IV.G.2 Lifecycle Verification of Polymeric Storage Liners

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Projected End Date: Project continuation and direction determined annually by DOE

Objectives

Perform durability qualification measurements on specimens of Type IV storage tank liners (polymers) at the nominal working pressure using thermal cycling commensurate with the design lifetime, followed by permeation measurements to determine if the steady-state leakage rate in the tank could potentially exceed the specification for hydrogen fuel cell passenger vehicles.

Technical Barriers

The project addresses the following technical barriers from the Hydrogen Storage section (3.2.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan [1]:

(D) Durability/Operability

Technical Targets

This project addresses the following technical targets for on-board hydrogen storage systems research and development:

- Cycle life variation, expressed as % of mean (min) at % confidence:
  - Fiscal Year (FY) 2010: 90/90; FY 2015: 99/90
- Environmental Health and Safety:
  - Permeation and leakage: meet or exceeds applicable standards.
  - Loss of usable H_2 (g/h/kg H_2 stored): FY 2010: 0.1; FY 2015: 0.05.

Accomplishments

- Completed 3,000 temperature cycles on a specimen of Lincoln Composites Type IV tank liner (high-density polyethylene, HDPE) and performed periodic permeation measurements on liner specimen to assess temperature-cycling induced changes in permeation coefficients.
- Verified that permeability coefficients have changed only slightly through 3,000 temperature cycles.
- Observed small systematic changes in activation energy E_A and constant P_0 in the liner during temperature cycling.
- Designed and assembled improved temperature-cycling apparatus. First temperature cycling results with new apparatus expected in 4th quarter of FY 2010.

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Introduction

Modern high-pressure hydrogen storage tanks use a polymeric liner as a permeation barrier to hydrogen, typically HDPE. Storage tank liners can, however, be stressed by cyclical excursions between temperature extremes, and the cumulative effects of repeated stress could harm the tank's durability. Ultra-high environmental temperatures can promote large hydrogen permeation rates and hydrogen saturation in the liner material. Ultra-low environmental temperatures can severely stress liner materials and possibly induce microcracking. In addition, increasing the pressure of gas in such a tank during filling necessarily raises the temperature of the gas and therefore the enclosing tank. Over the course of many fill cycles during the lifetime of the tank this might affect the permeability characteristics of the liner. Failure modes for the liner's performance based on the interaction of high pressure and extreme temperature cycling–might be possible. Hydrogen leakage through a liner microcracked by extreme temperature cycling could accelerate under sustained high temperature and pressure, or hydrogen saturation of the reinforcement layers external to the liner could put backpressure on the liner as the tank pressure decreases during vehicle operation, thereby causing the liner to separate from the reinforcement layers. Minimum temperatures during winter months in northern states may reach -40°C, and maximum temperatures after filling during summer months may reach 125°C. Thus, the purpose of this project is to cycle typical tank liner materials between these temperature extremes to determine whether such a degradation in properties occurs, and, if so, its extent.

Approach

Hydrogen permeation verification measurements for storage tank liner materials are being carried out using ORNL's internally heated high-pressure permeation test vessel (IHPV). The IHPV was previously used in the Hydrogen Delivery sub-program to measure real-time hydrogen permeation in low-carbon steels and polymer materials *at constant temperatures*. Materials properties such as the temperature- and pressure-dependent hydrogen solubilities, diffusion coefficients and permeation coefficients are extracted from measurements of real-time hydrogen flux through steels and polymers. In the previous project year we modified the IHPV to enable rapid temperature cycling in polymer specimens.

We are using the relevant portion of the test protocol specified in SAE J2579 to guide our performance of durability test cycling measurements of high-pressure polymeric tank liners [2]. The J2579 test protocol for compressed hydrogen storage systems prescribes long-term thermal cycling at high pressures of hydrogen. The requirement is to subject tank liner specimens to 5,500 thermal cycles over the temperature range -30 to 85°C at hydrogen pressurizations of 43 MPa (6,250 psia) and then 86 MPa (12,500 psia). Testing at 43 and 86 MPa, with cycling between -30 and 85°C, requires an automated temperature control strategy. To replicate the rapid temperature rise in the tank liner during fill cycles (approximately 100°C rise in 3 minutes) we decoupled the cooling and heating control systems in the IHPV. A low-temperature chiller with low-temperature refrigerant circulating to and from a sealed reservoir cools the IHPV's exterior containment vessel to approximately -40°C. A resistive heater situated in the permeation cell is used to ramp the specimen temperature from -30°C to 85°C. A heater controller controls the thermal cycling of the polymer specimen in the cell by applying and removing power to the heater. Process control software that was developed for the temperature controlled permeation measurements in steels and polymers was modified to provide automated, unattended operation and internet access so the tests can be remotely monitored and controlled. A complete heating and cooling cycle requires 33.3 minutes (see temperature cycle profile in Figure 1), and approximately 127 days are required to perform 5,500 temperature cycles.

The verification measurements occur at regular intervals during the 5,500 temperature cycles. The hydrogen flux is to be measured at three temperatures (-30, 25 and 85°C) at each interval, if practicable. The first measurements occur after the completion of 250, 500, 750, 1,000, 1,250 and 1500 cycles. The remaining measurements occur at 500 cycle intervals until 5,500 temperature cycles have been reached. A second verification test on a fresh tank liner specimen will be carried out at 86 kPa following the same protocol.

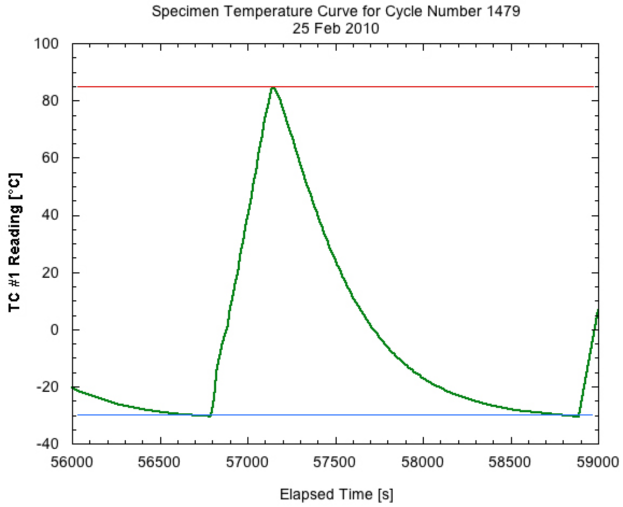

FIGURE 1. Each 33.3-minute-long temperature cycle consists of a 5.7-minute-long heating interval followed by a 27.6-minute-long cooling interval. The heating rate was selected to provide a 20°C per minute temperature rise similar to what might occur in a storage tank liner during filling.

Results

Permeation measurements on the specimen of Lincoln Composites Type IV tank liner (HDPE) indicate that permeability coefficients P are relatively unchanged through 3,000 temperature cycles (see Figure 2). Small systematic changes in activation energy E_A and constant P_0 in Arrhenius relationship $P = P_0 \exp(-E_A/kT)$ as a function of the number of temperature cycles were observed, which could indicate microstructural changes are occuring in the polymer during temperature cycling (see Figures 3 and 4). Assembled and tested an improved temperature-cycling apparatus that will enable us to complete cycling measurements faster. First results temperature cycling results using new apparatus expected in 4th quarter of FY 2010.

Conclusions and Future Directions

Through 3,000 temperature cycles we have observed no statistically significant departures from the Arrhenius relationship between permeation coefficient and temperature that would indicate the occurrence of microcracking or changes in glass transition temperature in the Lincoln Composites HDPE liner specimen.

FY 2010

- Complete initial lifecycle verification measurements and report durability assessments of Lincoln Composites specimen through 5,500 cycles.

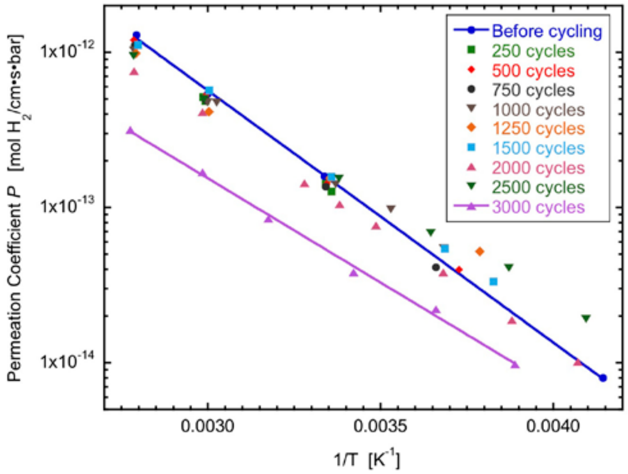

FIGURE 2. Permeation coefficients *P* for hydrogen in Lincoln Composites tank liner specimen, measured at 430 bar and performed at 250- and 500-cycle intervals.

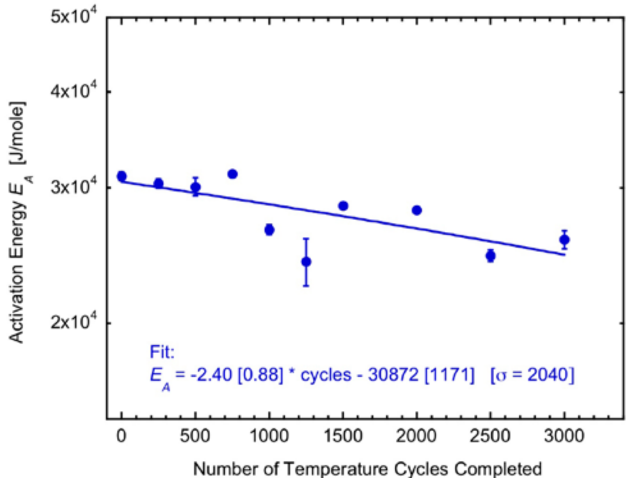

FIGURE 3. Analysis of changes in activation energy E_A. Measurement results through 3,000 cycles indicate a statistically significant decrease in E_A is occurring, which could indicate that the polymer is undergoing small changes in its microstructure.

- Begin temperature cycling of Lincoln Composites specimen at 860 bar (12,500 psia).
- Begin temperature cycling of Quantum Technologies specimen at 430 bar (6,250 psia).

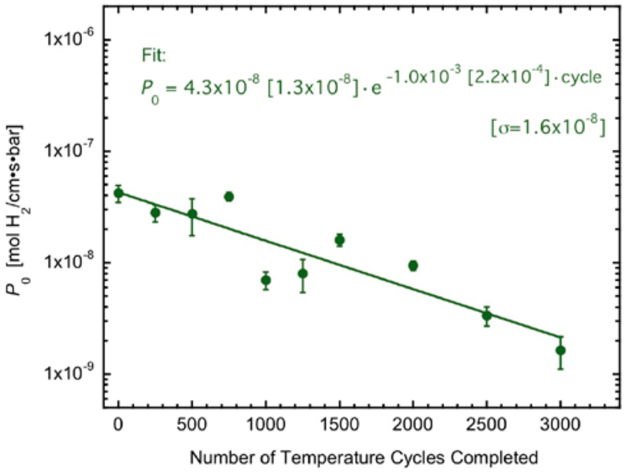

FIGURE 4. Analysis of changes in pre-exponential factor P_0. Measurement results through 3,000 cycles indicate a statistically significant decrease in P_0 is occurring, which could also indicate that the polymer is undergoing small changes in its microstructure.

FY 2011

- Complete all lifecycle verification measurements and report assessments for Lincoln Composites and Quantum Technologies.
- Complete temperature cycle testing of an alternative liner material (PA-6, PA-11, PPS) and compare to HDPE liner materials.
- Measure hydrogen solubility in tank liner materials.

FY 2010 Publications/Presentations

1. 2010 DOE Hydrogen Program Annual Merit Review – Washington, D.C. – June 9, 2010. Presentation ST053.

References

1. HFCIT MYRDD Plan, Table 3.3.2, “Technical Targets: On-Board Hydrogen Storage Systems,” October 2007.

2. SAE J2579, “Technical Information Report for Fuel Cell and Other Hydrogen Vehicles (January 2009),” Fuel Cell Standards Committee, SAE International.