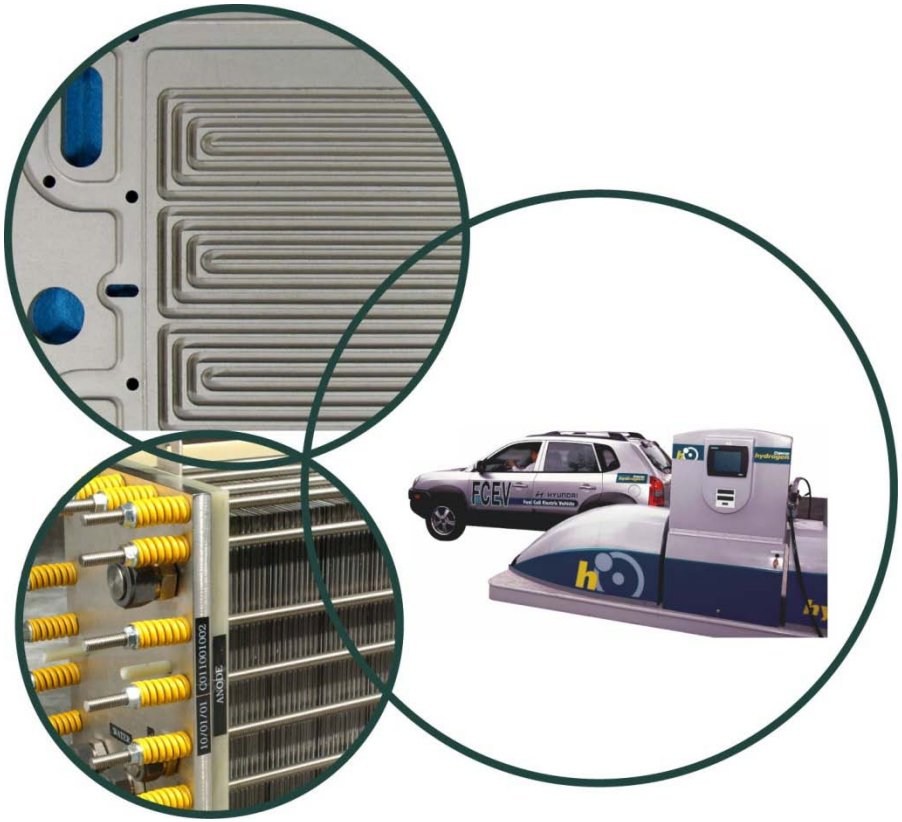
Lifecycle Verification of Polymeric Storage Liners



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Project ID #: ST053

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Overview

Timeline

- Start: June 2008
- Finish: Project continuation & direction determined annually by DOE

Budget

- Total project funding
  - DOE: $600k
- Funding received in FY10
  - $200k

Barriers

- D. Durability/Operability
- Technical targets

	430 bar	860 bar
Liner Durability	5500 cycles	5500 cycles

Partners & Collaborators

- Lincoln Composites
- Quantum Technologies
- Ticona

Relevance - Objective

Project goal: Perform durability qualification measurements on polymeric tank liner specimens and assess ability of liner materials to maintain required hydrogen barrier performance.

Month-Year	Milestone or Go/No-Go Decision
April 2010	Milestone: Complete thermal cycling and permeation measurements in Lincoln Composites liner materials (75% complete)
July 2010	Milestone: Complete thermal cycling and permeation measurements in Quantum Technologies liner materials (15% complete)
July 2010	Milestone: Complete measurements of hydrogen solubility, uptake and effects of hydrogen-induced swelling in tank liner materials (10% complete)
September 2010	Milestone: Go/No-Go decision on acceptability of existing liner materials (20% complete)

Relevance - Objective

- **The Technical Plan for Storage* has durability targets for on-board storage for LDVs**
  - **Durability target for compressed storage tanks:**
    - **Lifecycle: 1500 fill cycles (cycle = 1/4 tank ↔ full tank)**
    - **Permeation and leakage of tank must meet applicable standards, *e.g.* 75 Ncc H_2/min**
    - **Cycle life variation for permeation and leakage must not exceed 99% of mean with a 90% confidence interval**
- **SAE J2579 does not specifically address lifecycle testing of the tank liner**
- **Project objective is to verify tank liner meets permeation and leakage standards throughout tank lifecycle**

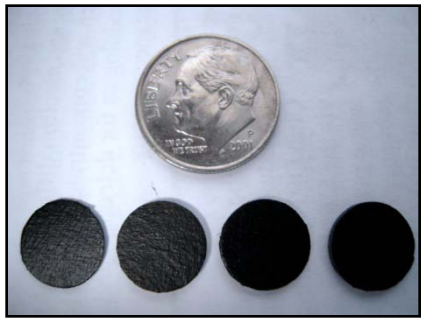
*Fuel Cell Technologies Program MYRDD Plan, Table 3.3.2, April 2009.

Relevance - Milestones

- Progress toward milestone completion was hampered by equipment failures in previous project year
- To overcome these failures we
  - Devised an improvement for the standard conical metal-on-metal seals in high-pressure make/break connections; the application of Kynar film to conical surface minimized leakage to a workable value at temperatures below -40 C
  - Devised a multilayer seal and pre-compression technique to prevent leaking at the sealing surface of the polymer specimen during temperature cycling

Technical Highlights

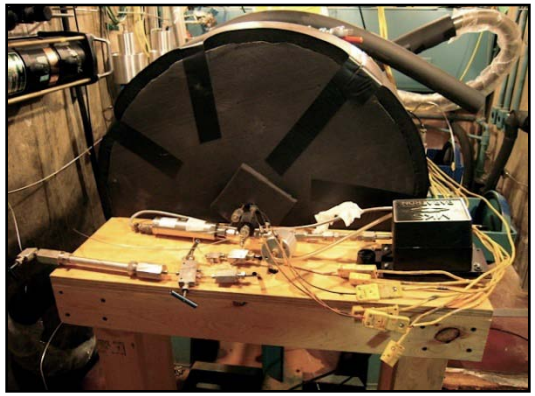
- **FY 2010**
  - **Permeation measurements on specimen of Lincoln Composites Type IV tank liner (HDPE) indicates that permeability coefficients are relatively unchanged through 2000 temperature cycles**
  - **Designed and assembled improved temperature-cycling apparatus; first results with new apparatus expected in 3rd quarter of project year**



1-cm dia. x 1-mm thk tank liner specimens

Technical Approach

- **Verify durability of polymer liners in high-pressure storage tanks**
  - **Subject polymer specimens to extreme-temperature cycling while specimens are differentially pressurized with hydrogen**
  - **Measure hydrogen permeation at prescribed intervals to assess the ability of the liner materials to maintain the required hydrogen barrier capability.**
  - **Use test protocol derived from SAE J2579, *Technical Information Report for Fuel Cell and Other Hydrogen Vehicles* (Jan 2008)**



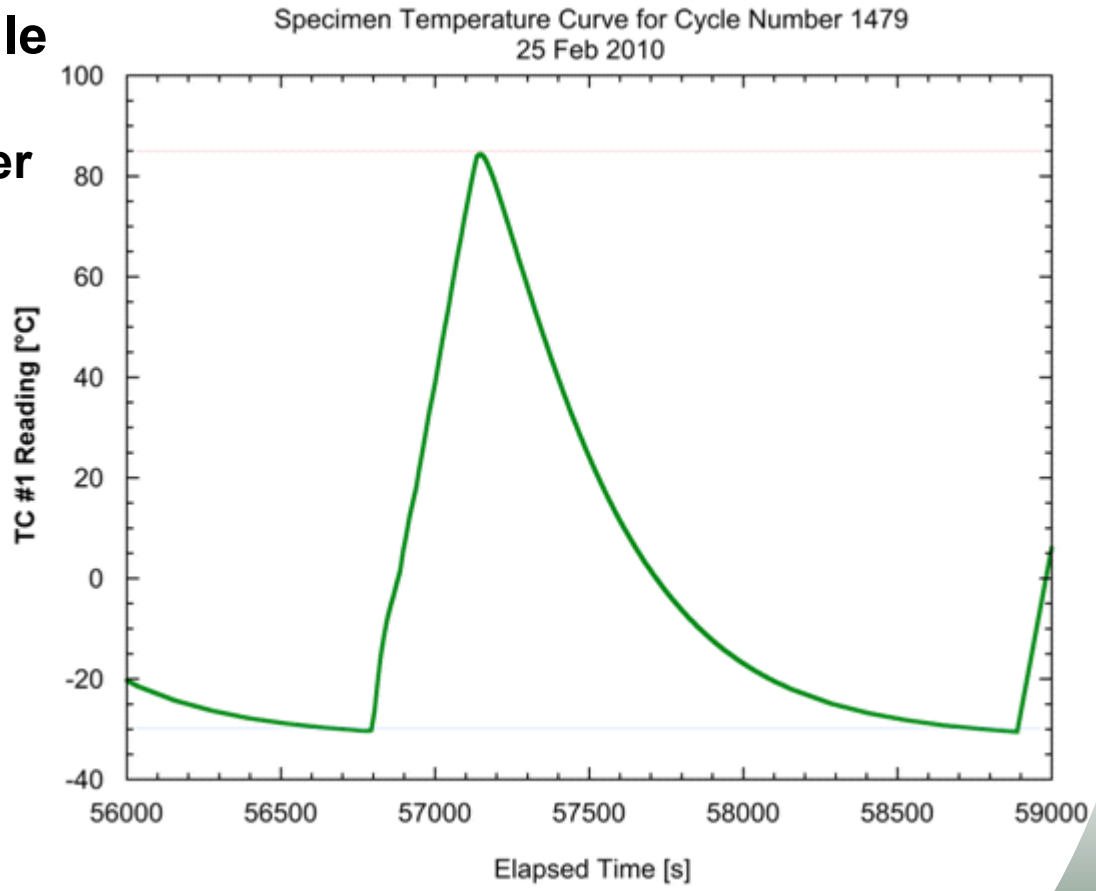
High-pressure temperature cycling test vessel

Technical Approach-Test Protocol

- From SAE J2579 § 5.2.2 (January 2008)
  - 5500 temperature cycles: -30 to 85°C
    - Upper temperature for specimen (85 C) is limited by glass transition temperature for polymer; lower temperature is determined by limitations of high-pressure seals in apparatus
    - Cycle consists of 5.75 minute heating interval (+20 C/minute), followed by 28 minute cooling interval (~2 cycles per hour)
  - Upstream hydrogen pressures: 430 and 860 bar (6,250 and 12,500 psia)
- Measure permeation rates at -30, 25, 60 and 85°C at completion of every 250 cycles (250-1500 cycles) and 500 cycles (2000-5500 cycles)

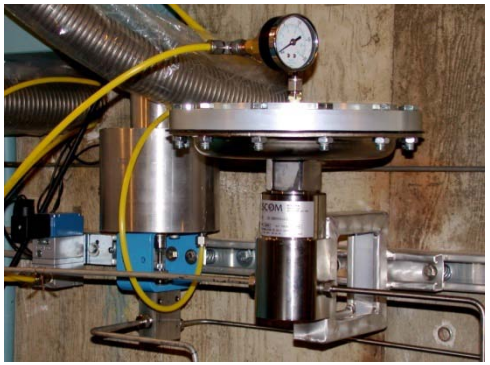
Technical Approach

- **Temperature cycling profile**
  - **5.75 min heating interval corresponds to a 20 C per min heating rate**
  - **27.6 min cooling interval determined by thermal mass of specimen holder**



Technical Approach

- Constant pressure differential maintained using computer-controlled accumulator/ regulator system
  - High upstream pressure maintained during temperature cycling using computer-controlled high-pressure regulator fed from high-pressure large-volume accumulators
  - Downstream pressure is maintained at a value below atmospheric pressure



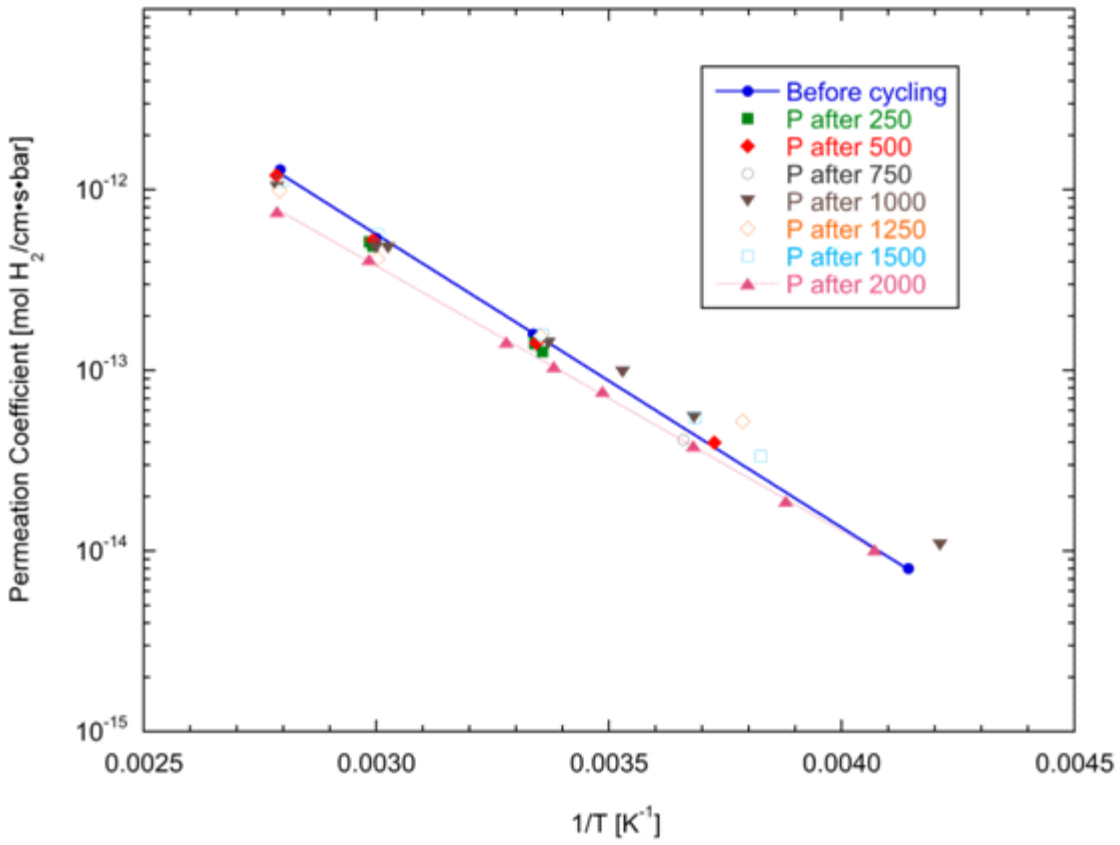
High pressure hydrogen regulator

High pressure hydrogen accumulators

Technical Progress

- **Completed permeation measurements* through 2000 temperature cycles**
  - **Temperature dependence of permeation coefficient is described by Arrhenius relationship**

    $$P = P_0 \exp(-E_P/RT)$$
  - **Measurment intervals: 0, 250, 500, 750, 1000, 1250, 1500 and 2000 cycles**
  - **Linear relationship in log *P* vs 1/*T* plot indicates that activation energy E_P remains constant**
- **Through 2000 cycles, no statistically significant departures from Arrhenius relationship that would indicate microcracking or changes in glass transition temperature in polymer**

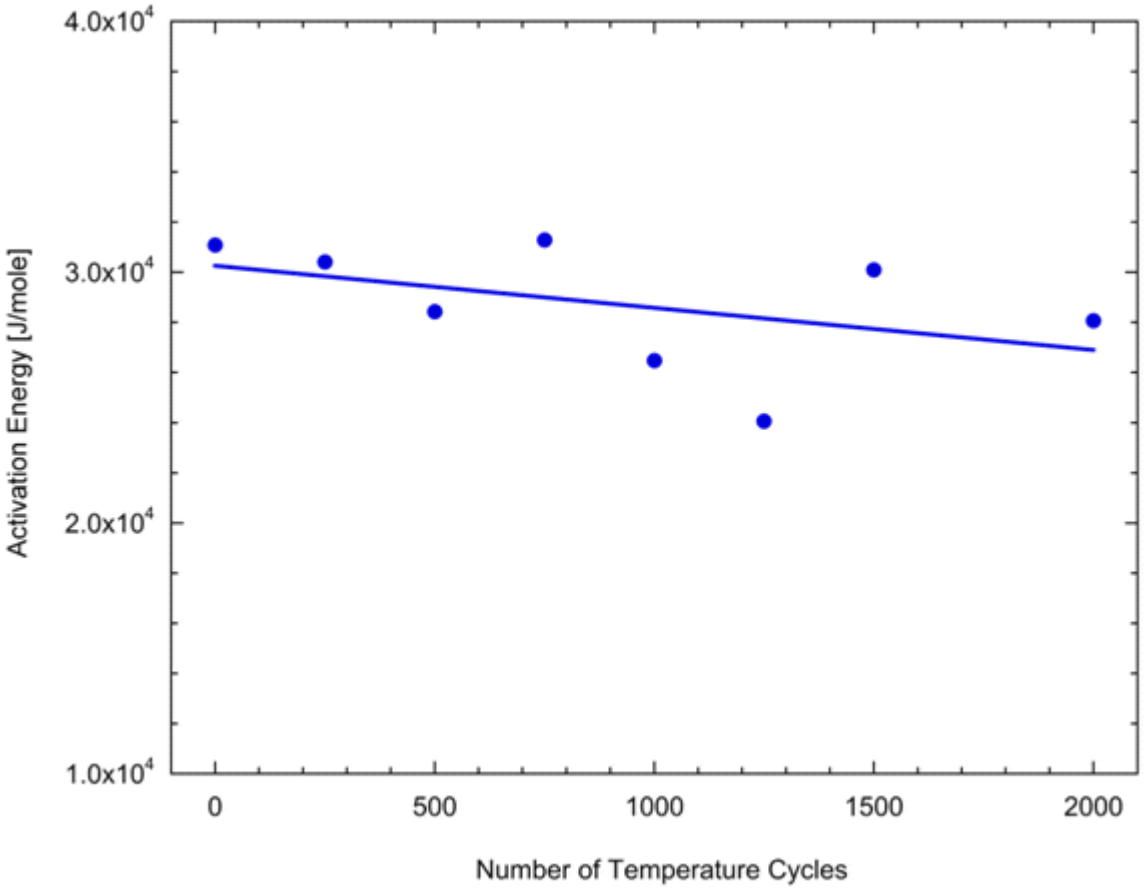


Permeation coefficients *P* for hydrogen in polymer specimen, measured at 430 bar.

*Measurements conform to ASTM D1434, *Determining Gas Permeability Characteristics of Plastic Film and Sheeting* (2003).

Technical Progress

- **Analysis of activation energy E_P**
  - **Changes in E_P as specimen is subjected to repeated cycling could indicate polymer is undergoing microscopic changes in polymer matrix**
  - **Measurements give slight indication that E_P could be decreasing, but at present decrease is almost statistically insignificant**



Collaborations

- Lincoln Composites – tank liner specimens
- Quantum Technologies – tank liner specimens
- Ticona – plastic pipeline grade PPS specimens

Future Work

- **FY 2010**
  - **Complete initial lifecycle verification measurements and report durability assessments of Lincoln Composites specimen through 5500 cycles**
  - **Begin temperature cycling of Lincoln Composites specimen at 860 bar (12,500 psia) pressurization**
  - **Begin temperature cycling of Quantum Technologies specimen at 430 bar (6,250 psia) pressurization**
- **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**

Project Summary

Relevance:	**Durability of polymeric tank liners over the performance lifetime of high-pressure storage systems must be verified and validated**
Approach:	**Use relevant portion of SAE J2579 to develop and carry out durability test cycling measurements**
Progress:	**Measurement of permeation coefficients through 2000 cycles suggests slight changes in polymer microstructure, but no indication that liner permeability has been adversely affected**
Collaborations:	**Lincoln Composites, Quantum Technologies, Ticona**
Future:	**Long-term measurements of multiple liners at 430 and 860 bar, possible measurements of alternative liner materials, measurements of hydrogen solubilities in tank liner polymers**