

IV.D.2 Thermomechanical Cycling of Thin Liner High Fiber Fraction Cryogenic Pressure Vessels Rapidly Refueled by LH₂ Pump to 700 bar

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Subcontractors

- Spencer Composites Corporation, Sacramento, CA
- Linde LLC, Hayward, CA

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Project End Date: January 2017

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section (3.3.5) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) System Weight and Volume

(D) Durability/Operability

(N) Hydrogen Venting

Technical Targets

This project specifically addresses three technical targets for onboard hydrogen storage in light duty fuel cell vehicles: system gravimetric capacity, system volumetric capacity, and operational cycle life. Previous projects on the development of the cryogenic high pressure storage technology achieved peak gravimetric and volumetric capacities of 0.074 kg H₂/kg system and 0.045 kg H₂/L system, respectively, using a 4,000 psi, 151 L (10.7 kg H₂ capacity), 25-in internal diameter, aluminum lined pressure vessel [1]. This current project aims at exploring designs with a 700 bar (10,000 psi) operating pressure, 63.5-L internal volume (5.6 kg H₂ capacity), 12-in internal diameter and a non-Al liner. FY 2015 efforts at designing, fabricating, and cryogenically strength testing pressure vessels produced a 63.5 L, non-Al liner Type III pressure vessel with 81% volume efficiency and 32 kg mass for 700 bar operating pressure, performance that would enable to meet our projected target of 0.090 kg H₂/kg system and 0.050 kg H₂/L system. Those projected performances will be demonstrated with a full size insulated system at the end of this project. Theoretical design calculations have also shown that this pressure vessel would have an operational life of at least 1,500 cycles. This cycle life will be experimentally tested through up to four full size prototype vessels in FY 2016. Table 1 summarizes our projected performance towards the three main technical targets addressed in this project.

Overall Objectives

- Develop ultra-light cryogenic pressure vessels with 12 in diameter and 700 bar rating
- Optimize metallic liner thickness, composite fiber fraction and ultra-thin vacuum jacket
- Quantify liquid hydrogen (LH₂) pump durability over 6,000 refuelings to 700 bar
- Demonstrate full scale system density of 50 g H₂/L_{system} and 9 wt% H₂, and a cycle life of at least 1,500 refills

Fiscal Year (FY) 2015 Objectives

- Submit safety plan for cryogenic H₂ cycling facility rated for 5 kg H₂ prototype vessels and obtain DOE/LLNL approval
- Fabricate 700 bar 163 L system using commercial vessel to test insulation and supports
- Complete civil construction of H₂ test facility
- Design and fabricate initial full scale (63.5 L) prototype 700 bar pressure vessel with a high ratio between inner and outer volume (80+% volumetric efficiency)
- Demonstrate 1,600 bar cryogenic (LN₂) strength of initial prototype (2.28 safety factor)

FY 2015 Accomplishments

- Sought and obtained LLNL safety approval of 65 bar containment for transient H₂ peak pressure and dynamic vessel wall loading of 2.5–5 kg H₂ over the full pressure and temperature range
- Completed civil site construction and control room installation for cryogenic H₂ cycling facility using 875 bar LH₂ pump

TABLE 1. Progress towards Meeting Technical Targets for Onboard Hydrogen Storage for Light Duty Fuel Cell Vehicles

Storage Parameter	Units	2020	Ultimate	Projected
System Gravimetric Capacity	kg H ₂ /kg system	0.055	0.075	0.090
System Volumetric Capacity	kg H ₂ /L system	0.040	0.070	0.050
Durability/Operability Operational Cycle Life	Cycles	1,500	1,500	1,500

- Designed and fabricated a 63.5 L thin lined carbon fiber overwrapped prototype vessel rated to 700 bar with 81% volumetric efficiency
- Demonstrated cryogenic strength of prototype vessel to 1,560 bar



INTRODUCTION

Storing cryogenic H₂ in a pressurized, insulated system has many benefits in terms of safety, volumetric and gravimetric densities and ownership cost that have been studied and demonstrated by LLNL [2,3] and external parties [4-7]. High utilization (>1,500 kg H₂/d) commercial scale fueling stations will likely require the use of liquid H₂ by means of a fast, energy efficient LH₂ pump. Until now, the development of cryogenic pressure vessels by LLNL has used “off the shelf” pressure vessels with an aluminum liner, a maximum operating pressure limited to 350 bar with large capacity (151 L, equivalent to 10.7 kg H₂) and large diameter (25 in). We believe that system densities (both volumetric and gravimetric), cycle life and manufacturability could be improved by developing pressure vessels specifically tailored towards cryogenic utilization, even at a 5.6 kg H₂ scale, by exploring: thin liner design (especially important for 12 in diameter), non-Al liner materials, high fiber fraction for the composite overwrap, 700 bar operating pressure and ultra-thin vacuum jacket designs.

APPROACH

Within the project, we are designing, manufacturing and cryogenically pressure testing full scale (65 L) 700 bar pressure vessels with a thin (<2 mm), non-Al liner and high fiber fraction. Our primary goal is to assess the *cryogenic* strength of these prototype composite vessels after 1,500 thermomechanical H₂ cycles, while secondary objectives will be accomplished in parallel to (1) measure LH₂ pump performance at 700 bar after 6,000 refuelings (~24 tonnes of LH₂), (2) demonstrate lightweight vacuum jackets for cryogenic H₂ pressure vessels, and (3) design and fabricate an experimental cryogenic H₂ storage system with 5.6 kg H₂ capacity.

In order to achieve the thermomechanical cycling, a LH₂ testing facility will be constructed next to the existing 875 bar LH₂ pump, capable of rapidly cycling full scale (63.5 L) non-certified cryogenic pressure vessels up to 700 bar and performing strength testing of those vessels up to 160 K, 1,300 bar. One to two vessels could be cycled at the same time in this single-manned, remotely operated facility that would also include a vent stack and a 40 kW heat exchanger.

RESULTS

The time period (July 2014 to July 2015) covered by this report focused on five tasks.

Development of Thin-Lined, High Fiber Fraction Vessels

Following the room temperature tensile testing done in FY 2014, ring burst tests, cryogenic tensile test, and pipe welding test completed the small-scale testing for the development of thin-lined high fiber fraction vessels. A design study was then carried out, including liner fatigue and finite element analyses.

The ring burst test procedure was used to evaluate liner buckling after autofrettage, where a liner “ring” (about 1.5 in wide) is overwrapped with a thin carbon fiber ring and then pressurized. This test enables to experimentally determine the minimum thickness the liner can have before it buckles. Thicknesses between 1.3 mm and 1.8 mm were shown to be sufficient for our conditions. Preliminary off-site cryogenic tensile strain testing was then conducted. This mechanical testing was necessary to determine basic variations of the properties of the liner material at cryogenic temperatures, such as Young modulus, elastic strain and tensile (ultimate) strength. It was observed that both the Young modulus and the elastic strain increase with decreasing temperatures. Also, the ultimate strength varied from 80 ksi at room temperature to almost 200 ksi at cryogenic LN₂ temperature. The results from the weld quality testing, tensile tests and ring burst tests showed that the selected material would perform as required.

A design study concerning the construction of the thin lined filament wound composite prototype pressure vessel was then carried out. The pressure vessel was designed based on the American Society of Mechanical Engineers

(ASME) Boiler and Pressure Vessel Code, Section X for Class III vessels with non-load sharing liners for gaseous hydrogen stationary service. A finite element analysis was also performed. The composite design was developed based on netting analysis and a helical-to-hoop fiber stress ratio of 75%. The hoop plies were consolidated into four groups to limit the number of elements required to uniquely model the helical and hoop layers. The dome shape for this pressure vessel was developed using geodesic-isotensoid theory. A winding table was generated.

Safety Analysis and Approval of 2.8 m³, 65 bar Vessel for Containment of Non-Certified Pressure Vessels during Pressurization and Cycling

Following the safety plan submitted to DOE in June 2014 and a visit from the DOE H₂ Safety Panel in August 2014, it was decided by DOE management that authorization for the design and operation of the containment of non-certified pressure vessels under cycling and strength testing conditions should ultimately be granted by LLNL's pressure safety committee. Internal reviews were performed with pressure and containment experts leading to the ultimate approval of the operation as initially proposed.

Civil Construction of the H₂ Vessel Test Facility

Civil construction of the H₂ vessel test facility started in early FY 2015, and was completed in February 2015. It consisted of the construction of several concrete pads next to the existing LH₂ pump to accommodate a 100 psi air compressor, a control room, support racks for cryogenic high pressure H₂ lines, instrumentation and control air, and a 30 ft by 30 ft pad where the H₂ equipment (containment vessels, vent stacks, heat exchanger) will be installed. Figure 1 is a picture of the completed civil construction together

with markers showing the future location of the main H₂ components.

Manufacture and Cryogenic Strength Test of the First Thin-Lined, Full Scale (63.5 L), 700 bar Pressure Vessel Prototype

The first thin-lined full scale 700 bar prototype vessel was fabricated by Spencer Composites then delivered to LLNL for cryogenic strength testing. Based on weight and geometrical measurements, we estimated that the vessel had 81% volumetric efficiency (ratio between inner and outer volume). The vessel was installed in an unmanned pressure test cell and initially filled with liquid N₂ at atmospheric pressure. It was then pressurized with room temperature N₂. Given the difficulty of maintaining a reasonable pressurization rate, the vessel underwent rather large pressure spikes (see Figure 2) before bursting at 1,560 bar and at an estimated temperature of 150 K. Based on the analysis of these results, DOE agreed to validate this go/no-go milestone.

Assembly of the H₂ Vessel Test Facility

Assembly of the test facility started after passing the first go/no-go milestone (previous task) and included instrumentation (pressure transducers, temperature sensors, vacuum transducer, H₂ sensor), air controlled valves (rated for cryogenic H₂ up to 30,000 psi), lines and fittings (rated for cryogenic H₂ up to 20,000 psi), vent stacks, 40 kW heat exchanger, and the containment vessel (Figure 3).

We anticipate completing construction of the H₂ test facility (without the heat exchanger, scheduled to arrive during the fall) by the end of FY 2015 allowing the beginning of prototype vessel cycle testing by that time.

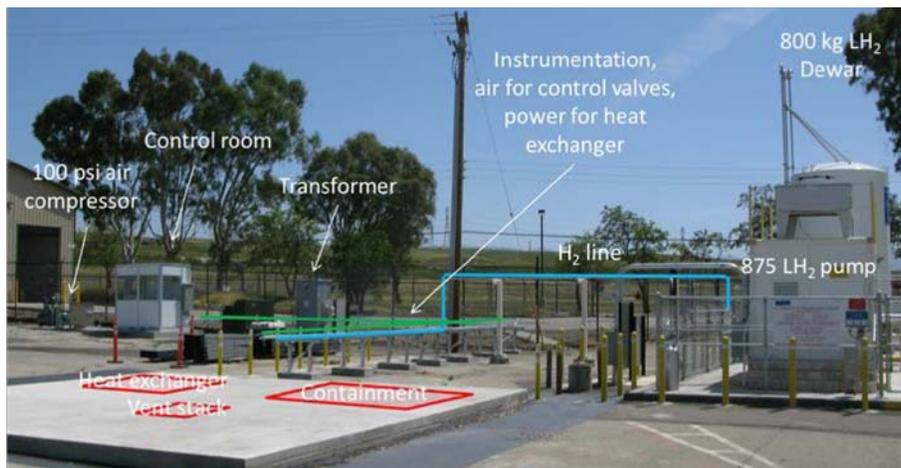


FIGURE 1. Completed site construction of the future H₂ test facility. Future locations of the main components (heat exchanger, vent stack, containment vessel and H₂ line) are shown.

efficiency when refueled at 72 g H₂/L density from the LH₂ pump will complete the second go-no go milestone

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Threaded Insert for Compact Cryogenic-Capable Pressure Vessels, Francisco J. Espinosa-Loza, Timothy O. Ross, Vernon A. Switzer, Salvador M. Aceves, Nicholas J. Killingsworth, Elias Ledesma-Orozco, US Patent 9,057,483 B2, June 16, 2015.

FY 2015 PUBLICATIONS/PRESENTATIONS

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2. Salvador M. Aceves, Francisco Espinosa-Loza, John W. Elmer, Robert Huber, “Comparison of Cu, Ti and Ta Interlayer Explosively Fabricated Aluminum to Stainless Steel Transition Joints for Cryogenic Pressurized Hydrogen Storage,” *International Journal of Hydrogen Energy*, Volume 40, pp. 1490-1503, 2015.

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2. Petitpas G, Aceves S.M., “Modeling of Sudden Hydrogen Expansion from Cryogenic Pressure Vessel Failure.” *International Conference on Hydrogen Safety*, San Francisco: 2011.
3. Aceves S.M., Petitpas G., Espinosa-Loza F., Matthews M.J., Ledesma-Orozco E. “Safe, long range, inexpensive and rapidly refuelable hydrogen vehicles with cryogenic pressure vessels.” *International Journal of Hydrogen Energy* 2013;38:2480–9. doi:10.1016/j.ijhydene.2012.11.123.
4. Kircher O., Greim G., Burtscher J., Brunner T. “Validation of cryo-compressed hydrogen storage (cch2)—a probabilistic approach.” *Proceeding of the International Conference on Hydrogen Safety*, San Francisco: 2011.
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