IV.G.1 Compact (L)H_2 Storage with Extended Dormancy in Cryogenic Pressure Vessels

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Objectives

- Build and test cryogenic pressure vessels.
- Demonstrate cryogenic vessel onboard a vehicle.
- Test thermal endurance and heat transfer rate.
- Test composite vessel outgassing and vacuum stability.
- Test vessel cycle life at liquid hydrogen (LH_2) temperature and high pressure.
- Test para-ortho and ortho-para conversion at cryogenic temperatures.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Weight and Volume
(D) Durability
(H) Balance of Plant (BOP) Components
(O) Hydrogen Boil-Off

TABLE 1. Progress toward Meeting DOE On-Board Hydrogen Storage Technical Targets

Lawrence Livermore Cryo-Compressed Vessels					
Storage Parameter	**Units**	**2010 Target**	**2015 Target**	**2007, 2nd generation§**	**2009, 3rd generation***
Specific Energy	kWh/kg	1.5	1.8	1.8	2.31
Energy Density	kWh/L	0.9	1.3	1.04	1.42
Storage System Cost	$/kWh	4	2	13.6	13.6

§ From Argonne and TIAX [1,2]
* Preliminary estimates being certified by independent analysis

Accomplishments

- Demonstrated generation 3 cryogenic pressure vessel that stores hydrogen at 45 gH_2/L and 7.5% H_2 weight fraction, thereby meeting the DOE 2015 targets.
- Conducted vacuum stability tests and chemically analyzed composite outgassing.
- Designed experiment for cryogenic cycle test.
- Designed experiment for para-ortho conversion.

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Introduction

As a universal transportation fuel that can be generated from water and any energy source, hydrogen (H_2) is a leading candidate to supplant petroleum with the potential to ultimately eliminate petroleum dependence, associated air pollutants and greenhouse gases. The predominant technical barrier limiting widespread use of hydrogen automobiles is storing enough hydrogen fuel onboard to achieve sufficient (500+ kilometers) driving range in a compact, lightweight, rapidly refuelable, and cost-effective system. Cryogenic pressure vessels may contribute to solving this challenge. In collaboration with industry, we are currently addressing the remaining hurdles to enable future commercialization.

Approach

Cryogenic pressure vessels being developed at LLNL have potential for enabling practical range through a combination of dense hydrogen storage (LH_2) and efficient packaging density. Cryogenic pressure vessels can store LH_2 with dramatically improved thermal endurance – the main challenge facing conventional low-pressure LH_2 tanks. Cryogenic pressure vessels have reduced sensitivity to heat transfer and can therefore operate with reduced insulation thickness (~1.5 cm vs. ~3 cm for low-pressure LH_2 tanks), considerably improving packaging efficiency leading to vessels that meet DOE's 2015 weight and volume targets and approach DOE's ultimate weight target. Current work focuses on improving the technology through innovative designs, collaboration with industry, and system performance experiments.

Results

Cryogenic vessels often demand thick insulation (~3 cm) for adequate thermal performance, negatively impacting volumetric hydrogen storage capacity. Thermodynamic analysis and experiments [3] indicate that cryogenic capable pressure vessels are approximately an order of magnitude less sensitive to heat transfer than conventional low-pressure cryogenic systems, thus enabling thin thermal insulation (~1.5 cm) and hence much improved storage density.

Starting with the LLNL generation 2 design [3] and reducing thermal insulation thickness from ~3 cm to ~1.5 cm leads to the LLNL generation 3 design (Figure 1) that is 23% more compact (225 liters vs. 297 liters), meeting the very challenging DOE 2015 weight and volume targets. Ultra-thin insulation may suffice for controlling heat entry at ~5-7 Watts through careful vessel support and insulation design, maintaining ~3-5 days dormancy for a full tank and avoiding evaporative losses under typical utilization scenarios. Dormancy will increase rapidly as the vehicle is driven and the fill level drops.

Aside from vessel fabrication, we are conducting experiments to test critical performance issues that may limit commercialization. Vacuum stability is a key feature. Excessive outgassing from the composite vessel may degrade the insulation performance and drastically reduce dormancy. We are therefore testing the outgassing behavior of composite pressure vessels by storing them inside a steel vacuum chamber at specified temperatures (20, 60 and 80°C). We are testing four small-scale (~1 liter) composite pressure vessels with aluminum lining and carbon fiber reinforcement. The vessels have four different surface and curing treatments: 1) regular pressure vessel with no special surface treatment; 2) vacuum cured pressure vessel; 3) ultraviolet (UV) protection coated pressure vessel; and 4) vacuum cured and UV protection coated pressure vessel. The pressure vessels are placed one at a time inside the vacuum chamber that is connected to a vacuum pump (Figure 2). The amount and composition of outgassing from the composite vessel at the different temperatures are measured while keeping a high vacuum. This experiment has the purpose of identifying surface treatments that may reduce outgassing. Identifying the amount and composition of the outgassing will enable optimum selection of absorbent (getter) materials that will maintain high insulation performance in a commercial cryogenic pressure vessel.

FIGURE 1. Generation 2 (left) and generation 3 (right) cryogenic pressure vessels. Generation 3 vessel is 23% more compact through reduced insulation thickness (1.5 cm vs. 3 cm).

The experiments are in progress and have identified detailed outgassing composition including a large family of hydrocarbons in the range of a few to 100 parts per billion. The main hydrocarbon species for the regular vessel (no surface treatment) have remained consistent between experiments at different temperatures, although vessels with other surface treatments are yet to be analyzed. Water is the main component of outgassed samples, and its concentration can be greatly reduced by baking. Hydrocarbons, however, are produced by the vessel even after baking.

Successful commercialization of cryogenic pressure vessels demands cycle life testing. Composite wrapped pressure vessels are typically not designed for cryogenic operation, and fatigue failure may result during repeated cycling. We have therefore proposed a cycle test procedure to address the need for validating composite pressure vessel endurance when pressure cycled at cryogenic temperature (Figure 3). The proposed test includes three operating points identified as most critical for cryogenic vessel operation: minimum temperature (20 K) and low pressure (point 2 in Figure 3), maximum working pressure at low temperature (point 3), and maximum working pressure at below ambient temperature (point 10). We estimate that the overall cycle can be efficiently conducted in ~3 hours when heating the vessel by circulating warm hydrogen (or helium) through the in-tank heat exchanger (2-5 kW depending on vessel temperature). We are planning to repeat the test cycle 300 times.

Finally, we have defined an experimental sequence to test the conversion between the para and ortho

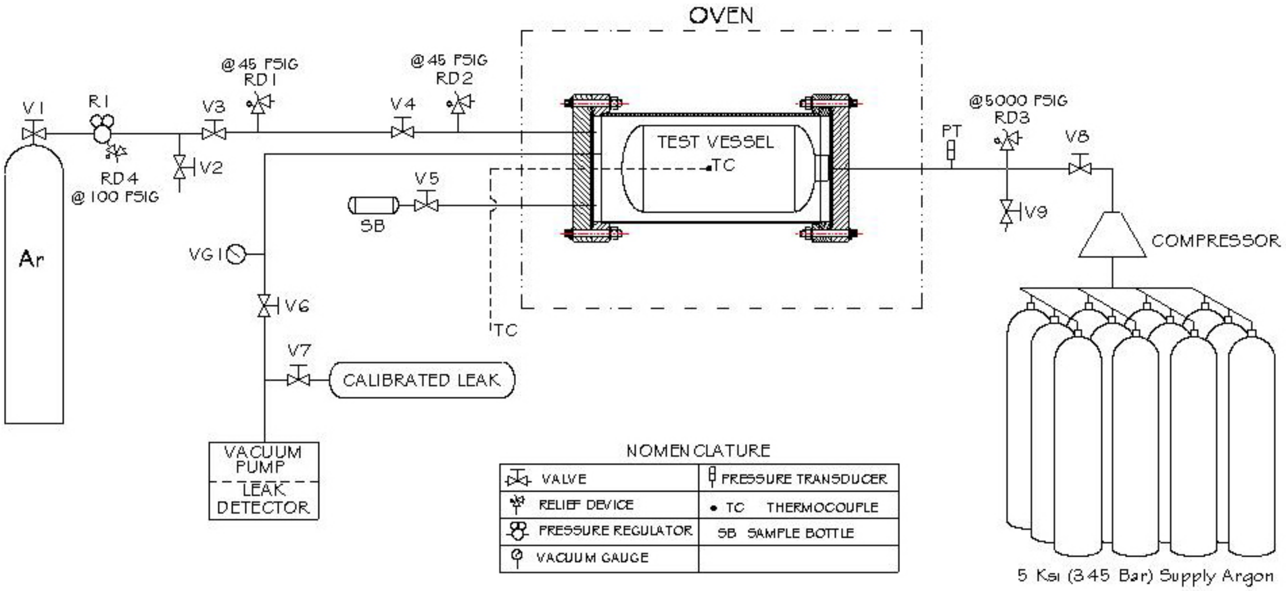

FIGURE 2. Schematic of experimental system for characterization of composite pressure vessel outgassing. The composite vessel is located inside a vacuum vessel, which is then positioned inside an oven for elevated temperature testing.

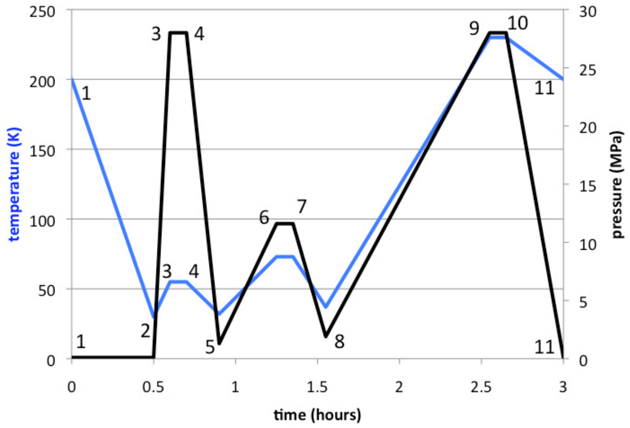

FIGURE 3. Experimental cycle test for cryogenic pressure vessel consisting of multiple steps: LH_2 fill (points 1-2), cryogenic pressurization by heat transfer (points 2-3), equilibration (points 3-4), depressurization by venting (points 4-5), second pressurization by heat transfer (points 5-6), and equilibration (points 6-7), second depressurization by venting (points 7-8), final pressurization by heat transfer (points 8-9), equilibration (points 9-10), and depressurization to ambient pressure (points 10-11).

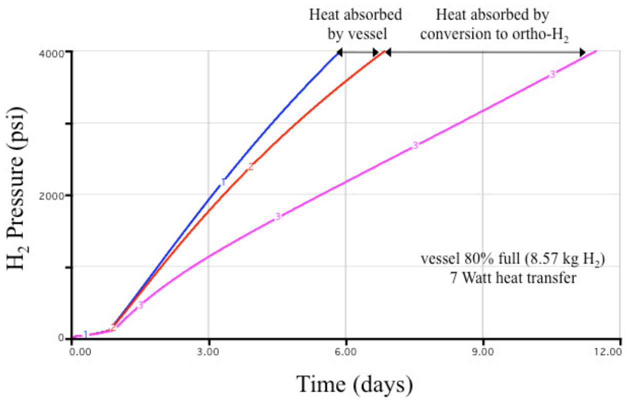

FIGURE 4. Possible effect of para-ortho conversion in cryogenic pressure vessel pressurization, assuming a pressure vessel initially filled with 8.57 kg of LH_2 (80% fill level) at ambient pressure with 7 Watts environmental heat transfer rate. The figure shows three lines: (1) pressurization neglecting vessel thermal mass and para-ortho conversion (blue), (2) pressurization neglecting para-ortho conversion and including vessel thermal mass (red), and (3) pressurization including vessel thermal mass and assuming phase equilibrium between para and ortho hydrogen phases (purple). Actual pressurization experiment will yield a line between the red and purple lines due to partial (kinetics-limited) para-ortho conversion.

states of nuclear spin of the hydrogen molecule. This is important because there is a potential synergy between cryogenic pressure vessels and the conversion of para-hydrogen into ortho-hydrogen as the vessel warms up: para-ortho conversion absorbs energy (because ortho is the higher energy form) and therefore increases the thermal endurance of the cryogenic vessel. This effect is present when most needed: for a nearly full vessel where para-ortho conversion may double the thermal endurance of the vessel if the conversion process is fast relative to the warming process so that the composition remains near phase equilibrium (Figure 4). However, kinetics of conversion from *para* to *ortho* is not well characterized for the broad temperature and pressure ranges in cryogenic pressure vessel operation. Our sequence of experiments will allow us to estimate the rate of para-ortho conversion at the conditions typically found in a cryogenic pressure vessel as it warms from 20 K (where the equilibrium concentration is approximately 100% para-hydrogen) to 200 K (where equilibrium concentration is near the ambient temperature mixture of 75% ortho and 25% para). Para-ortho conversion can be calculated from thermodynamic analysis of the pressure and temperature data collected as the tank warms up. Comparison with a helium warm-up test will allow for benchmarking and improved conversion estimation.

Conclusions and Future Directions

- Cryogenic pressure vessels can exceed 2015 DOE storage targets for weight and volume, with promising dormancy and cost relative to conventional LH_2 tanks and ambient pressure vessels.
- In collaboration with industrial partners, we are addressing interactions between pressure, temperature, and materials by conducting outgassing, cryogenic cycling, and cryogenic burst tests experiments.
- We are investigating fundamental operational aspects at full scale: internal heat exchange, dormancy and dormancy recovery, para-ortho conversion, and higher density (pressurized) refueling.
- Safety advantages of cryogenic pressure vessels are yet to be assessed. Possible advantages may originate from very low burst energy, fill vs. dormancy safety factor, protective vacuum jacket, and material strength at cryogenic temperatures.

FY 2009 Publications/Presentations

1. High Density Hydrogen Storage in Cryogenic Capable Pressure vessels, Salvador Aceves, Invited presentation, Purdue Hydrogen Symposium, April 2009.

2. Hydrogen-Fueled Carbon-Free Transportation, Salvador Aceves, Invited Presentation, Engineering Solutions for Sustainable Development: Materials and Resources, an international workshop organized by AIME and ASCE, Lausanne, Switzerland, July 22–24.

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2. Lasher, S., McKenney, K., Sinha, J., Rosenfeld, J., “Analyses of Hydrogen Storage Materials and On-Board Systems,” Proceedings of the DOE Hydrogen and Fuel Cell Annual Merit Review, Crystal City, Virginia, 2008, http://www.hydrogen.energy.gov/pdfs/progress08/iv_e_1_lasher.pdf.

3. Aceves, S.M., Berry, G.D., Espinosa-Loza, F., Ledesma-Orozco, E., Ross, T., Switzer, V., Weisberg, A., “Automotive Cryogenic Capable Pressure Vessels for Compact, High Dormancy (L)H_2 Storage,” Proceedings of the DOE Hydrogen and Fuel Cell Annual Merit Review, Crystal City, Virginia, 2008, http://www.hydrogen.energy.gov/pdfs/progress08/vii_6_aceves.pdf.