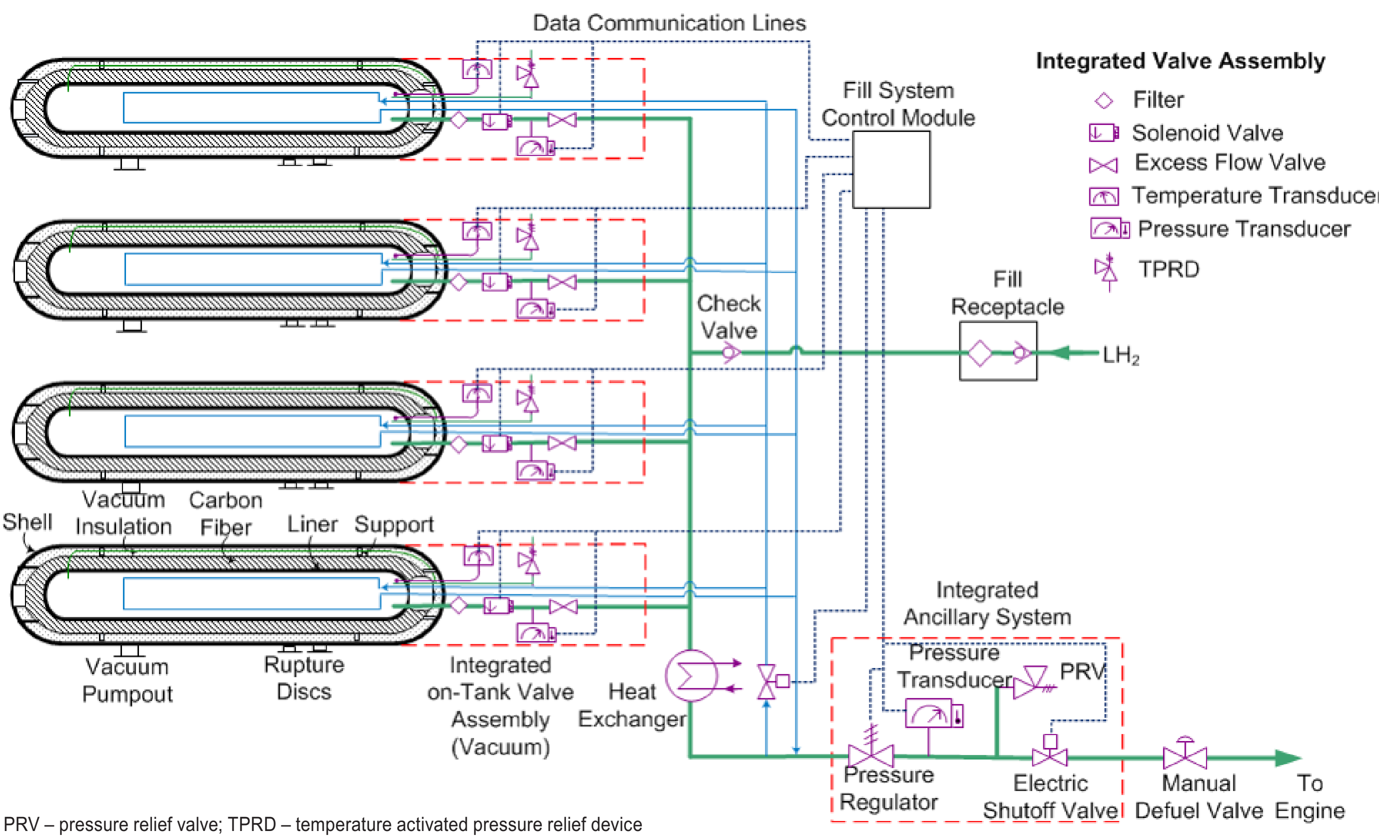

FIGURE 1. Cryo-compressed hydrogen storage system for fuel cell buses

separated from the inner tank by two G-10 space rings, completes the main vessel. The thickness of the insulation was determined so as to limit the heat transfer rate from the ambient to 10 W.

We considered two options for extending the fatigue life of the cryo-compressed tank: AF1 – the tank is autofrettaged at room temperature, then cooled to cryogenic temperature; AF2 – the tank is first cooled to cryogenic temperature before autofrettage is carried out. Results show that in AF1 the liner is in compression following autofrettage, but thermal stress induced during cool-down causes it to be in tension. In AF2, the liner is in tension after cool-down but reverses to compression post-autofrettage, and the cylinder section has undergone plastic deformation due to thermal stress during the cool-down step. Figure 2 shows the fatigue life for tanks with a SS liner and length-to-diameter (L/D) ratio of 5, storing 10 kg usable H_2 at 84 K. Two liner thicknesses (1 mm and 2 mm) and three storage pressures (350 bar, 500 bar, and 700 bar) were analyzed. For fixed liner thickness, the fatigue life decreases with increasing storage pressure because of higher cycling stress amplitude. If autofrettage is performed at cryogenic temperature, the fatigue life improves as a result of the increase in yield stress and strain hardening behavior of metals at low temperatures. The improvement over room temperature autofrettage (AF1) is more pronounced for the thicker liner. It is noted that fatigue is not an issue with a 2-mm SS liner because its fatigue life exceeds 15,000 cycles (red dashed line in Figure 2). For storage pressure up to 50 MPa, even a 1-mm SS liner meets the fatigue life requirement. We also analyzed aluminum liner and found that the liner needs to be thicker than 15 mm to meet the required 15,000 cycles. The thick liner adds excessive amount of weight and volume to the tank. Based on these results, the choice of liner material for a cryo-compressed storage tank strongly favors stainless steel over aluminum.

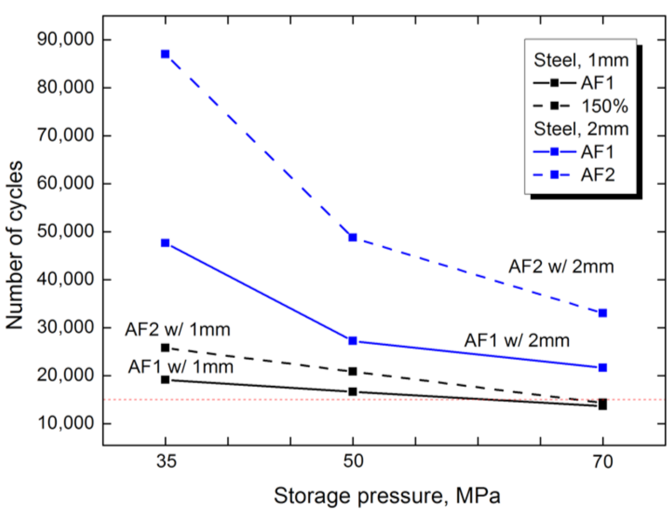

FIGURE 2. Fatigue life for Type III tanks with stainless steel liner

Table 1 shows the reference values and the range for the storage system parameters. The nominal storage pressure is 500 bar with an empty pressure of 5 bar. The storage temperature (107.9 K) and discharge temperature (47.1 K) are determined by liquid hydrogen (LH_2) refueling and the pump efficiency. In our analysis, the pump efficiency is derived from data gathered by BMW [2] on a 350-bar Linde pump as well as data gathered by Lawrence Livermore National Laboratory [3] on an 875-bar Linde pump. The pump isentropic efficiency is calculated from the flow rate, pump power, pump inlet and outlet pressure and temperature. Although LH_2 is used for refueling, hydrogen is stored in supercritical state in the tanks after being pumped to the storage pressure. In order to maintain the supercritical state at all times, a small amount of heat must be supplied to the tank during discharge to prevent liquid formation. Heat can be supplied via a small heater or an in-tank heat exchanger that recirculates a fraction of warm hydrogen back into the tank (see Figure 1). Our analysis shows that an average of 53 W is needed to maintain hydrogen in a single supercritical phase for a tank that discharges in one day, and 35 W is needed for a tank that discharges over three days.

Analysis was carried out for storage pressure ranging from 350 to 700 bar to compare the key performance metrics. For fixed empty pressure at 5 bar, the percentage of recoverable H_2 increases slightly with storage pressure. Because of pressure-volume work, the storage temperature is also higher at higher pressure; thus, the increase in storage density is not very significant. Doubling the pressure from 350 to 700 bar raises the storage density by just 16.7%. Although higher pressure results in higher storage density, it has little effect on the volumetric capacity. The improvement in storage density is negated by the increase in the amount of CF overwrap. In fact, the volumetric capacity is lower at 700 bar (42.2 g/L) than it is at 350 bar (42.4 g/L) or 500 bar (43.0 g/L). The added weight in CF reduces the gravimetric capacity from 8.4 wt% at 350 bar to 7.3 wt% at 500 bar and 6 wt% at 700 bar. CF and liner dominate the weight and account for 73% of the tank weight at 500 bar. The liner and shell thicknesses are the same for all storage pressures, so their weights vary only slightly in relation to tank size. Hydrogen has the largest share of volume. At 500 bar, the volumetric efficiency (H_2 volume divided by tank volume) is 73%. Compared to the current baseline 350-bar compressed hydrogen storage (ambient temperature) for fuel cell buses, the 500-bar cryo-compressed storage option can achieve 66% improvement in gravimetric capacity, 132% increase in volumetric capacity, and 36% savings in CF composite.

The dormancy, measured in watt-days, for the three storage pressures is shown in Figure 3a as a function of the initial amount of H_2 in the tank. Venting is initiated when the tank pressure reaches 1.25 times the nominal storage pressure. The effect of endothermic para-to-ortho conversion is included in dormancy calculations. While dormancy

TABLE 1. System Parameters for Cryo-Compressed Hydrogen Storage in Fuel Cell Buses

System Parameter	Reference Value[1]	Range[1]	Comment
Storage Pressure	500 bar	350–700 bar	Type III carbon fiber wound tank
Empty Pressure	5 bar	5–10 bar	Minimum delivery pressure set by fuel cell system
Storage Volume[2]	4 x 169 L	4 x 155–183 L	40 kg usable H_2
Storage Temperature	107.9 K	93–123 K	Determined by LH_2 refueling and LH_2 pump efficiency
Discharge Temperature	47.1 K	47.1–49.5 K	Function of duty cycle, 1–3 day discharge time
Heat Rate	4 x 53 W	4 x 52–70 W	Repeat charge-discharge cycle
Refueling Rate	1.6 kg/min	5 kg/min target	Set by LH_2 pump capacity
Tank Aspect Ratio	L/D = 5	L/D = 3-5	
Liner Thickness	2-mm SS	9.5–15.2 mm Al	SAE J2579: 11,250 duty cycles; ABAQUS FE-SAFE Model
Autofrettage Pressure	1.5 x NWP		Same as proof pressure
Carbon Fiber Amount	4 x 64.2 kg	4 x 43.2–96.2 kg	T700 CF; SAE J2579: 2.25 Safety Factor; ABAQUS-Wound Composite Modeler.
Insulation Thickness	7.4 mm	6.9–8.1 mm	10 W heat gain, MLVSI

[1] Unless noted otherwise, results are for SS liner and high-efficiency LH_2 pump
[2] Refers to gas (empty tank) volume
NWP – nominal working pressure

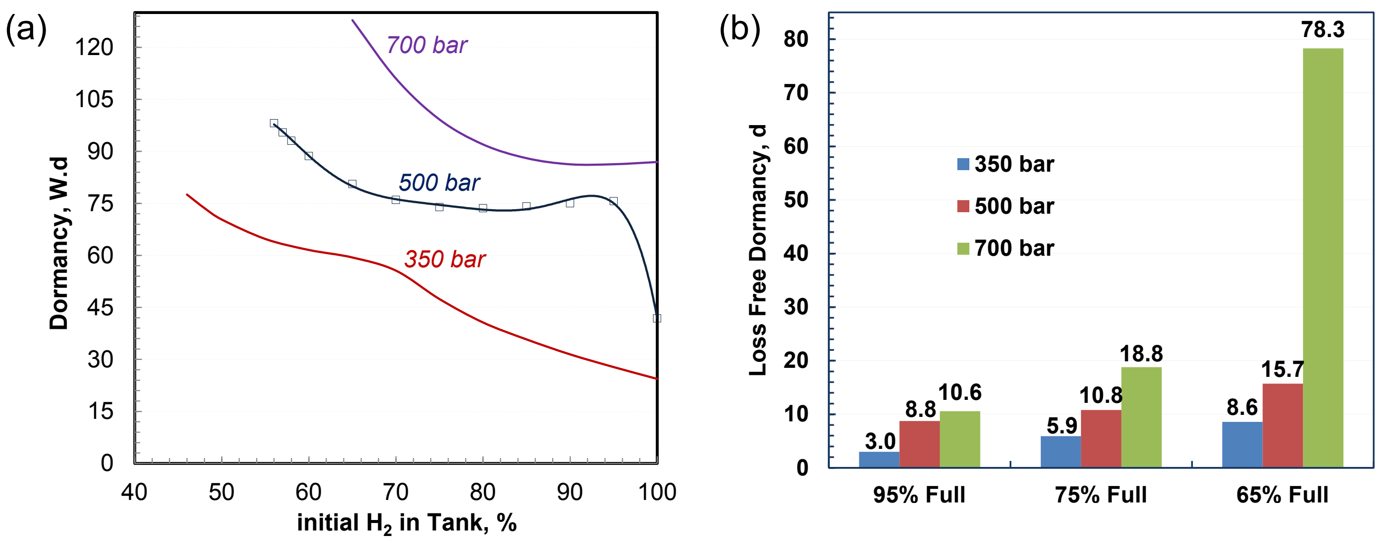

FIGURE 3. Dormancy measured in (a) watt-days and (b) days for various amounts of H_2 in tank

increases with increasing pressure, the increase also depends on the amount of H_2 stored, as shown in Figure 3b. Compared to 350-bar storage, the dormancy for a 700-bar tank is higher by a factor of 3.5 when the tank is 95% full, and by a factor of 9 if the tank is 65% full. At the reference 500-bar pressure, the dormancy for 95% full tank exceeds the 7-day target.

Physical Storage – 700 bar Compressed

We updated the key system parameters for 700-bar compressed hydrogen storage to incorporate changes in (1) ambient temperature, (2) storage tank empty pressure, and (3) tank design. The ambient temperature was changed from 20°C to 15°C to be consistent with SAE[2] regulations [1]. The tank empty pressure, previously set at 20 bar with a one-stage pressure regulator, was reduced to 15 bar and 10 bar with a two-stage pressure regulator (used on current 700-bar tanks). Finally, an alternate tank design similar to the Mirai tank [4] was adopted to take advantage of the CF savings. These changes and their impact on system gravimetric and volumetric capacities as well as CF usage are summarized in

[2] SAE International, formerly known as the Society for Automotive Engineers, is a body that sets standards to help ensure the safety, quality, and effectiveness of products and services across the mobility engineering industry.

Table 2. These changes are also expected to affect the system cost. The lower cost due to smaller tank size and less CF is partially offset by the higher cost for a two-stage pressure regulator. The CF savings are highlighted below.

- Reducing the ambient temperature from 20°C to 15°C reduces the CF amount by 1.1% because of a smaller tank size.
- Reducing the tank empty pressure increases the usable hydrogen and reduces CF usage by 1.1%–2.1%.
- The alternate tank design produces the largest savings in CF of nearly 5%.

Hydrogen Storage in Sorbents

We updated our reverse engineering analysis for hydrogen storage in sorbents. We analyzed the adsorption isotherm data for MOF-5, which was acquired and provided to us by the Hydrogen Storage Engineering Center of Excellence [5]. The data for both powder and pellets of various compact densities with and without expanded natural graphite (ENG) additives, and measured over a wide range of temperatures (77–295 K), were included in our analysis. To utilize the data for our reverse engineering study, the data were fitted to a single Langmuir equation of the form

$$N_e = \left(N_{\max} - V_a \rho_g\right)\left(\frac{K_1 P}{1+K_1 P}\right) = N_{\max}\left(1 - v_a \rho_g\right)\left(\frac{K_1 P}{1+K_1 P}\right) \quad (1)$$

$$K_1 = \frac{C_1}{\sqrt{T}} e^{\frac{E_1}{RT}} \quad (2)$$

The single-Langmuir equation is very appealing for reverse engineering since it only has four parameters (N_{max}, v_a, C_l, E_l), three of which can be related to physical material properties. N_{max} may be regarded as the sorption capacity (g-H_2/kg) of the sorbent, i.e., the maximum absolute uptake if all the active sites are occupied with H_2. Figure 4 shows the reference onboard system used in the reverse engineering analysis. Within our system performance analysis model, the heat transfer analysis was improved to incorporate (1) the temperature dependence of the medium thermal conductivity with various amounts of ENG, (2) a series-parallel thermal resistance model for MOF-5 and random ENG additives, and (3) a parallel resistance model for heat transfer in layered ENG structures. Table 3 summarizes the results of the reverse engineering analysis. Compared to our previous analysis, there is >25% smaller target uptake with improved thermal conductivity, lower ENG weight fraction, and more compact heat exchanger.

CONCLUSIONS AND UPCOMING ACTIVITIES

- The fatigue analysis shows that a 2-mm SS liner in a cryo-compressed tank for fuel cell buses meets the fatigue cycle life requirement for storage pressure up to 700 bar. Aluminum liner is not a good choice because its thickness exceeds 15 mm and it adds excessive amount of weight and volume to the tank.
- Autofrettage carried out at cryogenic temperatures (AF2) enhances the fatigue life of the liner over room temperature autofrettage (AF1). The improvement is more pronounced for thicker liners.
- Compared to the baseline 350-bar cH_2 tanks currently in use for fuel cell buses, 500-bar CcH_2 can achieve 66% improvement in gravimetric capacity, 132% increase in volumetric capacity, and 36% savings in CF composite.
- Dormancy is a function of storage pressure and the initial H_2 amount in tank. At the reference 500-bar pressure, the dormancy for 95% full tank exceeds the 7-day target.
- For 700-bar cH_2 storage, reducing the ambient temperature from 20°C to 15°C and the empty tank pressure from 20 bar to 10 bar reduces the CF amount by 3.2%.
- Compared to our previous reverse engineering analysis of hydrogen storage in sorbents, there is >25% smaller target uptake with improved thermal conductivity, lower ENG weight fraction, and more compact heat exchanger.

TABLE 2. System Parameters for Various Combinations of Ambient Temperature, Tank Empty Pressure, and Tank Design

	A	B	C	D	E	F
Empty pressure, bar	20[(1)]	20	15[(2)]	10[(3)]	15	10
Ambient temperature, °C	20	15	15	15	15	15
Tank design	Conv.	Conv.	Conv.	Conv.	Alt.	Alt.
CF composite, kg	97	95.9	94.9	93.9	90.3	89.3
Gravimetric capacity, wt%	4.19	4.23	4.26	4.29	4.41	4.45
Volumetric capacity, g-H_2/L	24.38	24.64	24.88	25.13	25.23	25.48

(1) Quantum two-stage pressure regulator
(2) Aerodyne Controls two-stage pressure regulator
(3) JTEKT two-stage pressure regulator used in Toyota Mirai, empty pressure unknown
Conv. – conventional; Alt. – alternative

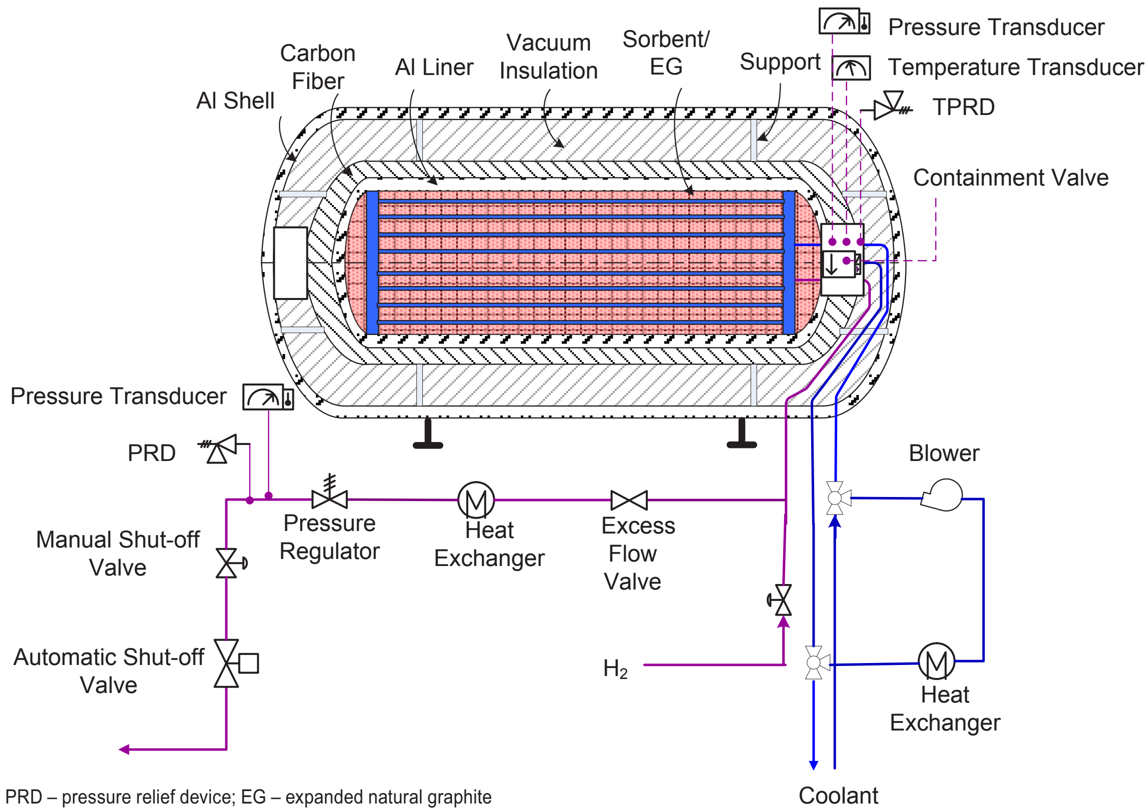

FIGURE 4. Reference onboard system for hydrogen storage in sorbents

TABLE 3. Reference Values for Meeting Onboard Targets

	Material Targets 2014	Material Targets 2017	Comments
Operating Pressures and Temperatures			
Storage Pressure (P)	100 bar	100 bar	
Storage Temperature (T)	155 K	155 K	20 K above coolant T
Discharge Pressure (P_d)	5 bar	5 bar	In addition to P swing, 60-K
Temperature Swing (DT)	60 K	60 K	DT allowed for 95% usable H_2
Off-board Coolant T (T_f)	135 K	135 K	55% well-to-tank efficiency
Material Properties			
Peak Excess Uptake at 77 K	190 g-H_2.kg^{-1}	**150 g-H_2.kg^{-1}**	5.5 wt% gravimetric capacity E_1 = 5 KJ.mol^{-1}
Excess Uptake at Storage P and T	120 g-H_2.kg^{-1}	**90 g-H_2.kg^{-1}**	V_a = 0.0125 $m^3 \cdot kg^{-1}$ C_1 = 0.0053 atm.$K^{0.5}$
Medium Bulk Density	500 kg.m^{-3}	**530 kg.m^{-3}**	40 g.L^{-1} volumetric capacity
Bed Thermal Conductivity	1 W.m^{-1}.K^{-1}	**5.5 W.m^{-1}.K^{-1}**	
Added ENG	20-wt% Random	**5-wt% Layered**	

- In FY 2018, we will validate the impact damage model against Hexagon Lincoln test data and apply the model to determine the burst pressure after impact (degradation of tank safety factor).
- In FY 2018, we will validate the ABAQUS model against Pacific Northwest National Laboratory cryogenic burst test data for cold gas storage.

- In FY 2018, we will expand the system analysis of hydrogen storage in high-pressure, low-enthalpy metal hydrides.
- In FY 2018, we will analyze system performance with compacted sorbents using Hydrogen Storage Engineering Center of Excellence data for materials and prototypes.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. R.K. Ahluwalia, J.K. Peng, and T.Q. Hua, "Cryo-Compressed Hydrogen Storage," Chapter 5 in Compendium of Hydrogen Energy, Vol. 2: Hydrogen Storage, Distribution and Infrastructure, R. Gupta, A. Basile, T.N. Veziroglu (Editors), Woodhead Publishing, 2016, 119–144.

2. N.T. Stetson, R.K. Ahluwalia, J.K. Peng, and G. Ordaz, "Characteristics of Low-Enthalpy Metal Hydrides Favorable for High-Pressure Hydrogen Storage Applications," 15th International Symposium on Metal-Hydrogen Systems, MH2016, Interlaken, Switzerland, August 7–12, 2016.

3. 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, January 9, 2017.

4. T.Q. Hua, H.S. Roh, and R.K. Ahluwalia, "Performance Assessment of 700-bar Compressed Hydrogen Storage for Light Duty Fuel Cell Vehicles," Int J Hydrogen Energy 2017; 42:25121-25129.

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1. SAE TIR J2579. Standards for Fuel Systems in Fuel Cell and Other Hydrogen Vehicles. USA: Society of Automotive Engineers; 2016.

2. BMW, Personal Communication.

3. Salvador Aceves, Lawrence Livermore National Laboratory, Personal Communication (2016).

4. 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.

5. M. Veenstra and J. Purewall, Ford, Personal Communication (2016).