IV.G.1 Extended Dormancy, Vacuum Stability, and Para-Ortho Hydrogen Conversion in Cryogenic Pressure Vessels

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Objectives

- Test thermal endurance and heat transfer rate.
- Test composite vessel outgassing and vacuum stability.
- Test para-ortho conversion at cryogenic temperatures and full scale (10 kg H_2).

Technical Barriers

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

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

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

Lawrence Livermore Cryogenic Pressure Vessels					
Storage Parameter	**Units**	**2010 Target**	**2015 Target**	**2007, Gen-2§**	**2009, Gen-3§**
Specific Energy	kWh/kg	1.5	1.8	1.8	2.36
Energy Density	kWh/L	0.9	1.3	1.04	1.48
Storage System Cost	$/kWh	4	2	9	8

§From Argonne and TIAX [1,2,3]

Accomplishments

- Held 10.2 kg liquefied hydrogen (LH_2) in a 95% full vessel for eight days with no evaporative losses or hydrogen extraction.
- Demonstrated that para to ortho hydrogen conversion stabilized vessel temperature for about one week.
- Demonstrated capacity to maintain 75% of the liquid hydrogen stored in vessel after one-month parking.
- Directly measured para-ortho hydrogen conversion with rotational Raman spectroscopy.
- Developed and tested a kinetic model for para-ortho hydrogen conversion.
- Conducted vacuum stability tests and chemically analyzed composite outgassing.

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Introduction

Cryogenic pressure vessels have potential for enabling practical vehicle 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. Low sensitivity to heat transfer enables 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. Further increases in thermal endurance may result from endothermic para-ortho conversion during long parking periods.

Approach

In previous years we dedicated our effort to demonstrating cryogenic pressure vessel weight and volume performance by building a prototype that met the DOE 2015 targets. This year we directed our attention to other critical issues: evaporative losses and long-term vacuum stability. The key experiment consisted on parking a vehicle with a nearly full (95%) cryogenic pressure vessel for a month to determine (1) heat transfer rate; (2) vacuum stability; and (3) para-ortho conversion. The results indicate that high performance thermal insulation, heat absorption due to para-ortho conversion, and favorable thermodynamics enabled completion of the 30-day experiment while retaining 75% of the initial hydrogen.

Results

Hydrogen has two phases of nuclear spin orientation: para-H_2 and ortho-H_2. Para-H_2 is the low energy form stable at liquid hydrogen temperature (20 K). As the hydrogen heats up from 20 K equilibrium shifts toward ortho-H_2, reaching normal composition (25% para and 75% ortho) at room temperature [4]. Liquid hydrogen (typically delivered as para-H_2 for stability) will therefore convert to ortho-H_2 as it warms up, absorbing considerable thermal energy (700 kJ/kg – comparable to vaporization) in the process. Para-ortho H_2 conversion has therefore much potential for augmenting thermal endurance.

While it may be possible to detect and quantify para-ortho H_2 conversion from calorimetry alone, LLNL has directly measured para-ortho population ratios using rotational Raman spectroscopy. In this approach, a hydrogen sample is collected inside a Raman cell (a small pressure vessel with windows at each end). A frequency-doubled Nd-YAG laser enters through a window in the Raman cell and the light is analyzed after interacting with the hydrogen (Figure 1). Most of the light leaving the Raman cell has the same frequency as the laser. This is filtered out leaving only light of different frequencies (inelastic scattering). A very small portion of the incident laser light scatters off the hydrogen molecules. An even smaller portion of the scattered photons give up some of their energy to the molecules. Thus they scatter with slightly less energy and are therefore shifted to slightly longer wavelengths. This is the Raman effect. The amount of this Raman scattered light is directly proportional to the number of molecules in each rotation energy state. Each energy state yields a slightly different Raman wavelength. Thus we are able to make a direct measurement of the relative populations of para (even quantum number rotational energy states) and the ortho (odd quantum number energy states) molecules.

The para-ortho conversion experiment was conducted onboard LLNL's hydrogen-fueled Prius. The vessel was filled to 95% capacity (10.2 kg) with LH_2 and parked outside, exposed to the daily sun, to capture worst-case conditions. The vessel warmed due to ~4.5 Watts of environmental heat transfer, until reaching maximum working pressure of 5,000 psi after 8.25 days of parking (Figure 2). At this point, we released 1.2 kg H_2. This both reduced the pressure to 3,000 psi and cooled the remaining 9 kg of H_2 from ~70 K to ~60 K.

Para-ortho conversion occurred during the second pressurization cycle (days 12-24) as indicated from rotational Raman spectroscopy measurements (blue line in Figure 2). During this time, endothermic para-ortho conversion absorbs most of the environmental heat transfer, leading to a considerable reduction (from ~4.5 Watts to ~1 Watt) in apparent heat transfer into the vessel. Apparent heat transfer is calculated from the pressurization rate assuming no para-ortho conversion. Calculating the total internal energy absorbed (blue area in Figure 2) and dividing it by the baseline heat transfer rate (4.5 W), we were able to determine that para-ortho conversion increased vessel dormancy by ~1 week.

After day 24, para-ortho H_2 conversion was nearly complete as the composition approached equilibrium (Figure 3), and apparent heat transfer returned to the baseline level (4.5 W). After a few more H_2 extractions,

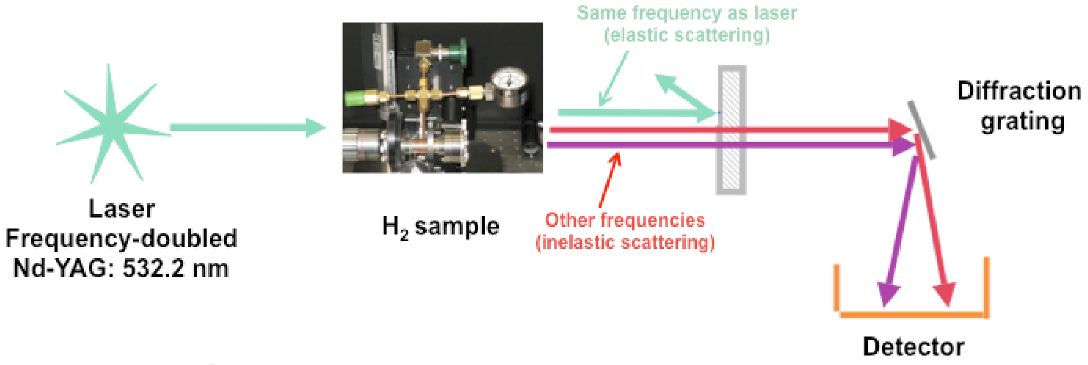

FIGURE 1. Experimental Setup for Measuring Para-Ortho Composition with Raman Spectroscopy

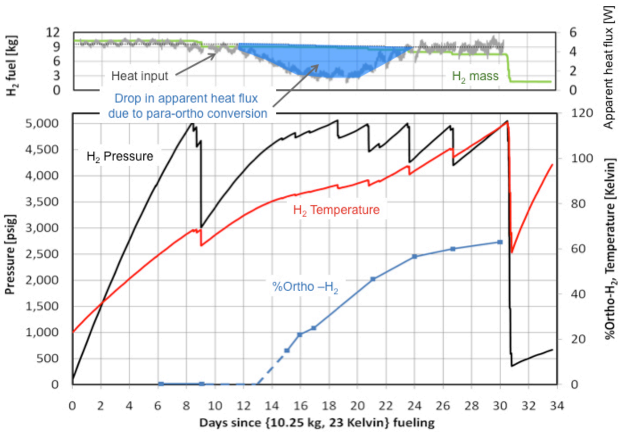

FIGURE 2. Results from month-long para-ortho conversion experiment. The figure shows pressure (black line, left scale), temperature (red line, right scale), ortho concentration (blue line, left scale), hydrogen mass (green line, left scale, upper chart), and apparent heat transfer (gray line, right scale, upper chart).

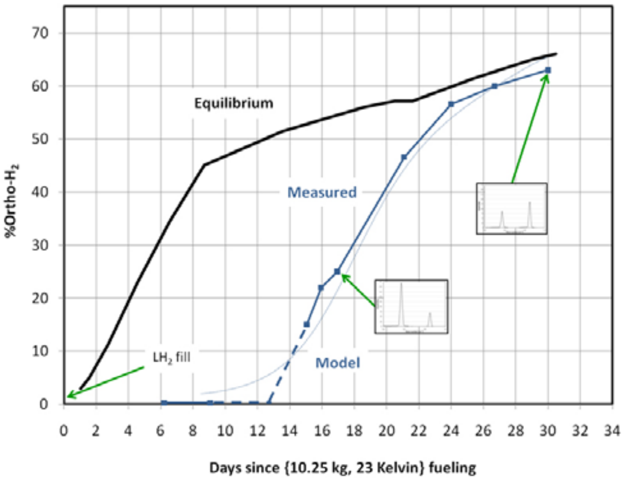

FIGURE 3. Para-ortho behavior during month-long experiment. The figure shows measured (blue line with symbols), equilibrium (black line), and model (thin line) ortho concentrations.

the experiment ended after 30 days with the vessel still retaining 7.65 kg H_2. Extracting 2.5 kg H_2 was therefore sufficient to avoid evaporative losses during a month. Considering that LLNL's H_2 Toyota Prius is an efficient vehicle (50 miles/kg H_2), 2.5 kg H_2 is enough for driving 125 miles. It is therefore concluded that very little driving (125 miles/30 days ~4 miles per day) is enough to avoid evaporative losses, even in the very challenging set of conditions used in the experiment (vehicle parked out in the sun with a very full vessel). Minimum daily driving distance for avoiding evaporative losses will drop considerably if the vehicle is parked with the vessel at a lower level of fill.

In addition to conducting the first (to the authors' knowledge) full-scale para-ortho hydrogen conversion experiments, we also developed and tested a para-ortho conversion model. This model is derived from ortho-para conversion experiments in a small vessel (2 cm^3) [4] and solves a set of differential equations that determine para-ortho composition as a function of density, temperature, and initial composition. After appropriate tuning, the model performed well for the full-scale vessel (Figure 3) accurately predicting para-ortho composition during the experiment. Further experiments are planned to validate the model under varying densities, with the final goal of determining how to best design cryogenic pressure vessels that take advantage of para-ortho conversion for considerable increases in thermal endurance.

In addition to the para-ortho experimental and modeling activities, we also completed outgassing experiments from fiber-wound pressure vessels. In these experiments, we tested the outgassing behavior of composite pressure vessels by storing them inside a steel vacuum chamber at specified temperatures (20, 60 and 80°C). We tested 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 results can be summarized as follows:

1. Temperature is the most important factor in determining outgassing.
2. Vacuum quality remains high if the vessel remains cold (below 250 K).
3. Pressure cycling plays a relatively minor role in outgassing.
4. Vacuum curing did little to reduce outgassing and it is most likely not worth the effort. UV coating considerably increased outgassing and is therefore not recommended for cryogenic pressure vessels.
5. Chemical composition reveals a series of ~10 hydrocarbons that are produced in all experiments. The main species produced are n-heptanone, acetic acid butyl ester, and acetone – all oxygenated hydrocarbons most likely derived from the epoxy used in the tank.

Detailed composition and outgassing amounts are now being used for selecting appropriate getters that may preserve vacuum during long periods of operation.

Conclusions and Future Directions

- Demonstrated 1-month cryogenic vessel dormancy while extracting only 2.5 kg H_2.

- Para-ortho conversion proved synergistic with cryogenic pressure vessel operation, extending vessel dormancy by approximately 1 week by absorbing heat during endothermic conversion.
- Developed and tested a kinetic conversion model of para-ortho conversion.
- Completed outgassing experiments that characterized the effect of temperature, surface treatment, and pressure cycles. Outgassing composition was also determined and is being used to find appropriate getters for long-term vacuum stability.

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

3. Hydrogen-Fueled Carbon-Free Transportation, Salvador Aceves, Invited Presentation, Engineering Solutions for Sustainability: Materials and Resources, Lausanne, Switzerland, July 2009.

4. Hydrogen Storage in Cryogenic Capable Pressure Vessels, Salvador Aceves, Invited Presentation, Spanish National Hydrogen Research Center, Puerto Llano, Spain, March 2010.

5. Hydrogen Storage in Cryogenic Capable Pressure Vessels, Salvador Aceves, Invited Presentation, International Conference on Hydrogen Production and Storage, Istanbul, Turkey, June 2010.

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