VI.A.6 Storage of Hydrogen in Cryo-Compressed Vessels

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Objectives

- Construct and test cryogenic capable pressure vessels.
- Demonstrate cryogenic capable vessel on board a vehicle.
- Obtain performance data to meet density and dormancy targets.
- Test low temperature cycle life of composite vessels.

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 6: Validate on-board cryo-compressed storage system on a technology development vehicle achieving 1.5 kWh/kg and 1.0 kWh/L.** Our Prius cryo-compressed hydrogen vehicle has exceeded these performance targets.

Accomplishments

- Designed and built a new cryo-compressed vessel that meets the 2007 DOE weight goal and is within 10% of the 2007 DOE volume goal including all system accessories.
- Tested prototype cryo-compressed vessel to verify vacuum performance, pressure performance and satisfactory operation at cryogenic temperature (down to 20 K).
- Installed cryo-compressed vessel in a Toyota Prius prototype vehicle.
- Demonstrated flexible refueling with both compressed and liquid hydrogen.
- Conducted drive test demonstrating 650 miles on a single liquid hydrogen tank (under atypical driving conditions).
- Conducted dormancy test and measured ~10 Watt heat leak at 20-30 K.

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Introduction

One of the fundamental hurdles to the widespread commercialization of hydrogen (H_2) vehicles is storing enough hydrogen on-board for a reasonable range (more than 300 miles). LLNL is working on a hydrogen storage concept that may demonstrate an advantage over existing technologies. The concept is a cryo-compressed pressure vessel that can store liquid hydrogen (LH_2) with dramatically improved thermal endurance, the main challenge facing conventional low pressure LH_2 tanks (for example those developed over the past 30 years by BMW and Linde). In addition, cryo-compressed vessels offer refueling and infrastructure flexibility since they can fill with ambient temperature compressed gaseous hydrogen (GH_2), to reduce fuel cost or energy intensity while expanding the number of potential refueling locations.

Approach

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

Results

Last summer we built a new cryo-compressed vessel design (151 liter internal volume) that stores 10.7 kg LH_2 within a compact package. The insulated vessel was then tested at cryogenic conditions (Figure 1). We also tested the vacuum insulation. The vessel is rated for 34.5 MPa (5,000 psi).

After satisfactory pressure, cryogenic and vacuum testing, we proceeded to install the vessel into our prototype hydrogen vehicle, a Toyota Prius hybrid vehicle converted to hydrogen by Quantum Technologies of Irvine, CA (Figure 2). Vessel installation was a labor-intensive effort that required the dedicated contribution of many LLNL participants: a designer, an analyst, two high-pressure inspectors, an electrician, a programmer, and a welder.

FIGURE 1. Cryogenic Testing of Vessel in LLNL High-Pressure Laboratory

Once the vessel and accessories were installed in the vehicle, we weighed and measured all components to determine the system volumetric and gravimetric performance. Considering a total hydrogen storage capacity of 10.7 kg, equivalent to 356 kWh of energy storage, and system weight and volume of 176 kg and 323 liters, we obtain a system that meets the DOE 2007 weight target (6% weight fraction of hydrogen vs. 4.5% for the DOE target) and is within 10% of the 2007 DOE volume target (33 grams of hydrogen per liter vs. 35 g/L for the DOE target). These performance parameters include all system components. The system also exceeds Milestone 6 from the Technology Validation program plan: *Validate on-board cryo-compressed storage system on a technology development vehicle achieving 1.5 kWh/kg and 1.0 kWh/L.*

The next step in the process consisted of fueling the car with compressed and liquid hydrogen (Figure 3) and operating the vehicle within the LLNL site. The vehicle was refueled multiple times with compressed and liquid hydrogen at LLNL's fueling station, demonstrating the fuel flexibility of the system.

After filling the vessel to full capacity with liquid hydrogen, we conducted a driving test and drove the vehicle 650 miles on a single tank of fuel–the longest ever for any hydrogen vehicle. The drive was conducted at low speed under low traffic conditions, and does not represent typical driving. Under typical driving we would expect a ~500 mile range based on the EPA fuel economy rating for the Prius and the capacity of the storage tank.

We also conducted a thermal endurance test, where the cryo-compressed vessel was filled with 4.2 kg of liquid hydrogen and then the vehicle was left parked for

FIGURE 2. Cryo-Compressed Vessel Installed Onboard the Prius Hydrogen Fueled Hybrid Vehicle

FIGURE 3. Prius Prototype Vehicle Being Refueled With Liquid Hydrogen at LLNL Fueling Station

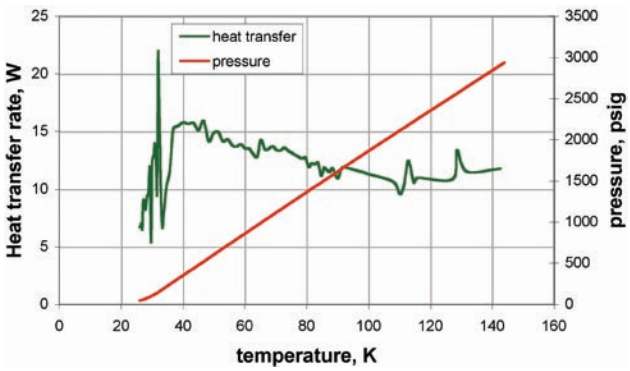

FIGURE 4. Heat Transfer Rate and Pressure as a Function of Vessel Temperature During the Parking Test of the Cryo-Compressed Vessel

2 weeks as the pressure increased due to heat transfer from the environment. At the end of the experiment we analyzed the pressure and temperature data to calculate heat transfer into the vessel. The results are shown in Figure 4. Heat transfer rate is ~10 W at 20-30 K. From this point, the heat transfer rate increased as the temperature increased. This is an unexpected result that was attributed to hydrogen leaking into the vacuum space and reducing the performance of the multilayer insulation. Our current vessel design includes a check valve inside the vacuum space (to reduce conduction of heat into the vessel), and this valve leaked when subjected to low temperatures and high pressures. Future designs will not incorporate valves into the vacuum space, avoiding leakage and keeping a good thermal performance.

Cryo-compressed vessels are very insensitive to heat transfer (an order of magnitude higher thermal endurance than a liquid hydrogen tank) and the parking experiment was concluded without fuel losses, even at the relatively high heat transfer rate calculated in the experiment.

Conclusions and Future Directions

- We have installed a cryo-compressed vessel into our prototype hydrogen vehicle, a Toyota Prius hybrid vehicle converted to hydrogen.
- The vessel system meets the DOE 2007 weight target (6% weight fraction of hydrogen vs. 4.5% for the DOE target) and is within 10% of the 2010 DOE volume target (33 grams of hydrogen per liter vs. 35 g/L for the DOE target), including all system components.
- The system also exceeds Milestone 6 from the Technology Validation program plan: *Validate on-board cryo-compressed storage system on a technology development vehicle achieving 1.5 kWh/kg and 1.0 kWh/L.*
- We conducted a driving test with a full tank of liquid hydrogen and drove the Prius 650 miles without refueling, which is the longest ever for any hydrogen vehicle. The drive did not represent typical driving conditions, and we anticipate ~500 mile range for more typical driving.
- A dormancy test revealed 10 W of heat transfer into the vessel at 20-30 K. The vessel demonstrated a long period of dormancy when filled with liquid hydrogen, due to the intrinsic thermodynamic advantage of cryo-compressed vessels when compared to liquid hydrogen tanks.

Special Recognitions & Awards/Patents Issued

1. Storage of H2 by Absorption and/or Mixture within a Fluid, Gene Berry and Salvador Aceves, US Patent 7,191,602, March 20, 2007.

FY 2007 Publications/Presentations

1. Advanced Concepts for Vehicular Containment of Compressed and Cryogenic Hydrogen, Salvador M. Aceves, Gene D. Berry, Andrew H. Weisberg, Francisco Espinosa-Loza, Scott A. Perfect, Proceedings of the 16th World Hydrogen Energy Conference, Lyon, France, June 10-15, 2006.

2. Vehicular Storage of Hydrogen in Insulated Pressure Vessels, Salvador M. Aceves, Gene D. Berry, Joel Martinez-Frias, Francisco Espinosa-Loza, International Journal of Hydrogen Energy, Volume 31, pp. 2274-2283, 2006.

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

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