

IV.F.2 Lifecycle Verification of Polymeric Storage Liners

Barton Smith (Primary Contact) and
Lawrence M. Anovitz
Oak Ridge National Laboratory (ORNL)
P. O. Box 2008
Oak Ridge, TN 37831
Phone: (865) 574-2196
E-mail: smithdb@ornl.gov

DOE Manager
Ned Stetson
Phone: (202) 586-9995
E-mail: Ned.Stetson@ee.doe.gov

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FY 2011 Accomplishments

- Permeation measurements on specimen of Lincoln Composites Type IV high-density polyethylene (HDPE) tank liner show progressive changes in the slope and pre-exponential scaling factor of the permeation curves that occur as the specimen undergoes simulated lifecycle temperature variations.
- Characterization of liner specimen using neutron scattering and electron microscopy (small angle neutron scattering [SANS], ultra small angle neutron scattering [USANS], scanning electron microscopy/back scattered electron mode [SEM/BSE]) show significant structural changes were induced by temperature cycling or hydrogen exposure or both.
- Using permeation coefficient data, the Lincoln Composites HDPE liner in a 350-bar tank can be expected to maintain an H₂ leak rate that meets applicable leakage standards throughout its lifecycle history.



Fiscal Year (FY) 2011 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

This 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:

(D) Durability/Operability

Technical Targets

This project addresses the following technical targets for on-board hydrogen storage systems research and development [1]:

- Cycle life variation, expressed as percent of mean (min) at percent confidence:
 - FY 2010: 90/90; FY 2015: 99/90
- Environmental Health and Safety:
 - Permeation and leakage: meets or exceeds applicable standards.
 - Loss of usable H₂ (g/h/kg H₂ stored): FY 2010: 0.1; FY 2015: 0.05.

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 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 Society of Automotive Engineers standard J2579 [2] to guide our performance of durability test cycling measurements of high-pressure polymeric tank liners. 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 -40 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 -40 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, 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 measured at multiple temperatures in the range -30 to 85°C at each interval. The first measurements occur after the completion of 250, 500, 750, 1,000, 1,250 and 1,500 cycles. The remaining measurements occur at 500 cycle intervals until 5,500 temperature cycles have been reached.

Results

We completed permeation measurements on a Lincoln Composites Type IV tank liner specimen (HDPE). The permeation coefficients P have the temperature dependence of an activated process, $P = P_0 \exp(-E_A/kT)$, where the pre-exponential scaling factor P_0 and the activation energy E_A are presumed to be independent of temperature. We performed permeation measurements before cycling and after 250, 500, 750, 1,000, 1,250, 1,500, 2,000, 2,500, 3,000, 3,500 and 4,000 cycles. Semi-log plots of P versus $1/T$ are shown in Figure 1. Lines have been drawn through measurements at 0, 1,000, 2,000, 3,000 and 4,000 cycles to illustrate the systematic changes in E_A and P_0 . The decreasing slope and shift in scaling indicates that some physical change occurred in the polymer during cycling, but we did not observe a statistically significant departure from the Arrhenius relationship, which would indicate that microcracking or changes in glass transition temperature had occurred in the polymer. Figures 2a and 2b illustrate the changes in E_A and P_0 , respectively. E_A and P_0 each decreased as the specimen was subjected to repeated temperature cycles. The -2.21 J/mole slope for E_A versus number of cycles was approximately five standard deviations from a slope of zero, and the 4.6×10^{-8} mol H₂/cm·s·bar slope for P_0 versus number of cycles was approximately 4 standard deviations from a slope of zero.

Following completion of the temperature cycling we used neutron scattering analysis (SANS and USANS) to look for structural changes on the order 1 nm to 30 μm in

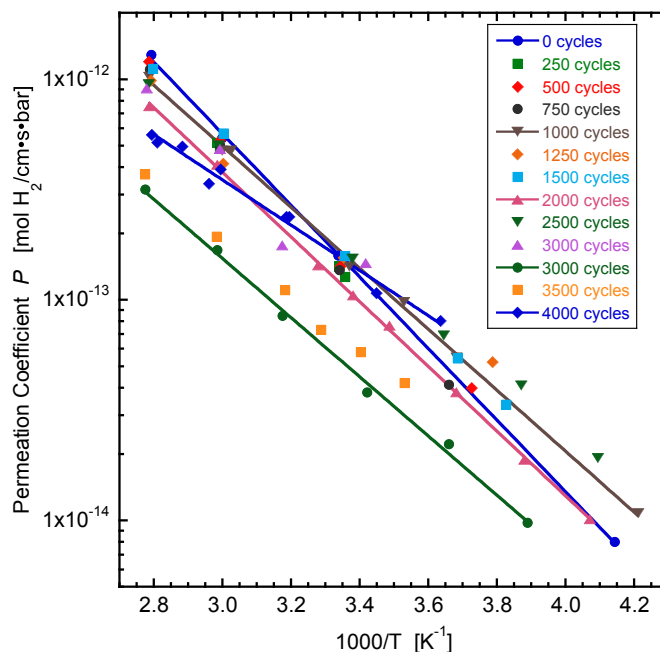


FIGURE 1. Permeation Coefficients P for Hydrogen in Polymer Specimen, Measured at 430 bar

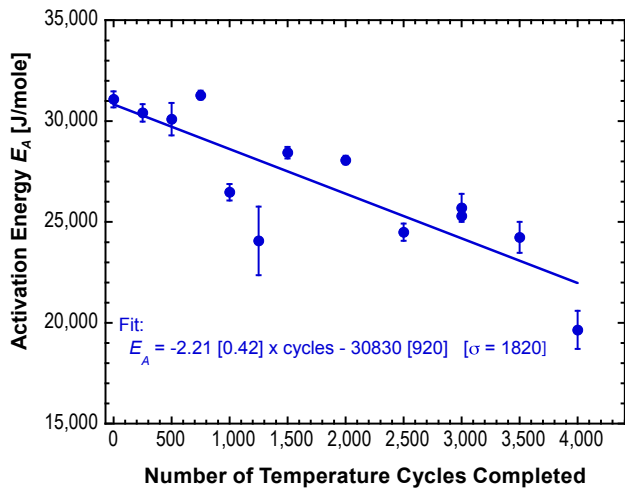


FIGURE 2a. The activation energy E_A of the HDPE specimen decreased through 4,000 temperature cycles, indicating that the polymer experienced small changes in its microstructure.

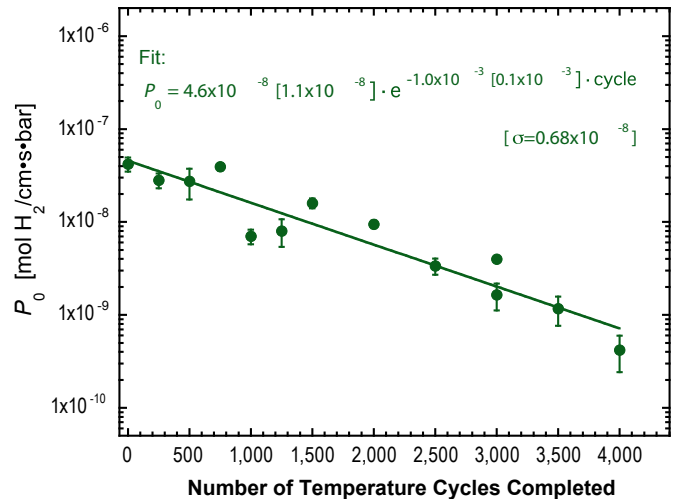


FIGURE 2b. The pre-exponential scaling factor P_0 also decreased through 4,000 temperature cycles, further evidencing small changes in polymer microstructure.

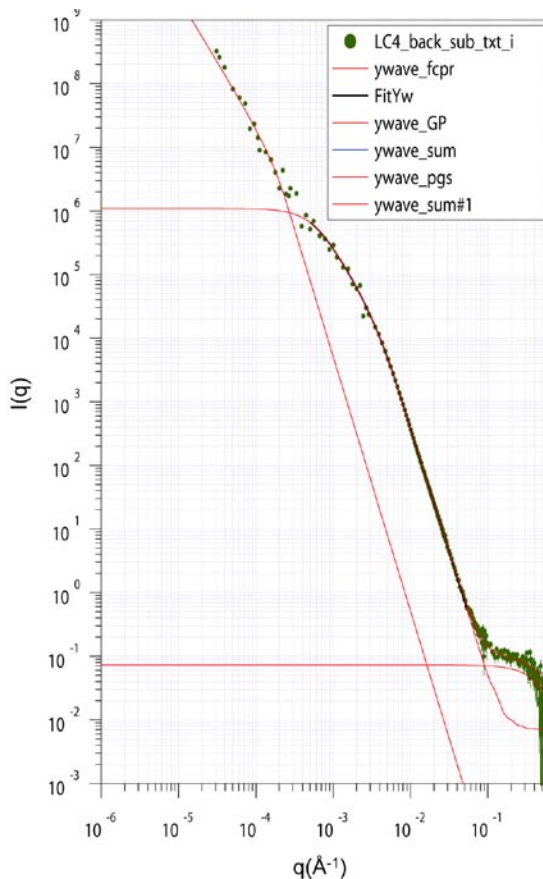
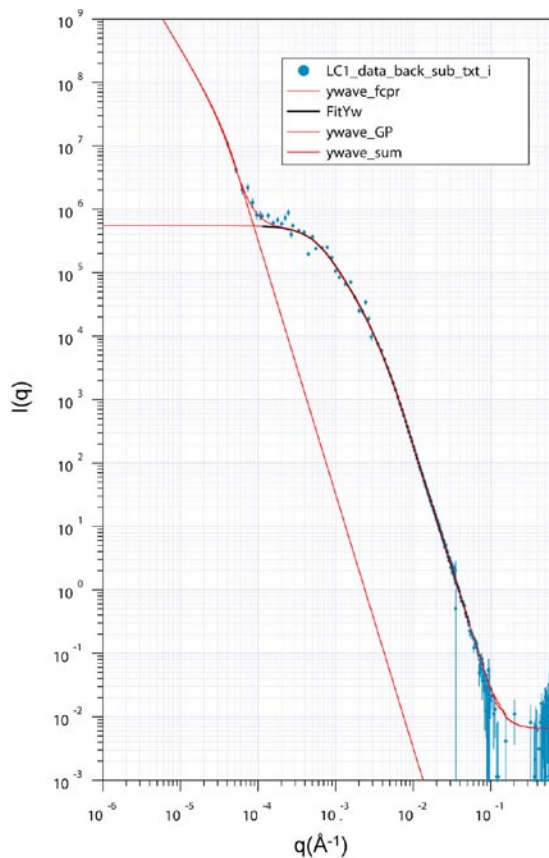


FIGURE 3. Neutron scattering data for Lincoln Composites tank liner specimens, before temperature cycling (left) and after 4,000 temperature cycles (right).

the polymer. We analyzed four HDPE tank liner specimens: 1) before temperature cycling, 2) after a few temperature cycles, 3) after 600 cycles, and 4) after 4,000 cycles. The

scattering data for the before-cycling and after-4,000-cycles specimens is shown in Figure 3. The scattering data was analyzed as follows [3]: the low- q section was fit using a

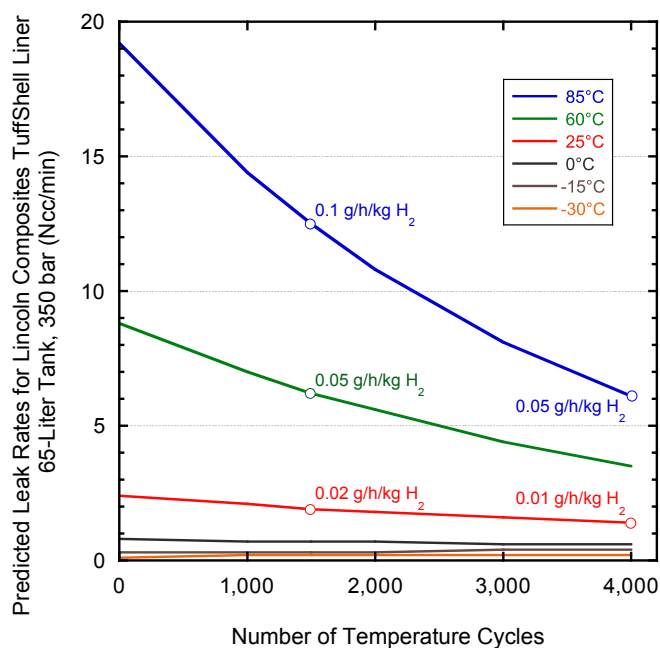


FIGURE 4. Predicted leak rate values for HDPE tank liner as a function of liner temperature and number of temperature cycles.

Guinier-Porod model, the central section was fit using a flexible cylinder with a polydispersed radius model (designed for treatment of polymers, see reference [3]), and the high- q section was fit to a polydispersed (Gaussian) sphere model. In the low- q section, the fit changes slope from -4 (Porod region) to -2 (Guinier region corresponding to plates or laminae). The transition from Porod to Guinier occurs with increasing number of temperature cycles. The presence of low- q scattering in the USANS data indicates the presence of large-scale ($>30 \mu\text{m}$) scattering features that change significantly with long-term exposure to hydrogen or increasing number of temperature cycles or both. Similarly, the presence of high- q scattering appears only after temperature cycling.

Conclusions and Future Directions

We used the values of P_0 and E_A obtained from measurements during the temperature cycling to model the behavior of the permeation coefficients P as a function of T and the number of cycles. This modeling shows that at all temperatures the values of the hydrogen permeation coefficients decrease with cycle count, thus implying that the hydrogen leak rate of the tank liner should decrease with the number of temperature cycles.

To obtain a quantitative prediction of the leak rate for an actual tank liner, we used the dimensional specifications for a Lincoln Composites TUFFSHELL[®] hydrogen fuel tank rated for 350 bar service and with a volumetric capacity of 65.3 liters (water volume). The HDPE tank liner is cylindrical with nearly hemispherical end caps, and the

liner wall thickness is about 7 mm. We obtained a family of leak rate curves using the cycle-dependent permeation coefficients in an analytical expression for the tank leak rate. These curves are shown in Figure 4. In this analysis the tank leak rate remains below 75 normal cubic centimeters per minute (Ncc/min) at all temperatures for the duration of 4,000 temperature cycles. Furthermore, for all liner temperatures less than about 60°C, the loss of useable hydrogen remains below 0.05 g/h/kg H₂ for a fully filled tank, i.e., at a 350 bar pressurization.

For the next project year we have crafted a research plan that addresses the findings made in the present year. A second verification test on a fresh tank liner specimen is being carried out at 86 kPa following the same protocol. We will again perform some post-cycling analysis of the specimen to determine the type of structural changes that take place in the polymers. Differential scanning calorimetry measurements, SEM/BSE microscopy, transmission electron microscopy (using microtome sectioning), and perhaps some additional SANS/USANS (neutron scattering) will be used. This analysis will allow us to determine the implications of the structural changes during the lifecycle of the tank liner. Furthermore, we will expand the investigation beyond tests of the existing tank liner materials to future materials, as several tank manufacturers have recently introduced liners made from new less expensive and potentially higher performance (lower permeation) materials. Also under consideration is the need to adequately address the durability of the liner when it is bonded to the tank reinforcement. To this end we are developing a test plan for temperature cycling sectioned specimens from tank structures while they are differentially pressurized with hydrogen (high pressure on the liner side, atmospheric pressure on the outside of the reinforcement). Obtaining a better understanding the adhesion and interaction between the liner and composite matrix layer over the lifetime of the tank would be very valuable for a complete assessment of the lifecycle durability of the Type 4 storage tanks. This measurement will require a significant amount of collaboration with tank manufacturers to obtain their advisement on the testing procedure and their provision of tank sections.

FY 2011 Publications/Presentations

1. 2011 DOE Hydrogen Program Annual Merit Review – Arlington, Virginia – May 9, 2011, poster 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.
3. B. Hammouda, The SANS Toolbox, NIST Center for Neutron Research, available at <http://tinyurl.com/SANStoolbox>