

## IV.F.1 Lifecycle Verification of Polymeric Storage Liners

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Project Start Date: June 2008  
Project End Date: September 2013

### Technical Targets

This project addresses the following technical targets for onboard hydrogen storage systems R&D [1]:

- Operational cycle life (1/4 tank to full):
  - FY 2017: 1,500 cycles; ultimate: 1,500 cycles
- Environmental health and safety:
  - Permeation and leakage: meets or exceeds applicable standards
  - Loss of useable H<sub>2</sub>: FY 2017: 0.05 g/h/kg H<sub>2</sub>; ultimate: 0.05 g/h/kg H<sub>2</sub>

### FY 2013 Accomplishments

- Temperature cycling and permeation measurements are in progress for four tank liner polymers.
- Demonstrated that permeation in polymers is not linearly dependent on pressure and is influenced by the compressibility of the polymers.



### Overall 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.

### Fiscal Year (FY) 2013 Objectives

Continue durability qualification measurements on specimens of novel polymers proposed for use as storage tank liners and hydrogen barrier materials.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan, section 3.3.5 - Hydrogen Storage:

- (D) Durability/Operability (of on-board storage systems – lifetime of at least 1,500 cycles)
- (G) Materials of Construction (vessel containment that is resistant to hydrogen permeation)
- (L) Lack of Tank Performance Data and Understanding of Failure Mechanisms

## INTRODUCTION

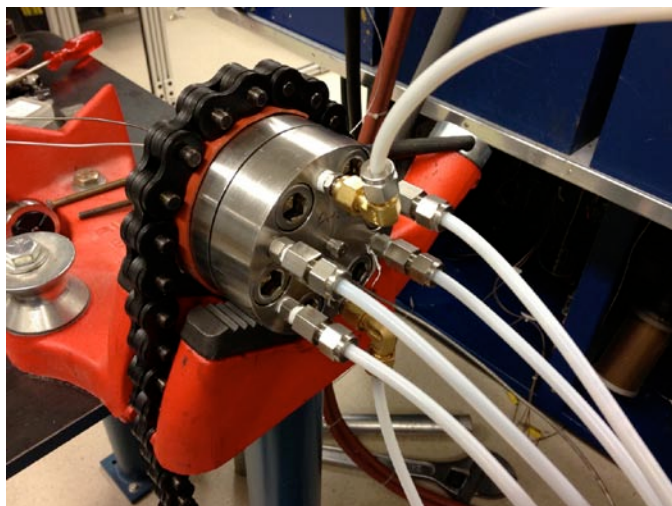
Type IV high-pressure hydrogen storage tanks employ polymeric liners as permeation barriers to hydrogen. The tank liners can be stressed by cyclical excursions between temperature extremes, and the cumulative effects of repeated cyclical stress could harm the tank's durability, i.e., its ability to maintain an acceptably low leakage rate. Furthermore, ultra-high environmental temperatures can promote large hydrogen permeation rates and hydrogen saturation in the liner material, while ultra-low environmental temperatures can severely reduce the elasticity of liner materials and induce microcracking. The rapid pressurization of hydrogen in the tank during filling operations raises the temperature of the gas, the liner, and the carbon fiber matrix reinforcement shell. Minimum temperatures during winter months in northern latitudes may reach -40°C, and maximum temperatures after filling during summer months may reach 125°C.

The hundreds or thousands of thermal cycles that occur during fill cycles over the operational lifetime of the tank could thus affect the permeability characteristics of the liner. Failure modes for the liner's performance—based on the interaction of high pressure and extreme temperature—must be considered and investigated. 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. The objective of this project is to evaluate the durability of polymer tank liners by cycling tank liner specimens between temperature extremes while monitoring the hydrogen permeabilities. Significant changes in permeability are expected to be prime indicators of whether such degradation occurs.

## APPROACH

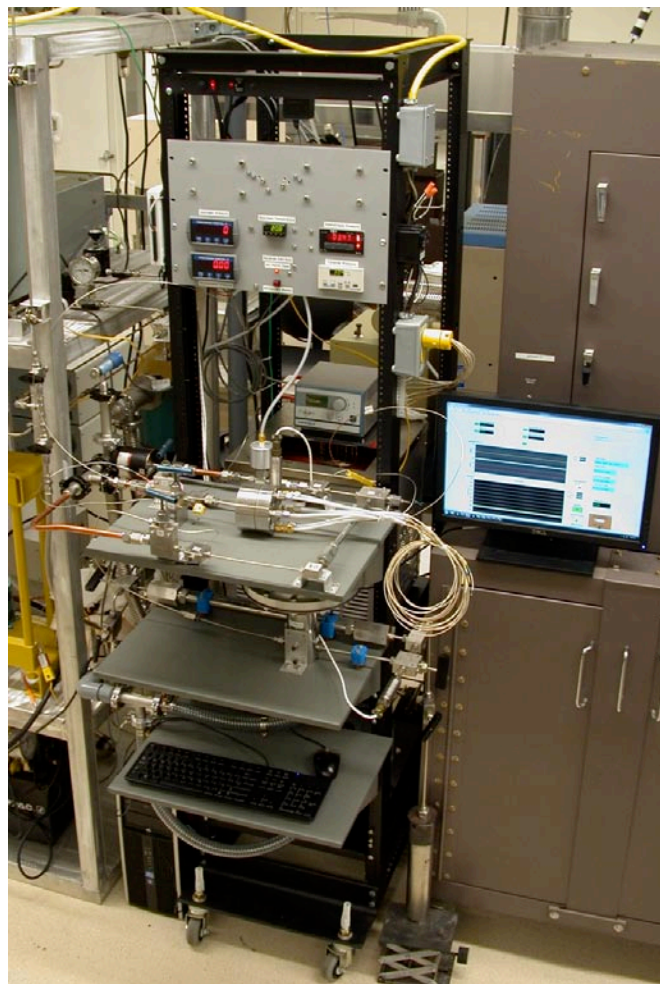
Hydrogen permeation verification measurements for storage tank liner materials are being carried out in a high-pressure permeation test vessel designed to measure hydrogen permeation in polymer materials at select intervals in the temperature cycling process. The pressure vessel (see Figure 1) is comprised of two stainless steel Type 316 flanges that are bolted together in a configuration designed to withstand working pressures up to 860 bar without leaking. The polymer specimen being evaluated is sealed by compression in an annular ring between pressure vessel flanges (10 cm<sup>2</sup> sealing area). The vessel is immersed in a chilled bath (reservoir) of ethylene glycol and distilled water at a temperature that varies from -30 to -50°C during the thermal cycle. The reservoir is the low-temperature heat sink for the temperature-cycling process and its temperature fluctuates as it absorbs heat from the vessel during the cooling interval. The vessel is internally heated with six 300-W (1,800-W total) cartridge heaters to accomplish the heating portion of the temperature cycle. The temperature cycling/permeation measurement apparatus is shown in Figure 2. The specimen is continuously differentially



**FIGURE 1.** Assembled pressure vessel showing water-tight electrical connections to cartridge heaters and bolt configuration.

pressurized during temperature cycling, with the high-pressure hydrogen on one side of the specimen and a sub-atmospheric pressure maintained on other side. The permeation measurements are performed with the specimen in the pressure vessel by calculating a gas transfer rate from the pressure rise rate in the fixed downstream volume.

The polymer specimens are prepared from liners provided by multiple manufacturers of Type IV storage tanks. The tank liners are too thick to use for lab-timeframe permeation measurements and are typically curvilinear in shape, so we prepare specimens by lathe-turning small sections of the liner to thicknesses of approximately 1 mm. The turning is done on the exterior (lower pressure) side of the liner. The thinned liner is then punched into a 5.7-cm diameter disc. The disc is then wet sanded with a succession of progressively finer grits through International Organization for Standardization P1200. The specimen disc is oriented in the pressure vessel so the liner interior (pristine surface) is exposed to the high-pressure hydrogen. A 4.5-cm



**FIGURE 2.** Temperature cycling and high-pressure permeation measurement apparatus.

diameter circular area is directly exposed to high-pressure  $H_2$ , and this is the area over which the gas transfer rate is determined.

Our temperature cycling protocol and methodology is based on the tank liner durability test protocol specified in SAE International J2579 [2]. The J2579 test protocol for compressed hydrogen storage systems prescribes long-term thermal cycling at the maximum allowable pressure of the storage tanks. We subject the tank liner specimens to 1,500 thermal cycles over the temperature range 40 to 85°C at constant hydrogen pressurizations of 350 bar (5,000 psia) and 700 bar (10,000 psia). Testing at these pressures, with cycling between 40 and 85°C, requires an automated temperature control strategy. Our heating rate replicates the rapid temperature rise in the tank liner during fill cycles (heating rate of approximately 20°C per minute). After heating, the low-temperature reservoir removes the heat from the pressure vessel until it reaches the low end of approximately 40°C. Process control software provides automated and unattended operation, and the test progress can be remotely monitored and controlled via the Web. A complete heating and cooling cycle requires approximately 20 minutes, and the completion of 1,500 thermal cycles with permeation measurements, at a single pressure, requires approximately one month to complete.

The permeation measurements are performed at regular intervals during the 1,500 temperature cycles. The permeation coefficients are measured at four temperatures (-40, -10, 30, and 85°C) at intervals of 0, 750, and 1,500 cycles. The coefficients are measured at the temperature extremes (40 and 85°C) at intervals of 250, 500, 1,000, and 1,250 cycles.

Our progress this year was slowed by numerous unexpected difficulties related to below-expected performance of components in the temperature cycling apparatus. The cartridge heaters produced less heat than specified by the manufacturer and it was necessary to modify the heating control and algorithm through extensive trials to compensate for the lower-than-expected heat output. We also found that it was necessary to cool the reservoir bath with a secondary, ultra-low-temperature recirculating bath to increase heat capacity and cooling power in the reservoir. We evaluated several candidate heat transfer fluids for the ultra-low temperature bath (ethylene glycol-water mixtures being far too viscous at temperatures below -40°C) and found that a specialty blend of a terpene hydrocarbon met our requirements for low viscosity, low freezing temperature, and non-flammable characteristics. The result was a decrease in the cycle time from approximately one hour to about 25 minutes. Additionally, we discovered that a significant amount of trial and error is required to perfect the procedure for sealing each type of polymer. Differences between thermal expansion of the polymer and the stainless steel vessel introduce numerous opportunities for gas leaks. The

variations in polymer hardness, modulus, and surface texture require a systematic approach to achieving a durable seal.

## RESULTS

The liner materials available for evaluation during FY 2013 are:

- Extrusion-molded high-density polyethylene (HDPE)
- Injection-molded HDPE
- Rotationally-molded HDPE
- Extrusion-molded polyamide-6 (PA-6)
- Blow-molded polyethylene terephthalate (PET)
- Extrusion-molded PA-6, with carbon black additive
- Injection-molded HDPE with nano-clay additive

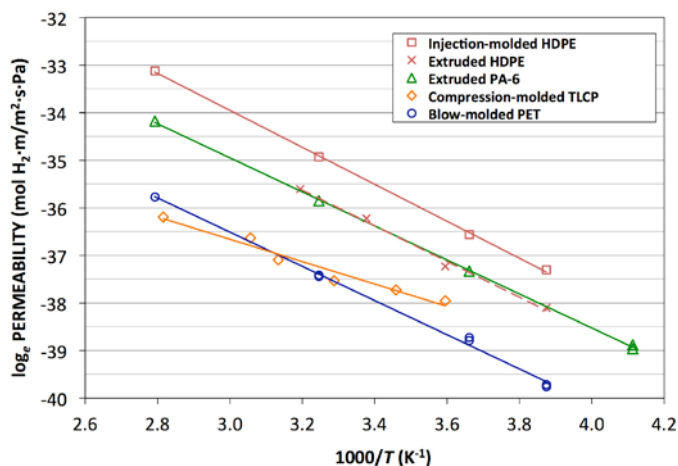
We completed a durability characterization of liner Material 1, extruded HDPE, in a previous project year, and results from this characterization are available in previous annual progress reports. The four highest-priority measurements are for liner Materials 2, 3, 4, and 6 because they are currently being used in Type IV tanks. Polymers 5 and 7 are being considered for use as liner materials.

Results on our evaluations of Materials 2, 3, 4, and 6 were not ready for publication at the time of this progress report. We intend to publish the results of these evaluations in the archival literature so they will be available to a wide audience.

In addition to the temperature cycling measurements we conducted an extensive series of hydrogen diffusion and permeation measurements on tank liner polymers to characterize the relative hydrogen-barrier capabilities of the polymers and the pressure-dependence of the permeability coefficients. Presentation of the entirety of the results of these measurements is beyond the scope of this report and they will be published in the near future in the archival literature. In this report we present highlights of the permeability measurements that we expect will be of use to researchers and technologists who are investigating the use of polymeric materials in hydrogen storage and delivery systems.

Figure 3 shows the temperature dependence of the hydrogen permeability coefficients for four polymers being evaluated for durability in the temperature cycling experiments, as well as the coefficients for a thermotropic liquid crystal polymer (TLCP). TLCPs have been proposed for use as a hydrogen barrier material due to their lower permeabilities. The TLCP evaluated was compression-molded DuPont HX 3000. The other polymers were proprietary formulations provided by storage tank manufacturers. The measurements shown were made at temperatures ranging from 30 to 85°C at a differential pressurization of approximately 135 bar (2,000 psia) with the





**FIGURE 3.** Temperature dependence of the hydrogen permeability for four tank liner polymer specimens and an additional specimen of TLCP. All measurements were made using a differential hydrogen pressure of 134 bar (13,400 kPa) with the exception of the roto-molded HDPE, which was measured at 345 bar (34,500 kPa).

exception of the rotationally-molded (roto-molded) HDPE, which was done at 345 bar (5,000 psia). Measurements of the permeability coefficient values were extremely reproducible for HDPE, PA-6 and PET polymers. Measurements of the TLCP permeability coefficients were much less reproducible, and reliable measurements could not be made at temperatures below 10°C. It was difficult to prepare specimens from the TLCP due to its brittleness and tendency to become friable at cut edges, and TLCP specimens exhibited a substantial amount of creep and deformation following pressurization at temperatures substantially above room temperature.

There were no statistically significant differences between the permeabilities of the HDPE produced by extrusion molding, rotational molding, and injection molding manufacturing processes. The permeability of PET was about an order of magnitude less than that of HDPE. The permeability of TLCP is comparable to that of blow-molded PET.

The temperature dependence of the permeability coefficients for a particular polymer at a specified hydrogen pressure can be modeled very accurately by the Arrhenius equation for an activated process, i.e.,

$$P = P_0 \exp(E_A/RT) \quad \text{Eq. 1}$$

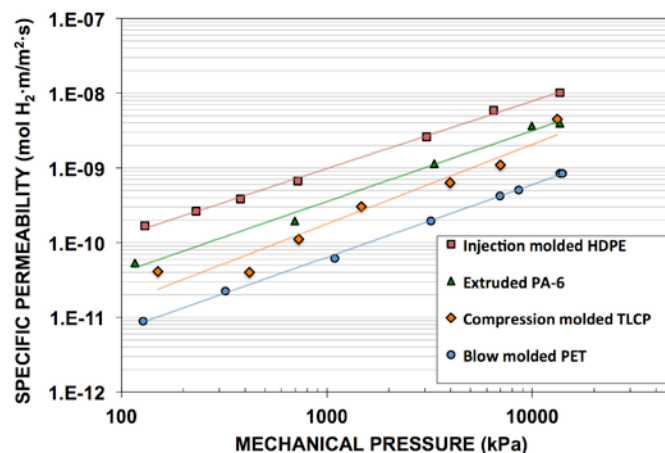
where  $E_A$  is the activation energy for permeation in J/mole,  $R$  is the gas constant,  $T$  is the temperature in Kelvin, and  $P_0$  is a pre-exponential scaling factor in mol H<sub>2</sub>·m/m<sup>2</sup>·s. Table 1 lists the  $E_A$  and  $P_0$  coefficients determined by a least-squares fit to the permeation measurements. The TLCP has activation energy and pre-exponential factor that are unusually low and high, respectively, when compared to the other polymers.

**TABLE 1.** Activation energies and pre-exponential scaling factors for calculating hydrogen permeability coefficients for select polymers using Eq. 1. The standard error for the  $E_A$  value is shown in square brackets.

| Polymer                 | Pressure bar | $E_A$ kJ/mol H <sub>2</sub> | $P_0$ mol H <sub>2</sub> ·m/m <sup>2</sup> ·s |
|-------------------------|--------------|-----------------------------|---|
| Injection-molded HDPE   | 134          | 32.3 [0.5]                  | $2.08 \times 10^{-10}$                        |
| Extrusion-molded HDPE   | 104          | 31.2 [1.7]                  | $5.51 \times 10^{-11}$                        |
| Rotomolded HDPE         | 345          | 32.1 [0.8]                  | $2.58 \times 10^{-10}$                        |
| Extrusion-molded PA-6   | 137          | 30.0 [0.2]                  | $3.38 \times 10^{-11}$                        |
| Compression-molded TLCP | 136          | 19.5 [2.0]                  | $7.09 \times 10^{-13}$                        |
| Blow-molded PET         | 137          | 29.9 [0.9]                  | $6.71 \times 10^{-12}$                        |

Hydrogen transport in polymers differs from that in metals in one important aspect: it is not necessary for the hydrogen molecule to dissociate prior to dissolution in polymers. Sieverts' Law, which predicts that the solubility of hydrogen gas in metals will be proportional to the square root of the partial pressure of the gas in thermodynamic equilibrium, is not applicable to polymers. Thus the concentration of hydrogen dissolved in a polymer should be linearly proportional to applied pressure rather than proportional to the square root of the applied pressure. The permeability is directly proportional to the solubility, and thus the permeability of hydrogen in polymers should likewise be linearly proportional to the pressure.

Figure 4 shows the dependence of the specific permeabilities  $P_{sp}$  of several tank liner polymers on hydrogen pressure (mechanical pressure, which translates into an applied force to the polymer). We observed slight deviations from a linear dependence of  $P_{sp}$  on pressures in the range 100 to 14,000 kPa. The amount of deviation roughly follows the Young's modulus of the polymer—the larger the modulus, the more compressible the polymer, and the less linear the dependence of  $P_{sp}$  on pressure. This deviation



**FIGURE 4.** Pressure dependencies of the specific permeabilities of four polymers.

from linear pressure dependence is evidenced by the data shown in Table 4. The slope of the  $P_{sp}$  versus pressure curves increases as the modulus  $E$  increases. It follows that the polymer is being elastically compressed by the hydrogen pressure, and the compression reduces the free volume in the polymer. Polymers with larger moduli are more resistant to compression and therefore have  $P_{sp}$  values that are more linear with pressure.

**TABLE 4.** Dependence of specific permeability of polymers on hydrogen pressure, correlated to approximate values of their moduli. The standard error for each dependency is shown in square brackets.

| Polymer                 | Pressure dependence of $P_{sp}$<br>(mol H <sub>2</sub> ·m/m <sup>2</sup> ·s/kPa) | $E$<br>(MPa) |
|-------------------------|--|--------------|
| Injection-molded HDPE   | 0.89 [0.02]  | 1,000        |
| Extrusion-molded PA-6   | 0.95 [0.05]  | 2,400        |
| Blow-molded PET         | 0.95 [0.01]  | 3,100        |
| Compression-molded TLCP | 1.06 [0.11]  | >8,000       |

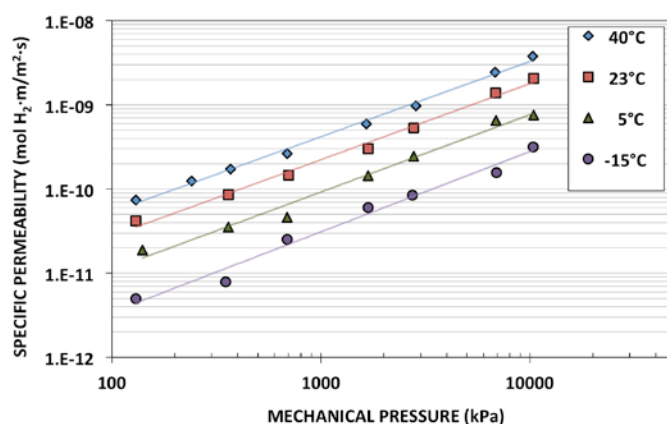
This compressibility effect is likewise evident in the case where the pressure dependence of  $P_{sp}$  for a single polymer is measured as a function of temperature, as shown in Figure 5. The modulus increases as the temperature decreases, making the polymer progressively less compressive and therefore having less free volume. The dependence of  $P_{sp}$  on pressure becomes more linear as the temperature decreases, as evidenced by the  $P_{sp}$  values

**TABLE 5.** Dependence of specific permeability on temperature for extrusion molded HDPE. The standard error for each dependency is shown in square brackets.

| Temperature<br>(°C) | Pressure dependence of $P_{sp}$<br>(mol H <sub>2</sub> ·m/m <sup>2</sup> ·s/kPa) |
|---------------------|--|
| 85                  | 0.89 [0.03]  |
| 23                  | 0.90 [0.04]  |
| 5                   | 0.92 [0.05]  |
| -15                 | 0.96 [0.06]  |

## CONCLUSIONS AND FUTURE DIRECTIONS

The measurements of hydrogen permeabilities for several polymers in current use as tank liners—or being proposed for future use for such applications—show that the polymers have permeabilities that differ by an order of magnitude or less. The activation energies measured over the temperature range 30 to 85°C were very closely grouped around 31 kJ/mol, the exception being the specimen of compression-molded TLCP which had an activation energy of 19.5 kJ/mol. All the polymers show promise as good hydrogen barrier materials, based on their permeability coefficient values. The TLCP exhibited a significant amount of pressure-induced creep when subjected to prolonged temperatures above room



**FIGURE 5.** Pressure dependencies of a specimen of extrusion-molded HDPE, measured at multiple temperatures.

temperature. Additional evaluation of the high-pressure stress behavior of TLCP is in order before it can be qualified as a realistic barrier material candidate.

Unforeseen delays brought about by instrumentation problems in the temperature cycling apparatus delayed completion of the lifecycle durability measurements. Our intent is to complete measurements on as many polymers as possible this year and to publish the test procedure along with the durability measurements early next year.

The use of disc specimens for the durability measurements is a useful screening method, but this methodology might not be sufficient for predicting the performance of polymer liners in actual systems. Liners in tank systems will be exposed to flexural and tensile conditions in addition to those brought about by thermal cycling, and interactions of the liner with the surrounding walls will add to the complexity of a real-world evaluation of the liner's durability.

A test methodology that incorporates an *in toto* temperature cycling evaluation of tank liner in contact with the composite reinforcement would:

- Provide a fuller understanding of how liners function when situated in proximity to the composite reinforcement.
- Address the issue of absorption of H<sub>2</sub> in the liner and the subsequent volumetric expansion of the liner or pressurization of the void between the liner and reinforcement layers, and how these conditions could pose a concern for delamination during rapid depressurization of the tank.
- Provide a direct measurement of tank liner leakage as a function of cycle life.

Additional future work, which is also beyond the scope of the current project, should address the impact of rapid depressurization on the liner and perform a number of

temperature cycling and permeation measurements using H<sub>2</sub> incorporating concentrations of likely contaminants.

### **FY 2013 PUBLICATIONS/PRESENTATIONS**

1. 2013 DOE Hydrogen Program Annual Merit Review – Crystal City, Virginia – May 15, 2013, oral presentation ST053.
2. Progress Update, “Lifecycle verification of polymer liners in storage tanks,” Hydrogen Storage Tech Team Meeting, USCAR, Southfield, Michigan, April 18, 2013.

### **REFERENCES**

1. Fuel Cell Technologies Program MYRDD Plan, Section 3.4 - Hydrogen Storage, September 2011 interim update.
2. SAE J2579, “Technical Information Report for Fuel Cell and Other Hydrogen Vehicles (January 2009),” Fuel Cell Standards Committee, SAE International.