VII.6 Automotive Cryogenic Capable Pressure Vessels for Compact, High Dormancy (L)H_2 Storage

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Start Date: October 1, 2004
Projected End Date: September 30, 2011

Objectives

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

Technical Barriers

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

(B) Hydrogen Storage

Contribution to Achievement of DOE Technology Validation Milestones

This project will contribute to achievement of the following DOE milestone from the Technology Validation section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- **Milestone 9: Validate on-board cryo-compressed storage system on a technology development vehicle achieving 1.7 kWh/kg and 1.2 kWh/L.**

The cryogenic capable pressure vessel onboard the Prius hydrogen vehicle meets the weight target when refueled with low-pressure liquid hydrogen (20 K and 1 bar) and it meets the volume target if refueled with high-pressure cryogenic hydrogen (20 K and 200 bar). Ongoing work will produce more compact vessels that will satisfy the volume milestone even with low-pressure liquid hydrogen.

Accomplishments

- Demonstrated longest LH_2 dormancy onboard a vehicle (six days) and potential for three weeks at ~3.5 Watts heat transfer rate.
- Conducted a vacuum stability test by cooling down the vessel and letting it warm up to ambient temperature while monitoring the vacuum.

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Introduction

One of the fundamental hurdles to the widespread commercialization of hydrogen vehicles is storing enough hydrogen on-board for a reasonable range (more than 300 miles). LLNL is working on a hydrogen storage concept that is demonstrating advantages over existing technologies. The concept is a cryogenic capable pressure vessel that can store LH_2 with dramatically improved thermal endurance, the main challenge facing conventional low pressure LH_2 tanks. In addition, cryogenic capable pressure vessels offer refueling and infrastructure flexibility since they can fill with ambient temperature compressed gaseous hydrogen, to reduce fuel cost or energy intensity while expanding the number of potential refueling locations.

Approach

We are designing, testing and demonstrating cryogenic capable pressure vessels that achieve the high density of liquid hydrogen without the evaporative losses typical of LH_2 containers. If fueled with LH_2, our cryogenic capable pressure vessels provide high storage density and low evaporative losses. If fueled with compressed hydrogen, cryogenic capable pressure vessels reduce the energy necessary for hydrogen densification. Cryogenic capable pressure vessels can efficiently be applied to hydrogen storage materials (high surface area adsorbents) in addition to physical hydrogen storage.

Results

Last year (Fiscal Year 2007) we installed a cryogenic capable pressure vessel onboard a hydrogen-fueled Prius (Figure 1). The cryogenic-capable pressure vessel meets the 2007 weight target and is within 10% of the 2007 volume target. The vehicle was refueled with compressed and liquid hydrogen, demonstrating flexible refueling, and was driven 650 miles on a single tank of liquid hydrogen–the longest distance ever for a hydrogen car.

In FY 2008 we conducted a thermal endurance test, where the cryogenic-capable pressure vessel was filled with ~10 kg of liquid hydrogen and then the vehicle was left parked for six days as the temperature and pressure increased due to heat transfer from the environment (Figure 2). Thermodynamic analysis of the pressure and temperature data enables calculation of heat transfer rate into the vessel. We report heat transfer rate in Figure 3, along with pressure in the vacuum insulation.

FIGURE 1. LLNL experimental hydrogen Prius with the cryogenic-compatible pressure vessel installed in the trunk.

The heat transfer rate is high during the first few hours of the experiment. We believe some portions of the vessel were initially not at liquid hydrogen temperature, and the thermal energy of the vessel heated the hydrogen, increasing the pressure and appearing in the analysis as "virtual" heat transfer. After the initial spike, the heat transfer rate dropped to ~3 Watts, and after a short excursion to ~7 Watts it dropped to ~3 Watts again. At this point heat transfer started increasing slowly as the pressure in the vacuum space increased due to permeation through a valve gasket. Permeation intensified as the pressure inside the vessel increased, resulting in a fast increase in heat transfer rate. The test ended after six days and one hour when the vessel reached the maximum operating pressure (5,000 psi). Even with the premature end, six days is the longest dormancy ever demonstrated in an automotive liquid hydrogen vessel. Most importantly, the vessel shows the potential for ~3 weeks of dormancy if the heat transfer rate can be maintained at 3-4 Watts (i.e., if a high quality vacuum can be maintained throughout the test).

We also tested vacuum stability–a key issue for long-term operability onboard a vehicle. The cryogenic-capable pressure vessel was cooled down with liquid hydrogen and then emptied. The vessel was allowed to warm up until reaching ambient temperature while we monitored the vacuum at discrete time intervals (Figure 4). The vessel warmed up over ~5 weeks and the heat transfer rate was 3-4 Watts, similar to the dormancy test.

Starting with a high quality vacuum (10^{-5} Torr), the vacuum remained quite stable for ~4 weeks. In the last week of the test (680-850 hours) the pressure in the

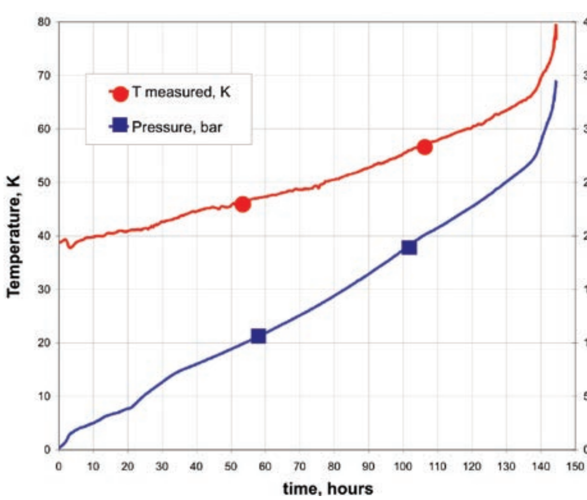

FIGURE 2. Pressure and temperature measured inside the vessel during the dormancy experiment.

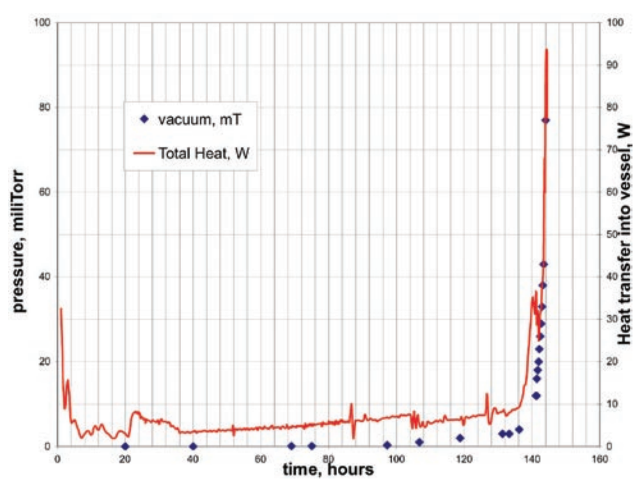

FIGURE 3. Pressure in the vacuum insulation (measured) and heat transfer into the vessel (calculated from the measured temperature and pressure, Figure 2) during the 6-day dormancy test.

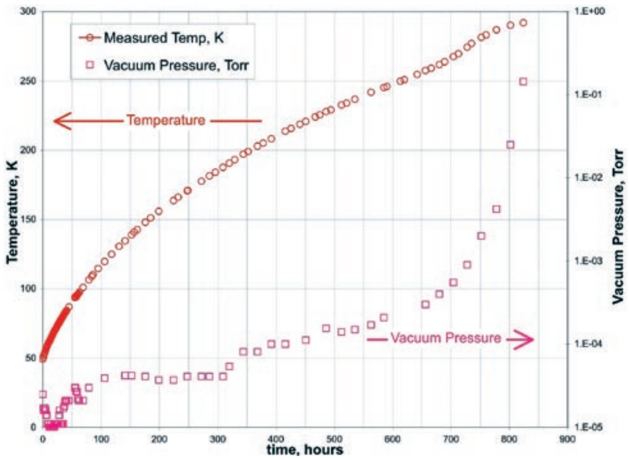

FIGURE 4. Vessel temperature and pressure in the vacuum space during a 5-week vacuum stability test.

vacuum space increased by ~3 orders of magnitude. This sudden increase in pressure occurred at the temperature range where water evaporates (250-273 K) at the low pressures of the vacuum space (10^{-4}-10^{-2} Torr), and we therefore anticipate that water evaporation may be responsible for the loss in vacuum. We collected samples of the gases contained in the vacuum and ongoing chemical analysis will reveal whether our prediction holds true. Chemical analysis will also help us determine practical approaches for maintaining vacuum stability over a long period of time (e.g., getter materials).

Conclusions and Future Directions

- We have installed a cryogenic-capable pressure vessel onboard LLNL's experimental hydrogen Toyota Prius vehicle. The cryogenic capable pressure vessel meets the 2007 weight target and is within 10% of the 2007 volume target. The vehicle was driven 650 miles on a single tank of liquid hydrogen.
- Starting with a vessel full of liquid hydrogen, we were able to contain the hydrogen for six days without evaporative losses. We also demonstrated the potential for containing hydrogen for ~3 weeks without evaporative losses by demonstrating 3-4 Watts of heat transfer at liquid hydrogen temperature (~30 K).
- A vacuum stability test revealed loss of vacuum quality as the vessel warmed up between 250-300 K. We attribute this sudden increase to water evaporation. Ongoing chemical analysis will help us determine practical approaches for long-term vacuum stability.

Special Recognitions & Awards/Patents Issued

1. Storage of H_2 by Absorption and/or Mixture within a Fluid, Gene Berry and Salvador Aceves, US Patent 7,191,602, 2007.

FY 2008 Publications/Presentations

1. Cryogenic Hydrogen Storage, Salvador Aceves, Invited Presentation, *Materials Science and Technology 2007 Conference and Exhibition*, September 2007.

2. Setting a World Driving Record with Hydrogen, Salvador Aceves, *Science and Technology Review*, June 2007, http://www.llnl.gov/str/June07/Aceves.html.

3. H_2 Going for Distance, Salvador Aceves, *Mechanical Engineering*, December 2007, p. 16.