IV.D.4 Key Technologies, Thermal Management, and Prototype Testing for Advanced Solid-State Hydrogen Storage Systems

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Fiscal Year (FY) 2011 Objectives

- Apply an understanding of storage system requirements for light-duty vehicles.
- Develop innovative on-board system concepts for materials-based storage technologies.
- Develop and test innovative concepts for storage subsystems and component designs.
- Identify technology gaps and identify trajectories to overcome technical barriers.
- Design, fabricate, and test subscale prototypes for each material-based technology.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan (referenced to 2015 targets, as revised 2009):

(A) System Weight and Volume: 5.5 $\%wt_{sys}$, 55 gH_2/kg_{sys}, 40 gH_2/L_{sys}

(C) Efficiency: 90% on-board/60% off-board

(D) Durability/Operability: <1% degradation @ 1,500 cycles, etc.

(E) Charging/Discharging Rates: 3.3 min fill, 0.02 g/kW-s minimum full flow

(G) Materials of Construction

(H) Balance-of-Plant Components

(I) Dispensing Technology

(J) Thermal Management

Technical Targets

Regarding the technical barriers addressed by JPL's activities within the Hydrogen Storage Engineering Center of Excellence (HSECoE), the main areas that would be the focus of technical efforts would be the nature of loss of useable H_2, thermal management, balance-of-plant components, efficiency, and durability/operability; the last of these will be evaluated directly by a phased effort of analysis and follow-on testing at JPL.

FY 2011 Accomplishments

Technical efforts at JPL during the previous year have been focused on the development and testing of novel thermal architectures for hydrogen storage systems. In particular, JPL's expertise with low-temperature system design and analysis has proved a good match for the unique demands presented by the cryo-adsorption system, which needs to operate at temperatures below 160 K, and as low as 60 K. The JPL project is a mixed approach of analytical modeling and follow-on experimental validation aimed at the development of thermal components and their interaction at the system level. JPL has also continued in the role of System Architect for cryo-adsorbent system technology development. In this role, JPL provides oversight and coordination of the various technology areas within the HSECoE that have responsibility for developing credible paths toward satisfying the DOE Hydrogen Storage targets (2010/2015/ultimate). This role also has direct responsibility toward system engineering outcomes, providing guidance and oversight for conceptual system design. Finally, JPL serves within the Center as Technology Area Lead for the Enabling Technologies team, providing technology management and coordination for overcoming technical gaps and incorporating emergent technologies and approaches.

Specific accomplishments:

- High-Isolation Cryogenic Vessel Design: In 2010, JPL identified multi-layer vacuum insulation (MLI) as a key design requirement for the cryo-adsorption storage vessel due to its high level of thermal isolation. Using analytical models validated by preliminary experiment, JPL demonstrated in 2011 a new design for a thermal architecture using MLI that improves thermal isolation, reducing heat loads on the storage medium by up to

44% over current designs, increasing dormancy ("hold") times for the idle vehicle.

- Cryogenic Fuel Energy Management: Via analytical modeling, JPL designed a compact onboard heat exchanger ("downstream H_2 HX") for cryogenic hydrogen fuel conditioning. This crucial device will utilize fuel cell waste heat in a closed coolant loop to raise the temperature of fuel supplied to the fuel cell. The JPL model has been incorporated into the overall HSECoE model framework, and has been shown to operate as designed across the complete operating envelopes of both AX-21 and MOF-5-based storage system designs.
- Loop Desorption Heating: Developed a design criteria and initial analytical model for H_2-loop desorption heating, identifying additional onboard efficiency gains and promoting the H_2 circulator as a technology gap for further investigation in Phase II.
- Cryo-Adsorbent System Phase 1 Transition: In the role of System Architect, JPL assisted in guiding the cryo-adsorbent system design team through the Phase 1-2 transition, which involved standardizing performance metrics of defined baseline systems and identifying technology development opportunities and challenges.

Introduction

JPL is engaged in developing enabling technologies for vehicular hydrogen storage systems for meeting DOE/FreedomCAR technical targets. During this project year, the enabling technologies area has been primarily concerned with low-temperature thermal management for the cryo-adsorbent system with emphasis in three areas: 1) parasitic heat transfer reduction in pursuit of the 2015 loss of useable H_2 target of 0.05 g h^{-1} kg^{-1} useable H_2, 2) downstream hydrogen heating to achieve the -40°C target for hydrogen delivered by the storage system, and 3) controlled heating of the cryogenic vessel for desorption (i.e., desorption heating) to meet the required 1.6 g s^{-1} requirement full flow rate for anticipated drive cycles. In each of these areas, the current state of the art was either extended in relation to the technical targets, or it was shown that the technical targets could be fully satisfied.

Approach

First-order heat and mass transfer models were constructed to quickly evaluate various technologies in the areas of dormancy, downstream hydrogen heating, and desorption heating. In the case of dormancy, detailed higher-order models were used for thermo-mechanical evaluation of cryogenic standoffs. In the dormancy area, the challenge is designing standoffs capable of withstanding shock loads exceeding 8 g while providing high conduction resistance. JPL has sought to improve on the state of the art in vehicular cryogenic storage by adapting the baseline G10 system proposed by Lawrence Livermore National Laboratory and others for liquid H_2 storage to the cryo-adsorption system, and also by proposing a new method of insulation relying on fibrous suspension of the pressure vessel inside the vacuum jacket, which has led to significant reduction in H_2 loss rate. JPL has investigated various methods for accomplishing downstream H_2 heating with the objective of mitigating frost risks and minimizing heat exchanger volume. As of March 2011, JPL has begun construction on a cryogenic test facility capable of spanning the temperature range projected for cryo-adsorption storage. The first use of this facility is to validate the parasitic heat transfer model used for dormancy calculations. The cryogenic test facility will also be used in Phase II of the project for additional experiments.

Results

The primary benefits of cryogenic adsorption storage are increased gas phase density and increased adsorption mass fraction near 80 K. Unfortunately, this low temperature can yield large parasitic heat transfer rates; only a few watts of parasitic heat transfer are needed to induce H_2 venting after a few days of idle. Mechanical models of thermal standoffs were built to size supports for a rigid G10 design and a second Kevlar™ design such that the components did not yield when subjected to loads of 8 g perpendicular to the axis of the tank with a safety factor of 2. Kevlar™ cables were sized to support the same loading; because Kevlar™ rope is available in discrete sizes, only cables that met or exceeded the mechanical requirements were used for heat transfer calculations.

Heat transfer models were built to estimate conduction across standoffs, radiative exchange across MLI, and conduction through tubing. These models were parameterized as a function of cold-side temperature at a hot-side temperature of 26°C, representing a summertime diurnal average. The component-level heat transfer for the G10 architecture (Figure 1a) revealed that standoff heat transfer is the most significant constituent of the ~5 W total parasitic. By replacing the G10 standoff design with Kevlar™, it was estimated that the total parasitic heat transfer could be reduced by up to ~44% (Figure 1b).

The reduced parasitics of the Kevlar™ design lead to reduced H_2 losses by venting and longer dormancy. To quantify these improvements, a model was constructed to relate parasitic heat transfer to tank temperature and vent rate; para- to ortho- conversion during tank heating is accounted for. Figure 2 shows that the average vent rate over a 30-day period is about ~0.52 g h^{-1} kg^{-1} for the G10 design compared with ~0.35 g h^{-1} kg^{-1} for the Kevlar™ design, and that the dormancy for Kevlar™ is approximately 70% longer. Figures 1-2 document a 70 bar aluminum pressure vessel with AX-21 adsorbent. A 200 bar Type-III carbon fiber vessel with MOF-5 adsorbent has also been modeled. MOF-5 shows slightly lower vent losses and

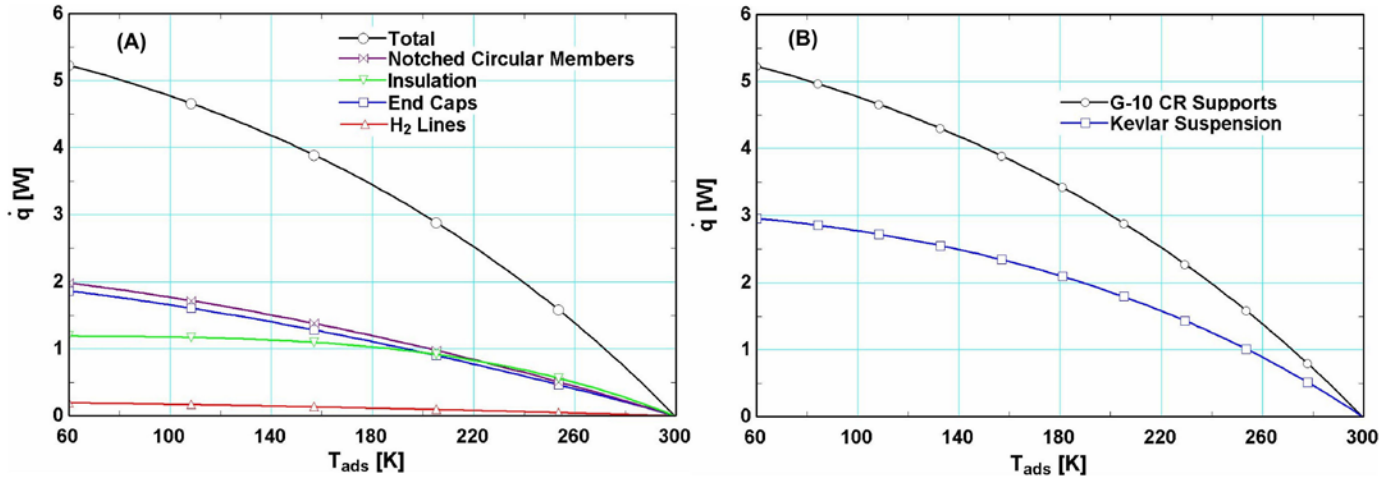

FIGURE 1. Breakout parasitic loads for G10 (state of art) and total parasitic loads for G10 and Kevlar™ (advanced) tank thermal isolation designs.

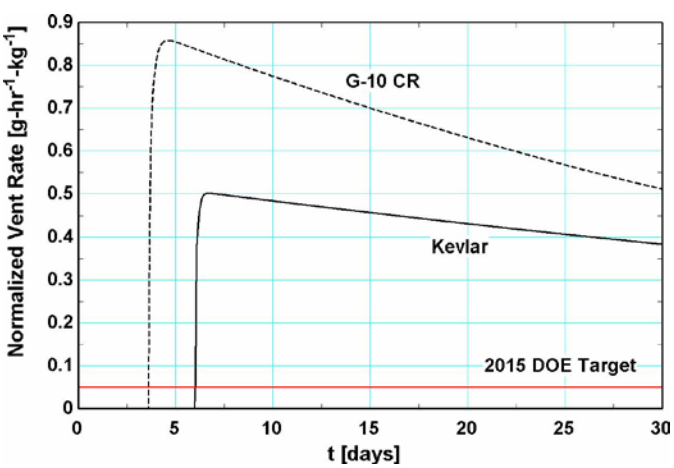

FIGURE 2. Vent rate histories for G10 (state of art) and Kevlar™ (advanced) thermal isolation designs.

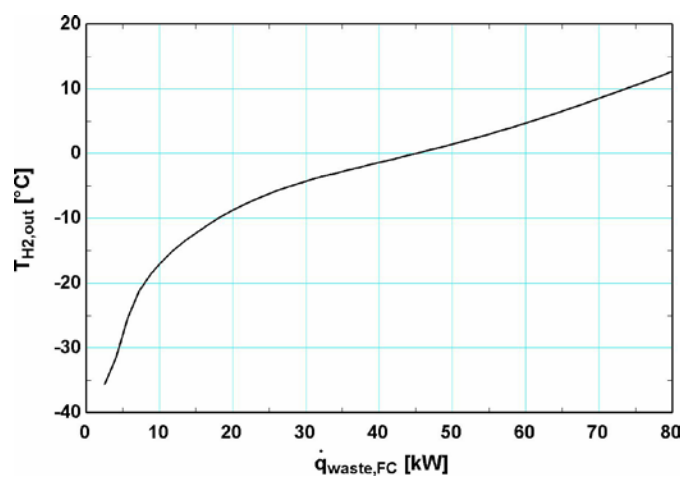

FIGURE 3. Delivered hydrogen temperature versus total fuel cell waste heat. Assumes 50% of waste heat is dissipated by coolant loop.

longer dormancy times, but the relative improvement of Kevlar™ over G10 is generally similar to the AX-21 case. Nevertheless, even the Kevlar™ design gives dormancy performance that falls short of the 2015 hydrogen loss target; the projected mass of hydrogen lost to venting is appreciable (~1 kg over 30 days) with the improved design. However, it should be noted that the scenario exercised in this model is a worst case and does not account for natural pressure relief through driving; a small amount of daily driving can extend dormancy indefinitely in this type of system.

In the downstream heat exchange area, three types of downstream heat exchange sub-systems were modeled with the common objective of heating stored low-temperature hydrogen to allowable temperatures en-route to the fuel cell or internal combustion engine. The modeled sub-systems included a direct air-coupled hydrogen heat exchanger with an air-side heater, a hydronic loop coupled to air, and a fuel cell coolant-coupled loop. The obstacles for each of these concepts were 1) the size and number of heat exchangers required, and 2) the potential for ice formation at various locations within the heat exchange equipment. The direct air-coupled heat exchanger model predicted frost build-up on the air side for most cases. The independent hydronic loop also showed the potential for icing at low temperatures in addition to requiring two dedicated heat exchangers. The fuel cell coolant-coupled loop is the leading design candidate. Waste heat from the fuel cell helps prevent icing on the coolant side, while the coolant loop axial flow fan and air-coupled heat exchanger are leveraged to reduce volume and parts count. At -30°C ambient and a hydrogen flow rate of 0.8 g s^{-1}, this system will deliver -40°C hydrogen with no waste heat input from the fuel cell. With a nominal amount of waste heat input, Figure 3 shows that this system exceeds the delivery target even in -40°C ambient conditions.

In desorption heating, a compressible flow network model was developed to model the flow-through heating

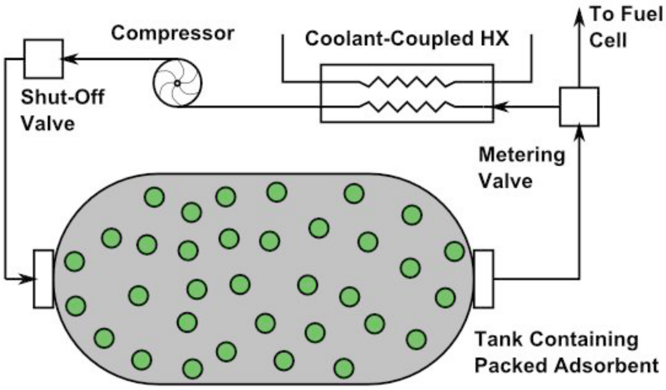

FIGURE 4. Flow-Through Desorption Loop Schematic

design shown in Figure 4. The most aggressive cases, delivering 1.6 g s^{-1} with a set point pressure of 20 bar, the H_2 circulation rate must be very large. For nominal quarter inch lines, pressure losses resulting from these flow rates can be significant; however, drive cycles incorporated into the framework model developed by Savannah River National Laboratory in conjunction with the United Technologies Research Center have suggested that such stringent cases do not exist in practice. Tank heating rates up to 1 kW should be realizable with this type of system. The model predicts that a circulator would need to provide 3 kPa of pressure rise in order to deliver ~1 kW of heating when transferring heat from fuel cell coolant at 52°C. The technology gap in this area, however, is procuring a circulator that is rated to operate at pressures exceeding 200 bar; investigations in this particular direction have already begun.

Conclusions and Future Directions

- Two thermal isolation architectures were studied in detail. A scaled parasitics experiment is being constructed to validate the predictive models, and in Phase II, a high-fidelity dormancy experiment based on the novel Kevlar™ architecture is planned. Pressure vessel outgassing experiments are also being developed, which will indicate the level of vacuum that is feasible.
- Various methods for downstream hydrogen heating were investigated, and it was determined that coupling to the fuel cell coolant loop offers the best protection against freezing while also meeting hydrogen conditioning requirements. JPL has started to develop higher-order models of this process and is in the planning stage of adapting an experimental facility to supplement those models.
- The HSECoE has identified flow-through heating as an alternative to Joule heating for desorption. A compressible flow network model was developed by JPL to model the flow-through design. Pressure-drops are reasonable current system configurations; however, the technology gap is the hydrogen circulator, which must operate at low temperature and high pressure. More work will be done to identify a path forward for desorption heating.
- During the next year, JPL plans to conduct a demonstration high-pressure burst test of a 200-350 bar composite pressure vessel at cryogenic (~77 K) temperatures. This proof-of-concept activity will begin a series of investigations that will include cryogenic pressure/temperature cycling as well as possible future burst tests. These investigations will be performed in conjunction with HSECoE partners Lincoln Composites, Pacific Northwest National Laboratory, and United Technologies Research Center, among others. The results will inform future investigations and safety/testing protocols during Phase II experimental work as well as eventual prototype storage system testing.

Patents Issued

1. Raymond A., Reiter J. (2011) Suspension for Thermal Isolation of Cryogenic Hydrogen Tanks for Terrestrial Applications. Provisional patent.

FY 2011 Publications/Presentations

1. Raymond, A. and Reiter, J. (2010) Parasitic heating and dormancy in cryo-adsorbent tanks for vehicular hydrogen storage. Poster Presentation. AIChE Annual Meeting. November 7–12. Salt Lake City, UT.

2. Raymond, A. and Reiter, J. (2011) Modeling and testing of cryo-adsorbent hydrogen storage tanks with improved thermal isolation. Cryogenic Engineering Conference. June 13–17, Spokane, WA.