III.11 700-Bar Hydrogen Dispenser Hose Reliability and Improvement

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Overall Objectives

By working closely with the original equipment manufacturer, Spir Star, NREL's 700-bar hydrogen fueling hose reliability R&D project aims to characterize, improve the reliability, and ultimately reduce the cost of dispensing hydrogen to fuel cell electric vehicles.

The high-cycling autonomous test apparatus is designed to reveal the compounding impacts of high-volume 700-bar fuel cell electric vehicle refueling that has yet to be experienced in today's low-volume market. The project scope includes performing physical and chemical analysis on the inner hose material before and after cycling to understand the relative changes in its bulk properties and material degradation mechanisms.

Fiscal Year (FY) 2014 Objectives

- Design, build, and begin operation of a test apparatus that unifies the stresses to which the hose is subjected during high volume back-to-back fueling events.
  - The stresses include use of hydrogen gas, high-pressure (up to 875 bar), low-temperature ($\geq$ -40°C), 3–5 minute refueling time and automated mechanical bending and twisting of the hose assembly to simulate the refueling process.
- Specify, down select and complete chemical and physical material analysis of inner hose material prior to cycling. This analysis will reveal chemical and property changes of the material between the pre- and post-cycle testing of the inner hose material.

Technical Barriers and Targets

This project is conducting applied research, development, and demonstration to reduce the cost of hydrogen delivery systems. This project addresses the following technical barriers from the Hydrogen Delivery section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(I) Other Fueling Site/Terminal Operations

(J) Hydrogen Leakage and Sensors

FY 2014 Accomplishments

- Completed multiple chemical and physical analysis techniques, using donated hoses and hose material from Spir Star, to establish the baseline (pre-cycled) characterization of the inner hose material.
  - The inner hose material was found to be polyoxymethylene and matched perfectly with a standard spectra provided by the literature.
- Completed burst testing of one of the donated hoses at Sandia National Laboratories.
  - The 9' long hose failed roughly in the middle at 58,800 psig.
- Designed, built and performed automatic cycling of a development robotics system interfaced to a main controller that operated valves and other system functions.
  - System cycled without operator intervention for over 1,000 cycles (goal was 100 cycles).
- Designed the high-pressure, low-temperature automated system by leveraging the NREL-funded 700-bar hydrogen refueling system and existing infrastructure at the Energy Systems Integration Facility (ESIF).
  - Hose cycling will begin in FY 2014 and post chemical analysis early in FY 2015.

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INTRODUCTION

NREL operates and maintains a unique user facility known as the ESIF. The ESIF houses a broad array of capabilities and laboratories focused on energy integration research. Fast and flexible swapping of research test articles is a hallmark of the facility.

NREL partners with DOE, industry, and market stakeholders from throughout the hydrogen, fuel cell, and utility industries in order to provide critical testing, validation, and refinement stages in the product research and development process. NREL's approach to integrated systems testing simplifies the interfaces between hydrogen production, compression, storage, delivery, and end use systems.

Operation and maintenance costs of compression, storage, and dispensing are significant, and NREL has found that about 19% of maintenance hours for 350-bar hydrogen fueling infrastructure are associated with dispensers. This data can be found in NREL's material handling equipment Composite Data Products MHE #52 and MHE #66 [1]. Stations dispensing at 350 bar are much more heavily used today than those dispensing at 700 bar. These composite data products provide an early look at maintenance and reliability issues of the prospective 700-bar vehicle refueling stations.

APPROACH

This project aims to perform long-duration accelerated life testing using high-pressure, low-temperature hydrogen. This work is unique in that it simultaneously stresses the hose assembly with realistic fueling conditions (hydrogen gas, pressure ramp rates, delays, low temperature, and time). In addition, the project applies mechanical stress (bending/twisting) to the hose and nozzle assembly to simulate people refueling vehicles. Finally, the system automatically completes the full fueling process by connecting and disconnecting the nozzle to the receptacle.

The project will perform accelerated life testing of hydrogen refueling hose assemblies by accomplishing the following:

- Long duration, unattended operation of an autonomous system
- 3–5 minute fills closely following SAE International technical specification SAE J2601 pressure profile
- Type A fills using low volumes of hydrogen (at -40°C)
- Simulation of the mechanical stress of a routine consumer refueling event, including the connection and disconnection of the nozzle to the vehicle receptacle, using a 6-axis robot.
- Leak monitoring around hose/nozzle connections to detect excessive leaking and failure.

The project will also include analysis of the physical and chemical property changes to the inner hose material after cycling. The following methods will be used:

- Burst testing the entire hose assembly with crimped connection fittings.
- Fourier transform infrared spectroscopy, attenuated total reflectance (FTIR-ATR) – Identifies molecular bonding and functional groups of molecules in solids, powders, gases, and liquids. ATR identifies the bulk property of the material.
- Thermogravimetric analysis (TGA) – Thermal analysis method that accurately monitors mass changes of materials during controlled temperature profiles. Unlike FTIR, TGA does not give detailed chemical information, but provides insight into the material degradation mechanism.
- Differential scanning calorimeter (DSC) – Thermal analysis method that accurately monitors changes of heat flow in/out of a material to identify physical transformations like melting points, glass transition and recrystallization. The heats at which these transformations take place allow for identification of the material. TGA is complementary to DSC and allows for decomposition of the material at higher temperatures.
- Scanning electron microscopy (SEM) – This analysis reveals changes of the inner hose material morphology between the pre- and post-cycle testing.
- Energy dispersive X-ray spectroscopy (EDX) – This analysis technique provides bulk elemental composition. EDX coupled with SEM provides a mapping of elements in the hose material.
- X-ray photoelectron spectroscopy (XPS) – XPS reveals changes in surface properties after testing with high pressure and low temperature in the hydrogen environment. Surface reactions, like embrittlement, of the polymer would be seen using this technique.

RESULTS

Automated Hose Cycling

A development robot was interfaced with a main controller to perform automated mating, activation and cycling using low-pressure nitrogen. The system was designed, built and cycled using 350-bar nozzle and completed over 1,000 cycles without operator intervention. The automatic cycling was terminated with a controlled user-initiated stop request once the milestone goal was exceeded by an order of magnitude. Furthermore, the system testing showed that the nozzle and receptacle mating, nozzle activation (i.e., 180° rotation), and required valve sequencing was sufficiently repeatable to enable unattended operation inside the ESIF's High Pressure Test Bay (HPTB).

Lessons learned, software, and safety systems provided by this development work were transferred to the 700-bar (nominal) system design. The new design will utilize a smaller robot and full suite of 700-bar (nominally rated) equipment that will be installed in the 10'x10' footprint of the HPTB.

Baseline (Pre-Cycled) Inner Hose Material Chemical and Physical Analysis

Spir Star donated three hose assemblies and a section of hose material—all from the same batch of material. One of the hose assemblies, complete with standard crimp end connectors, was given to Sandia National Laboratories for burst testing. The hose failed at 58,800 psig in the middle of its 9' length. Spir Star's burst rating specification is 50,800 psig with a 5% tolerance due to manufacturing and material variability.

A sample of the inner hose material was characterized by identifying and quantifying bulk and molecular species present through the implementation of a suite of analytical instrumentation and analysis techniques. The inner hose material was identified using FTIR to be polyoxymethylene and found to be a match with a standard spectra provided by literature. The black curve of Figure 1 is the spectra of the pre-cycled inner hose material and the red curve is the standard spectra for polyoxymethylene. FTIR testing of post-cycled inner hose material will expose any changes in the bonding structure.

A summary of the other chemical analysis results are:

- TGA resulted in 100% inner hose material being decomposed in two concurrent steps with a decomposition temperature of 302°C. TGA of post-cycled hose material revealed shifts in the decomposition temperature, indicating polymer composition changes.
- DSC shows melting temperature of polyoxymethylene in the range of 162–169°C, which matches the range provided by literature. During the cooling period of the test, the hose material recrystallized at 143°C. If the post-cycled hose material changes, by taking on impurities or hydrogen for example, DSC will identify the change because the melting point will likely also change.
- SEM shows the structure of new inner hose material resembling wrinkles/folds at 2,000 magnification. Post-cycled SEM scans will provide visual proof of pitting, embrittlement, or other surface morphology degradation.
- XPS analysis revealed that the inner hose material consists of carbon-carbon and carbon-oxygen bonds. EDX analysis showed that the bulk elemental composition of the inner and outer hose liner was 60–64% carbon and 39–36% oxygen.

CONCLUSIONS AND FUTURE DIRECTIONS

- **Conclusion:** Development of the controls, interfacing, and automated nozzle to receptacle process is very repeatable. Lessons learned from the 350-bar system were transferred to the 700-bar full system design, build, and operation.
  - **Future:** The system will be continuously cycled in unattended mode to achieve accelerated life testing of the hose assembly in the ESIF's HPTB using high-pressure, low-temperature hydrogen gas.
- **Conclusion:** Chemical and physical material analysis, aimed at revealing material changes between pre- and post-cycled hose material, was completed. Baseline (pre-cycled) chemical analysis identified the inner hose material to be polyoxymethylene. Burst test was completed with hose failing at 58,800 psig; well above the specification (50,800, ±5% psig) from Spir Star.

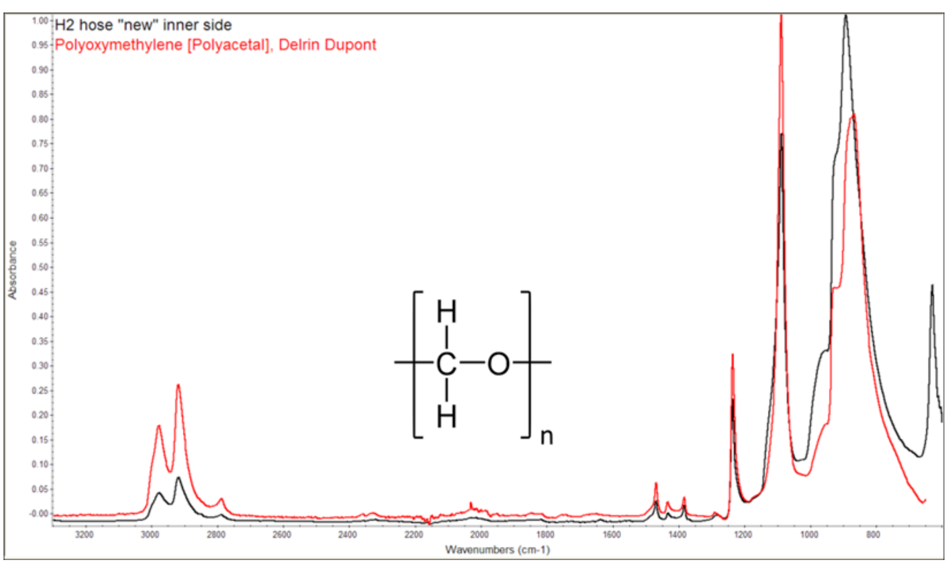

FIGURE 1. FTIR shows molecular bonding of inner hose material consistent with Polyoxymethylene

   - **Future:** Perform the same suite of analytic techniques on inner hose material after cycling with hydrogen at high pressure, low temperature and repeated bending/twisting to (potentially) reveal changes in bulk properties and elemental material composition.
- **Future:** Continue to work with industry partners like NanoSonic to test prototype hoses from their Small Business Innovation Research Phase II project, "Cryogenically Flexible, Low Permeability Thoraeus Rubber™ Hydrogen Dispenser Hose."

FY 2014 PUBLICATIONS/PRESENTATIONS

1. 1-Page Fact Sheet - http://www.nrel.gov/docs/fy14osti/61091.pdf
2. YouTube Video - http://www.youtube.com/watch?v=Rbc7f01oP8kA

REFERENCES

1. http://www.nrel.gov/hydrogen/proj_fc_market_demo.html