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

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Subcontractor:
California Institute of Technology, Pasadena, CA

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Project End Date: September, 2014

Fiscal Year (FY) 2012 Objectives

- Identify state-of-art concepts and designs for cryosorbent-based hydrogen storage systems
- Discover and characterize technical barriers to system development toward DOE targets
- Develop means and/or identify trajectories to overcome barriers using modeling techniques
- Describe and develop enabling technologies toward achieving targets
- Design, fabricate, and test hardware components for model validation

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 2017 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% Onboard
(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
(J) Thermal Management

Technical Targets

The JPL effort is currently focused on delivering beyond state-of-art cryogenic systems technologies and optimizations for the various cryo-adsorbent storage options being examined by the Center of Excellence. Table 1 summarizes recent progress and gives the current status for JPL tasks and milestones as measured against the specific targets that guide them.

TABLE 1. Current (FY 2012) Status of Target-Relevant JPL Tasks

Task Area	2012 Status	Main Relevant Target(s) (2017)	Comments
Advanced Vessel Thermal Isolation Design	Complete. Model validated, showing <2 W heat leak @ 77 K, improved from over 3 W	Loss of useable H_2 <0.05 g/h/kg	"Subscale" 77 K dormancy validation experiments planned late FY 2012
Outgassing of COPV Tank-Wall Materials	Partially Complete. Initial experimental results show strong temperature dependence.	Loss of Useable H_2 <0/05 g/h/kg Permeation and Leakage	Inadequate instrumental resolution and sensitivity; new bench-top facility to be ready fourth quarter of FY 2012
Downstream Cryogenic H_2 Heat Exchanger	Complete. Design satisfies targets at all but coldest (-40°C) environment for 77 K fuel supply	Min Delivery Temperature > -40°C Onboard Efficiency >90%	Bench-top cryogenic validation experiments in design stage; expected operation early FY 2013. Modeled device is 1.1 kg, 1.0 L
COPV Cryogenic Burst Test	Incomplete. Task shifted to later in FY due to resource allocation.	Safety Operational Cycle Life (>5,000 cycles)	Facility nearing completion; COPV tank articles have been provided by Lincoln Composites; initial burst at 77 K expected early FY 2013

COPV - Carbon-overwrapped pressure vessel

FY 2012 Accomplishments

- **Advanced Vessel Thermal Isolation Design:** In 2012, JPL performed detailed thermo-mechanical design of an advanced vessel isolation system for automotive use and experimentally validated the design at 80 K. The validated results indicate the design approach is capable of limiting parasitic heat load on a full tank to <2 W, a 38% improvement over the current state of the art. This improved performance is expected to consequently result in increased dormancy ("hold") times for the idle vehicle over the entire operating range, $-40°C < T_{amb} < 60°C$.

- **Vacuum Outgassing of COPV Materials:** As part of the effort to characterize the dormancy behavior of a vacuum-insulated COPV, JPL obtained outgassing data for carbon fiber tank-wall materials in vacuum over the range $170 K < T < 350 K$. Initial results from this "ad-hoc" experimental effort indicate a clear "vacuum spoiling" effect and a temperature-dependent outgassing rate.
- **Cryogenic Fuel Energy Management:** JPL developed a coupled, detailed analytical model for a downstream H2 fuel heat exchanger, necessary for cryo-adsorbent storage systems to raise the temperature of fuel supplied to the fuel cell. JPL's design utilizes both ambient air and fuel cell waste heat as necessary via a closed coolant loop. The compact design (1.1 kg, 1.0 L – a "soda bottle") has been modeled for 40 K and 80 K storage temperatures at steady-state and transient (cold-start) conditions, and satisfies DOE targets at all but the coldest ambient temperature (-40°C).
- **Cryogenic COPV Burst Testing:** in FY 2012, JPL completed the facility design for providing 15 kpsi burst for a medium-sized (5–20 L) Type 4 COPV at 77 K. Due to parallel tasks, resource allocation forced a shift of the completion to FY 2013, although procurements and some fabrication are taking place in the current FY. The facility has been designed to flexibly perform repeated burst events as well as provide a pressure cycling capacity with some modification.

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Introduction

Since the inception of the Hydrogen Storage Center of Excellence (HSECoE) in FY 2009, JPL has been engaged in developing advanced, enabling technologies for vehicular hydrogen storage systems to meet DOE/U.S. DRIVE technical targets. To this end, JPL also serves 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.

During FY 2012, JPL's technical effort has been primarily concerned with low-temperature thermal management and related technologies for cryo-adsorbent storage system options with emphasis in three areas: 1) parasitic heat transfer reduction in pursuit of the 2017 loss of useable H_2 target of <0.05 g h^{-1} kg^{-1} useable H_2; 2) downstream hydrogen heating to achieve the minimum delivery temperature target $T_{min} > -40^{o}C$ for hydrogen delivered by the storage system, and 3) demonstration of cryogenic burst failure performance of COPVs to address the safety and operational cycle life targets. These are the primary targets influenced by each activity; except for burst testing (shifted to FY 2013), the current state of the art was either extended in relation to the primary targets, or it was shown that the technical targets could be fully satisfied. In practice, each task area also addresses several additional subsequent targets in a cross-cutting fashion.

Approach

JPL has identified and filled a need for critical cryo-system engineering in Phase 2 of the Center's project. This renewed effort has allowed efficient use of manpower and resources following the de-scope of the metal hydride system in 2011 and suits the direction of the Center very well, supporting the development of gap-mitigating technologies critical to the implementation of a cryo-adsorbent-based onboard storage option. JPL's approach involves bootstrapping into advanced technology development via modeling and bench-top proof-of-concept validation. The FY 2012 technology program has been generally guided by the following technical milestones:

- Experimentally validate model results for high-isolation cryo vessel design at 77 K
- Measure and characterize outgassing from COPV materials from $300 K > T > 77 K$
- Refine coupled downstream heat exchanger (HX) model and predict performance for relevant drive cycles, conditions; fuel at 77 K and 40 K, 1.6 g/s (max)
- Implement cryo-burst facility and determine burst limit for sample COPV at 77 K

Results

As a direct result of discharging gaseous hydrogen at storage temperatures below 80 K, a heat exchanger is required downstream of the storage vessel. This device must enable the storage system to meet the required technical targets (fuel T_{min}: $-40^{o}C$; flowrate: 1.6 $g{\cdot}s^{-1}$; T_{amb}: -40 to $60^{o}C$) and be very compact. A coolant-coupled HX design was selected during mid-2011 to utilize the existing vehicle radiator and the large coolant flow rate to the fuel cell to mitigate frost formation while pre-heating H_2 fuel using waste heat. JPL's HX model assumes an off-the-shelf shell/tube configuration for the device, and predicts coupled inlet and outlet temperatures of three fluid streams: H_2, glycol-water (55/45) coolant, and ambient air. The model assumes a constant fuel cell $T_{FC} = 80^{o}C$ for the purposes of efficiency calculations, a conservative decision that actually minimizes available waste heat. Furthermore, it is assumed that cryogenic hydrogen is discharged from a full tank via isenthalpic expansion, giving the coldest possible fuel stream; this is also a conservative assumption. The steady-state predictive results show near-total compliance with targets for the prototype HX design at both 80 K and 40 K, as the colder storage temperature is only marginally more challenging from a fuel-heating perspective. Figure 1 shows these results, plotting fuel delivery temperature against fuel flowrate for several ambient temperatures. Only the coldest environment (-40°C) prevents the fuel from heating to the minimum requirement; optimization beyond the off-the-shelf design may enable even this requirement to be met. Figure 2 shows a visualization of the modeled device in a representatively sized benchtop storage system, indicating to good effect the truly compact nature of such a device (1.1 kg, 1.0 L, most of which is thermal insulation).

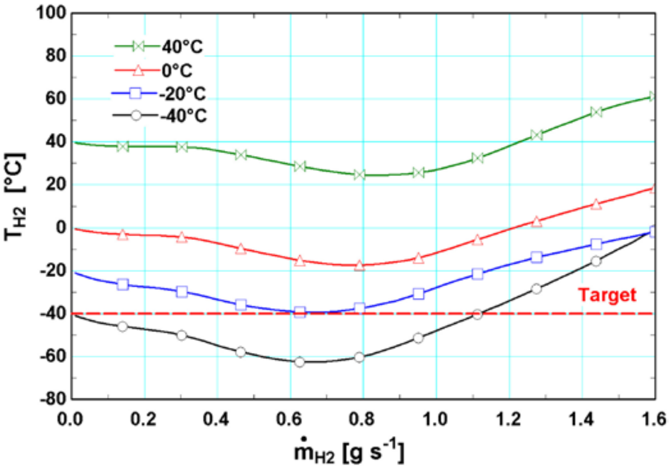

FIGURE 1. Curves showing performance of JPL's Downstream Fuel HX design; here, fuel delivery temperature at the fuel cell is plotted against fuel flowrate for several ambient temperatures. The 80 K storage case is shown here; the results for 40 K are categorically similar.

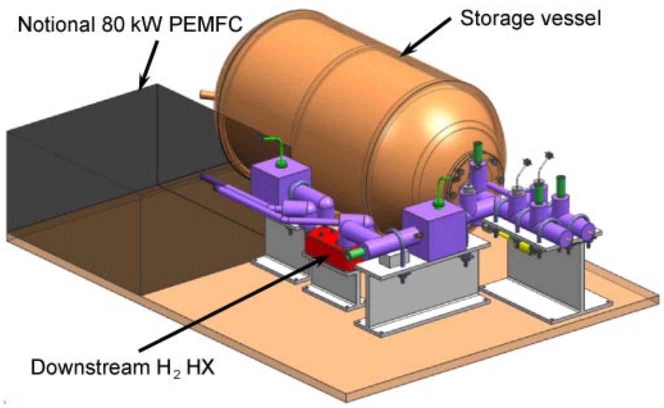

FIGURE 2. Computer-aided design visualization of JPL's Downstream Fuel HX design, showing the compact device (in red) installed in a representative hydrogen storage system. Sizes of components were defined by a design that optimally satisfies the 2017 targets using technology known to the Center in 2011.

The advanced Kevlar^{TM} "web" suspension design JPL introduced in 2011 was compared to the current state-of-art design using a detailed thermo-mechanical model that was later validated to within 10% by experimental data. In the model, the G-10 fiber-reinforced plastic (FRP) standoffs of the state-of-art vessel and the Kevlar^{TM} 29 cords of the advanced design were both sized for driving loads and conservatively designed for robust performance over long life. Thermally, the use of tensile cords to limit parasitic heating of the inner vessel is responsive to the fact that conduction of G-10 FRP is ~60% of the total heat load of such a vessel, while the use of Kevlar^{TM} can limit conduction to below 40% of the total. This approach improves the thermal design by attacking the "low hanging fruit" of conduction while avoiding a more difficult (i.e., expensive) radiation optimization. Modeling the multi-layer insulation blanket was via the "Lockheed equation" with gas effects for an assumed vacuum pressure of 10^{-4} torr, 40% more conservative than the absolute minimum. In the experimental setup, vessel heat load was simulated by a heated aluminum test coupon in a vacuum chamber suspended from a cold boundary by either G-10 FRP or Kevlar^{TM} 29 cord. Radiation was controlled by multi-layer insulation wrapped around the test coupon. Heat flows were measured for cold side temperatures of 80 and 150 K and hot side temperatures of -25, 10, and 45°C. The results of this experimental validation

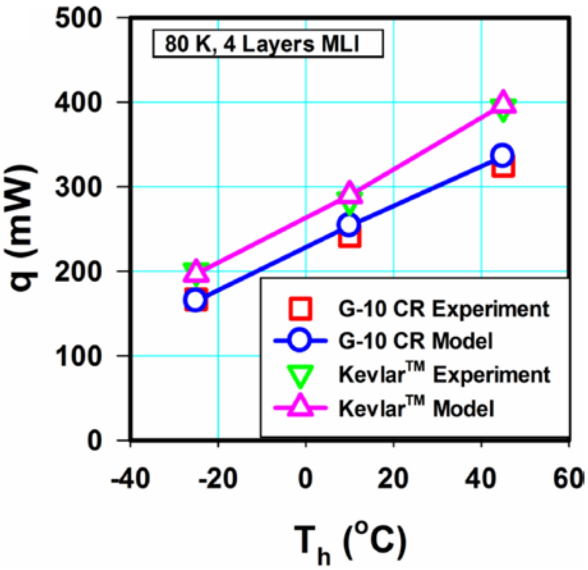

FIGURE 3. Curves indicating the correlation of model and experimental data for JPL's advanced thermal architecture design at 80 K. There is very good agreement (within 10%) between predictions and experimental results for both Kevlar^{TM} and G-10 materials. The mostly linear form of the curves shows the effect of T_{hot} on total heat transfer. The results are similarly well correlated for the 150 K storage temperature as well as for varying MLI layer count, indicating a robust design.

are shown in Figure 3. Dormancy cases were evaluated for the advanced vessel design using the validated model, showing an increase in "hold" time from 2 to 3 days for a full tank and no driving; these results are shown in Figure 4. In addition, an initial outgassing study of COPV material was performed as part of this effort to quantify the impact of volatile contaminant species on the integrity of the vessel's vacuum insulation, a critical system parameter. While the ad-hoc nature of the experimental setup yielded mostly qualitative results, a rise in pressure with increasing temperature was apparent. This result will be further investigated and quantified with a new experimental setup and approach.

Conclusions and Future Directions

JPL's conclusions from work in FY 2012 represent the initial steps in Phase 2 of the Center's top-level research project, in which key technologies were actively developed with a focus on bench-top component testing and model validation.

- A detailed thermo-mechanical design of an advanced vessel thermal isolation system has shown that thermal load on a cryogenic tank can be reduced by almost 40%; this result has been experimentally validated via coupon-scale testing at 80 K. Follow-on work has already begun, and will include validation of performance models at appropriate (i.e., larger) scales and environmental conditions. These data, along with demonstrated manufacturability methods for the advanced isolation system, will be provided to the Center and to DOE.
- Initial outgassing data for carbon fiber tank-wall materials were obtained over a temperature range of 170 K < T < 350 K; the results indicate that outgassing is a potential source of vacuum-spoiling species. Next steps involve completion, calibration, and commissioning of the new high-resolution test facility, after which higher-quality outgassing data will be acquired for a range of materials over a larger temperature range.
- A fully-coupled Downstream Fuel HX model was developed and utilized to obtain refined results showing potential mass/volume reductions of the HX device; this design was visualized using a computer-aided design model in a representative storage system. In FY 2013, this work will be supported by experimental verification via a new bench-top facility; this campaign may use the "full-sized" article, as it is already compact.
- An initial design review for a cryo-burst facility is complete, including safety reviews, burst energy calculations, and facility use; the test procedure was

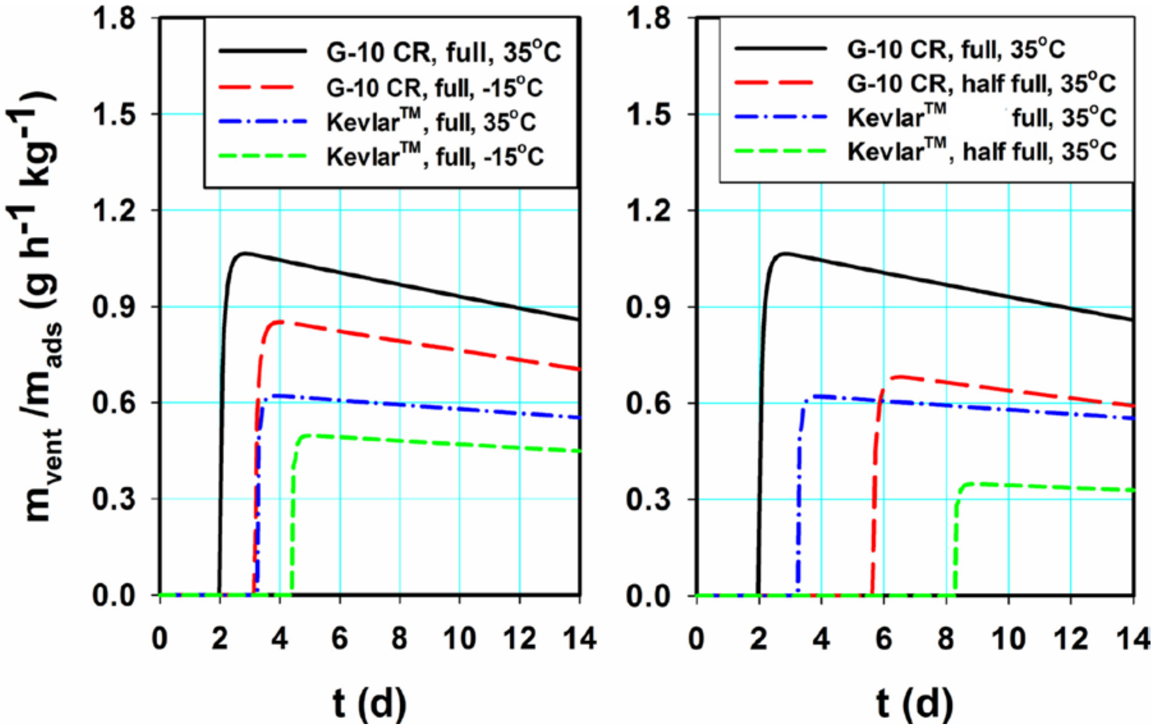

FIGURE 4. Plots comparing the validated dormancy performance of the advanced JPL design over the current state-of-art G-10 design, showing an improvement in dormancy times for a full (5.6 kg useable H_2) tank from 2 to 3 d with no driving of the vehicle. Here the curves indicate H_2 vent rates as heat ingress causes adsorbed H_2 to pressurize the vessel via thermal desorption. The effects of a "half-full" tank are also shown on the right hand side.

developed with assistance from industry (Lincoln Composites, National Aeronautical and Space Administration, etc.) and procurements have begun. By early FY 2013, the burst facility will have conducted its first burst of a small COPV provided by Lincoln Composites, on the way to additional tests examining cycled vs. un-cycled burst strength and other variations. Plans may be implemented to allow pressure-cycle testing to be conducted on this same facility at cryogenic temperatures.

FY 2012 Publications/Presentations

1. Reiter, J.W., Raymond, A., and Ramesham, R. Outgassing Rate and Species Measurement for Cryogenic Carbon Fiber Hydrogen Storage Vessels. Oral Presentation. AIChE Annual Meeting, October 16–21, 2011. Minneapolis, MN.

2. Raymond, A. and Reiter, J. “Modeling and Testing of Cryo-adsorbent Hydrogen Storage Tanks with Improved Thermal Isolation.” Proceedings of the 2011 Cryogenic Engineering Conference, in press.