IV.F.2 Lifecycle Verification of Polymeric Storage Tank Liners

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

Fiscal Year (FY) 2012 Objectives

- Continue temperature cycling and permeation measurements on tank liner polymers, and use permeation data to assess ability of tank liners to retain a steady-state hydrogen discharge rate that does not exceed 110% of the 75 normal cubic centimeters per minute (Ncc)/min permeation requirement of SAE International J2579 § 5.2.2.1.3
- Develop a method for temperature cycling on pressurized Type-4 storage tank sections to provide a lifecycle evaluation of the polymer liner when it is in contact with the composite matrix layer.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cells Technology Program Multi-Year Research, Development and Demonstration Plan [1]:

(D) Durability/Operability (of onboard storage systems – lifetime of at least 1,500 cycles)

(G) Materials of Construction (vessel containment that is resistant to hydrogen permeation)

(M) Lack of Tank Performance Data and Understanding of Failure Mechanisms

Technical barriers D and G are applicable to all storage approaches. Technical barrier M is specific to compressed gas systems.

Technical Targets

This project addresses the following technical targets for onboard hydrogen storage systems R&D [2]:

- 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_2 (g/h/kg H_2 stored): FY 2017: 0.05; Ultimate: 0.05

FY 2012 Accomplishments

- We observed that repetitive temperature cycling decreases H_2 permeability in specimens of extruded high-density polyethylene (HDPE) by increasing the size of the crystalline regions in the polymer.
- A new and improved temperature cycling and permeation measurement system is now online, providing temperature cycling between –40ºC and 85ºC, faster temperature cycles of ~20 minutes (40% shorter than cycling time in original apparatus), a maximum differential hydrogen pressure across specimen of ~900 bar (13,000 psia), and using less hydrogen and substantially less electrical power.

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Introduction

Modern high-pressure hydrogen storage tanks use a polymeric liner as a permeation barrier to hydrogen, typically HDPE or polyamide. Storage tank liners can 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 possibly induce microcracking. In addition, increasing the pressure of gas in such a tank during filling necessarily raises the temperature of the gas and the pressure-load-bearing carbon-fiber reinforced shell. Over the course of hundreds of fill cycles during the lifetime of the tank, these environmental stresses could affect the permeability characteristics of the liner and failure modes for the liner's performance–based on the interaction of high pressure and extreme temperature cycling–might be introduced. 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 well below 0°C, tank precooling before filling could reach -40°C, and maximum temperatures after filling during summer months may reach 85°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

To address this tank liner durability issue, ORNL is performing hydrogen permeation verification measurements on storage tank liner materials using specially designed experimental facilities that provide rapid thermal cycling of polymeric liner specimens between -40 and 85°C at rates of about two to three temperature cycles per hour. This cycling is done while the liner specimens are differentially pressurized to 430 or 860 bar (6,250 or 12,500 psi). (Pressures as high as ~1,000 bar and temperatures near the polymer softening points could be accommodated in the future.)

We are using relevant portions of the test protocol specified in SAE J2579 [3] to guide the implementation 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 as many as 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.

The permeation coefficient measurements occur at regular intervals intermittent during the temperature cycling. The hydrogen flux is to be measured at four temperatures (-40, -10, 30 and 85°C) at each measurement interval, when practicable. 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 a trend in permeation increase/decrease is observed or 5,500 temperature cycles have been reached, whichever occurs first.

Results

In the previous project year, permeation measurements on a specimen of extruded HDPE cut from the cylindrical portion of a tank liner, made during high-pressure hydrogen temperature cycling, showed progressive changes in the slope, E_A, and pre-exponential scaling factor, P_0, of the Arrhenius curves. As the number of temperature cycles increased, both the activation energy and the magnitude of the scaling factor decreased, implying that structural changes were taking place in the polymer as the temperature was cycled. Characterization of the polymer using neutron scattering (small angle neutron scattering, ultra-small angle neutron scattering), differential scattering calorimetry (DSC) and helium pycnometry indicated that temperature cycling slightly increases both the average size of the crystalline regions in the polymer and the polymer density. This year we repeated the temperature cycling on a specimen of extruded HDPE from the same liner but this time we used high-pressure argon gas instead of hydrogen. The results were very similar to those observed in the specimen cycled in hydrogen; this specimen also exhibited increased crystallinity, implying that it is the temperature cycling that is primarily responsible for the increases in crystallinity. The increases in density might be attributable to the differential pressurization, which effects a plastic compression of the specimen during testing.

Projections of the potential effect of temperature cycling on a complete tank liner, using modeling based on the permeation coefficients obtained as a function of temperature cycling history, predict that hydrogen leakage through the tank liner will not significantly increase during the tank lifecycle and will remain below the maximum allowable leak rate (see Figure 1).

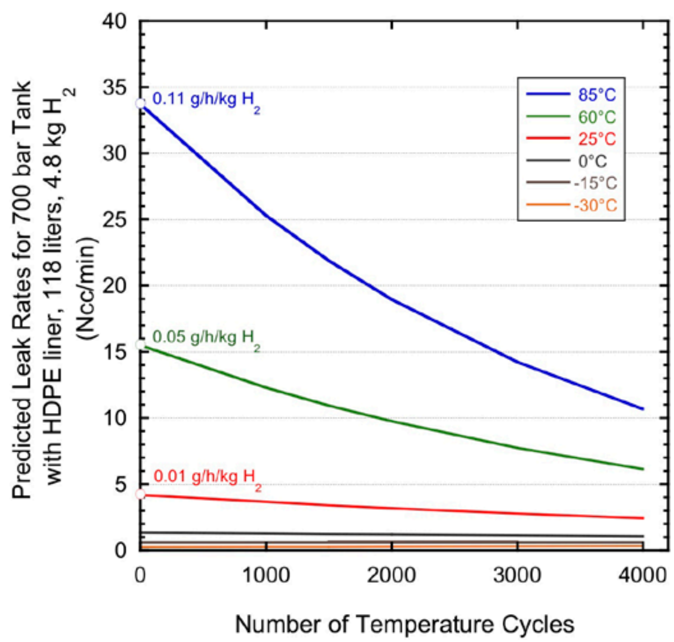

FIGURE 1. Prediction of tank liner durability (changes in hydrogen leak rates) using modeled permeability coefficients *P* to calculate leak rates in an HDPE-lined cylindrical tank with hemispherical end caps. A family of curves corresponding to predicted leak rates at varying temperatures are plotted as a function of the number of temperature cycles the tank is expected to experience due to fill operations and variations in ambient temperature.

Conclusions and Future Directions

To obtain a quantitative prediction of the leak rate for an actual tank liner, we used the dimensional specifications for a hydrogen storage tank rated for 700-bar service with a volumetric capacity of 118 liters (4.8 kg H_2 capacity). The HDPE tank liner is cylindrical with approximately hemispherical end caps, and the liner wall thickness is about 7 mm. 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 temperature and the number of cycles. This modeling shows that at all temperatures the values of the hydrogen permeation coefficients decrease with cycle count. Thus the hydrogen leak rate of the tank liner should decrease with the number of temperature cycles. In this analysis the tank leak rate remains below 75 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 H_2 for a fully filled tank (350 bar pressurization).

Future research will focus on measurements on additional tank liner materials, primarily those that promise to be significantly less expensive and with lower hydrogen permeation. Based on comments made by reviewers at the 2012 Annual Merit Review and by members of the Hydrogen Storage Tech Team, we have crafted our research plan to address the findings made in the present year and to accelerate the rate at which we can evaluate the materials. We would like to expand the scope of our investigation of the durability of the tank liners to an investigation of the durability of the tank liners when they are in physical contact with the reinforcement structure *in toto*. It is widely known by manufacturers of Type-4 composite tanks that the liner permeability of the tank liner tends to be significantly less in practice than predicted based on permeation coefficients and liner thickness. The fiber-epoxy reinforcement, which is the structural support for the liner, appears to enhance the liner's ability to retain hydrogen at high pressures. To adequately assess this contribution and to determine whether it persists during temperature cycling requires a lifecycle analysis of the structure.

We will continue to perform some post-cycling analysis of the specimens to determine the type of structural changes that take place in the polymers. DSC measurements, scanning electron microscopy/back scattered electron microscopy, transmission electron microscopy (using microtome sectioning), and perhaps some additional small angle neutron scattering, ultra-small angle neutron scattering (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.

FY 2012 Publications/Presentations

1. 2012 DOE Hydrogen Program Annual Merit Review, Arlington, Virginia, May 17, 2012, presentation ST053.

References

1. Fuel Cells Technology Program Multi-Year Research, Development and Demonstration Plan–Hydrogen Storage, pages 3.3-12–3.3-14 (2011, interim update).

2. Fuel Cells Technology Program Multi-Year Research, Development and Demonstration Plan–Hydrogen Storage, Table 3.3.1, "Technical System Targets: Onboard Hydrogen Storage for Light Duty Vehicles," page 3.3-8 (2011, interim update).

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