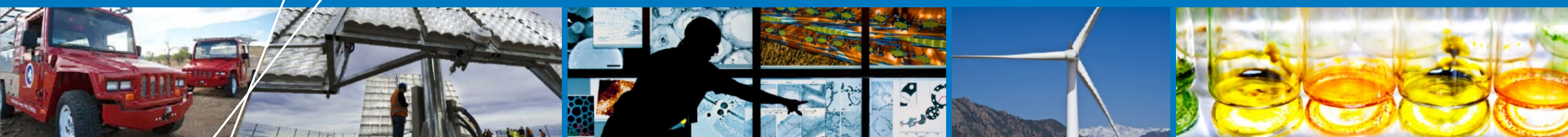
700 bar Hydrogen Dispenser Hose Reliability Improvement



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National Renewable Energy Laboratory
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Project ID # PD100

Overview

Timeline

Project start date: June 2013
Project end date: June 2015

Barriers

- **Reliability**
- **Safety**
- **Cost**

Budget

Total Funding Spent: $285k*

Total DOE Project Value: $775k

NREL Funding

- **$1.1M – 700 bar Fueling Station**
- **$20k – Compressors**

Spir Star: $5k

Partners

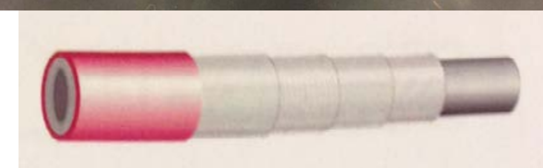
- **Spir Star**
- **NanoSonic**
- **Sandia National Laboratory**
- **NREL**
  - Hydrogen Sensor Group
  - Chemists
- **Colorado School of Mines**

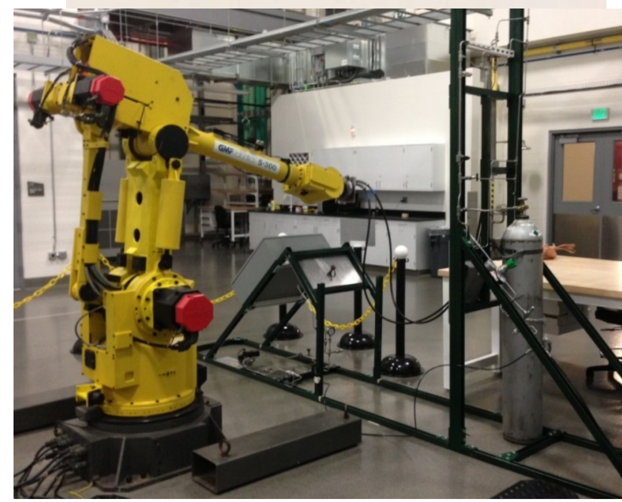
* As of March 31, 2014

Relevance & Project Objective

To characterize and improve upon 700 bar refueling hose reliability under mature market conditions

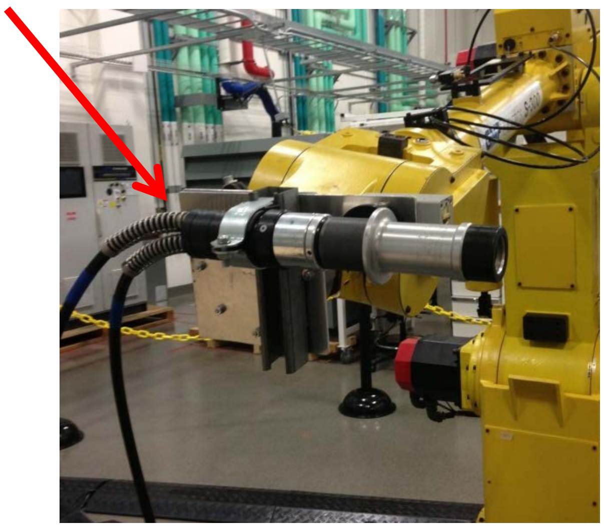
- By working closely with the original equipment manufacturer, Spir Star, NREL's hose reliability R&D project aims to improve the reliability and reduce the cost of 700 bar hydrogen refueling hose assemblies.
- NREL has designed a test system that unifies the four stresses to which the hose is subjected (Pressure, Temperature, Mechanical and Time)
- 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.





Approach

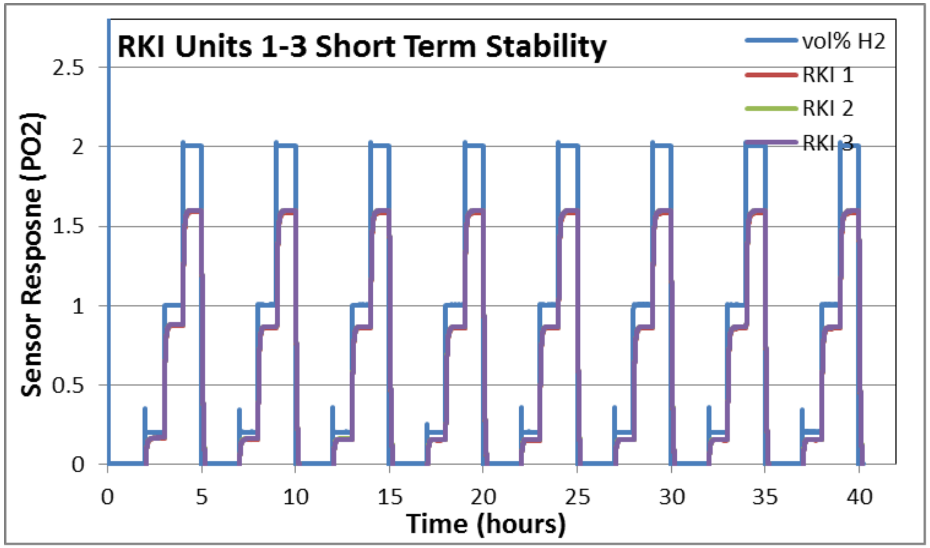
- **Long-duration accelerated life testing in hydrogen is accomplished autonomously to simultaneously stress the hose assembly with realistic fueling protocol conditions (pressure, temperature and time) and the mechanical stress applied to hose during the process of connecting and disconnecting the hose to the vehicle during the fueling event.**
  - NREL purchased (2) air-driven gas boosters to achieve 875 bar to support this project
  - Leak monitoring of hose/nozzle interface

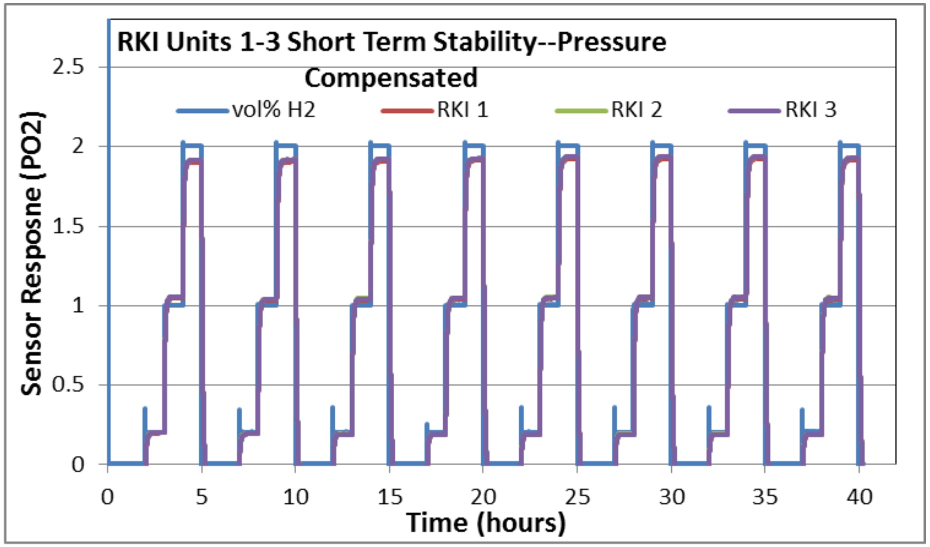


- **The approach includes performing physical and chemical analysis on hose material <u>before and after testing</u> to understand the relative changes in its bulk properties and material degradation mechanism.**

Approach: Test Protocol

- 3 minute fills based on SAE J2601 pressure profile, Type A fills using low volumes of hydrogen (at -40°C)
- A robotic arm is used to simulate the mechanical stress of routine consumer refueling. Including connecting and disconnecting the refueling nozzle to the vehicle receptacle.
- Leak monitoring is placed around hose/nozzle interface to detect failure.





Approach – FY2014 Milestones

Qtr	Due Date	Type	Milestones, Deliverables, or Go/No-Go Decision	Status
Q2	Originally 6/2014	Regular	Perform pre SEM, stress/strain and EGA on hose material under test, evaluate the ability of these analysis methods to determine the presence of micro-cracking and hydrogen impregnation in the subject hose materials.	Completed in Q2
Q3	6/2014	Regular	Distribute and gather feedback on hose test plan, including the chemical analysis plans, to at least three (3) interested industry leaders. Modify test plan with feedback that will enhance the project without adding significant costs or delays.	
Q4-1	8/2014	Regular	Install other major equipment and safety systems to achieve 700 bar (nominal) filling down to -40C.	
Q4-2	9/30/2014	Regular	Perform accelerated hydrogen cycling to 700 bar (nominal) on a hose sample to failure or 25,000 cycles, whichever occurs first.	
FY15 Q1	12/2014	Regular	Perform post SEM, stress/strain and EGA on hose material under test, or other tests as deemed appropriate.	

Technical Accomplishment - Automation

- Development 350 bar system exceeded (by 10x) milestone of 100 autonomous cycles
- System controller, software developed and handshaking with robot controller
- Automated nozzle actuation and filling sequence
- Transfer lessons learned to 700 bar system hardware

Play Video
Here

Technical Accomplishments – Hose Burst Test Results

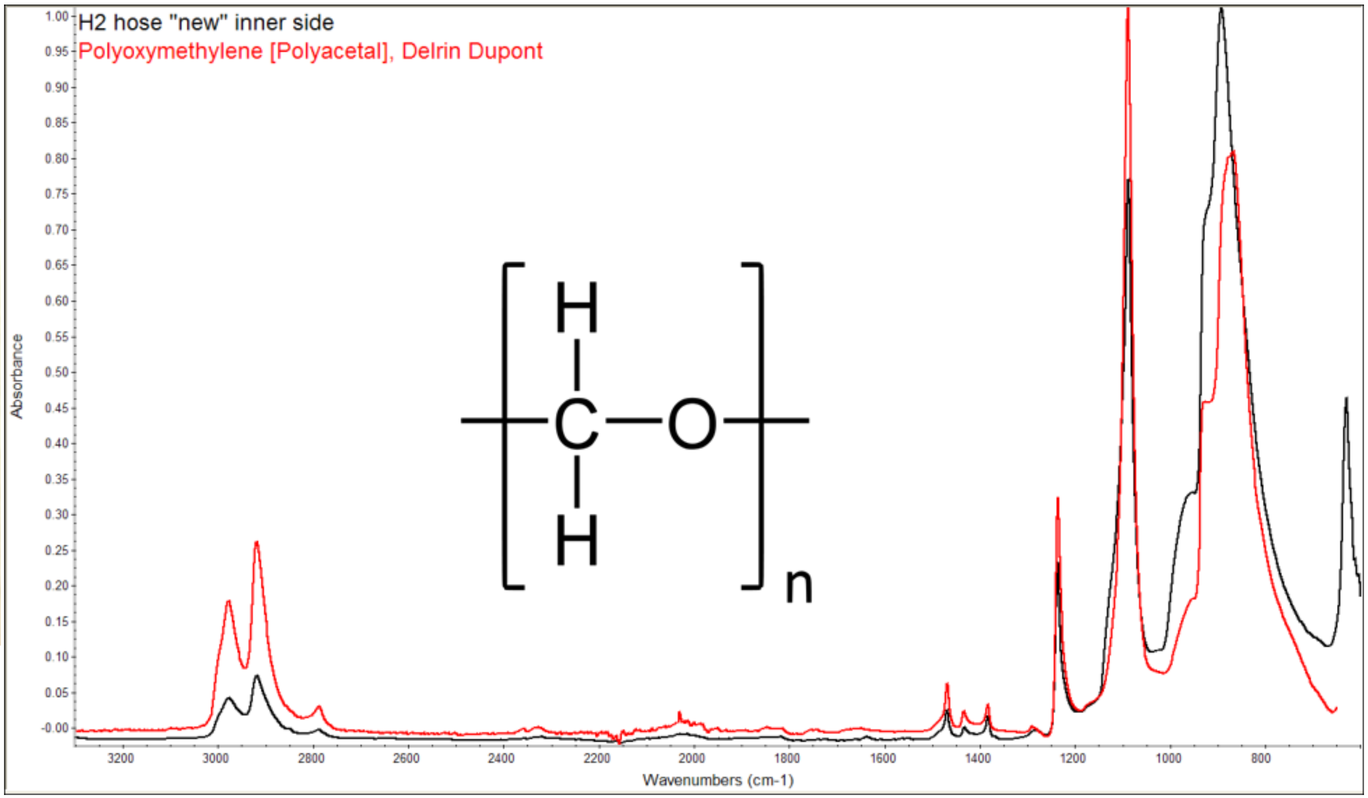
- **Results:** Hose failed at 58,800 psig
- **Location:** Middle of hose section, hose had end connectors
- **Burst Specification:** 50,800 psig burst pressure with 5% variation

<u>SpirStar Hose Specifications</u>

- Inner Core: Low permeation POM
- Pressure Support: 4 layers of high tensile steel wire
- Outer Cover: preven Polyamide (PA)
    - Non-conductive
- Temperature: -40 to +65C
- Working pressure 12,700 psig
- ¼” ID and ½” OD
- Minimum bend radius 7.09”
- Electrical resistance from end fitting to end fitting is < 0.3 Ω/m

Technical Accomplishments – FTIR-ATR

FTIR shows molecular bonding of inner hose material consistent with Polyoxymethylene [POM]



FTIR-ATR = Fourier Transform Infrared Spectroscopy Attenuated Total Reflectance
(identifies bonding and functional groups of molecules in solids, powders, gases, and liquids)

Technical Accomplishments –
TGA - Initial degradations inner hose inert/air

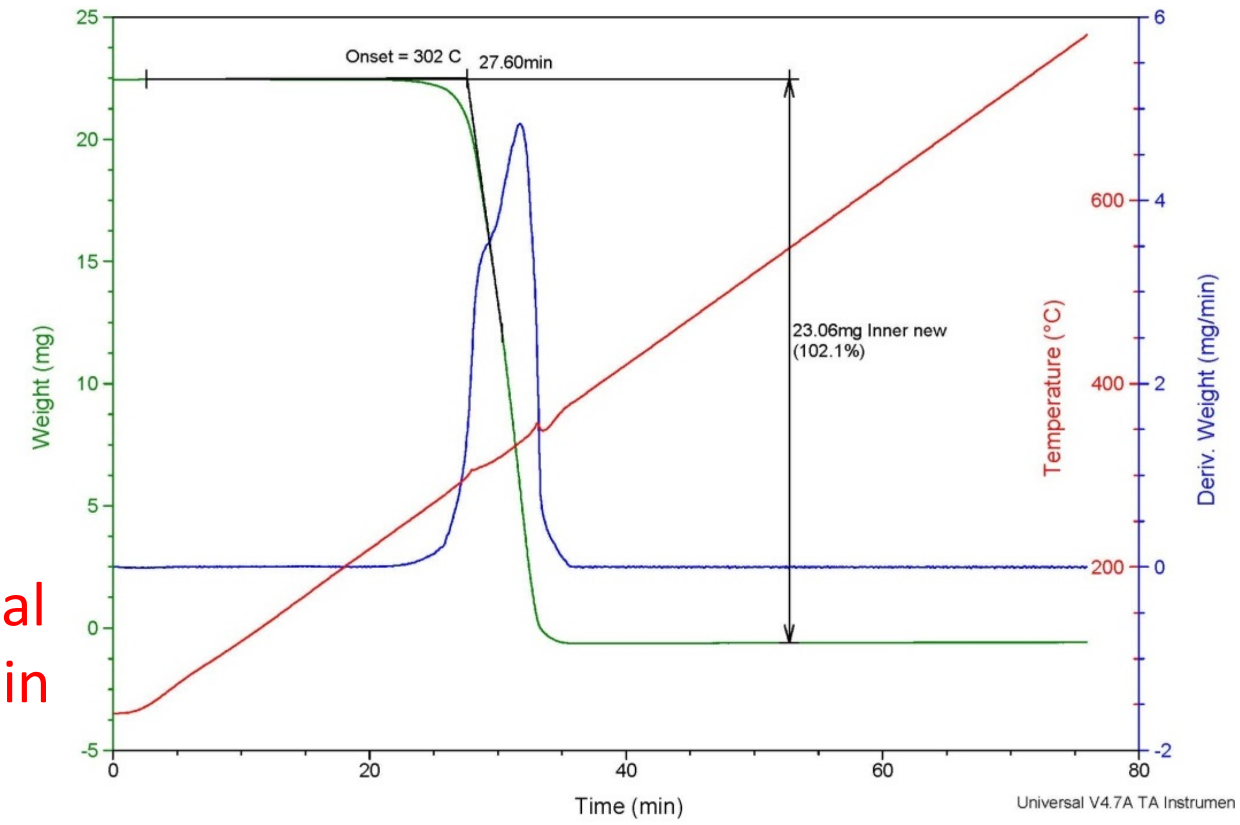
This analysis will be used to show degradation or material changes between the pre- and post-cycle testing of the inner hose material

T_d = 302^{o}C

Two concurrent steps

100% material loss

Will the same material degradation be seen in the cycled hose material?



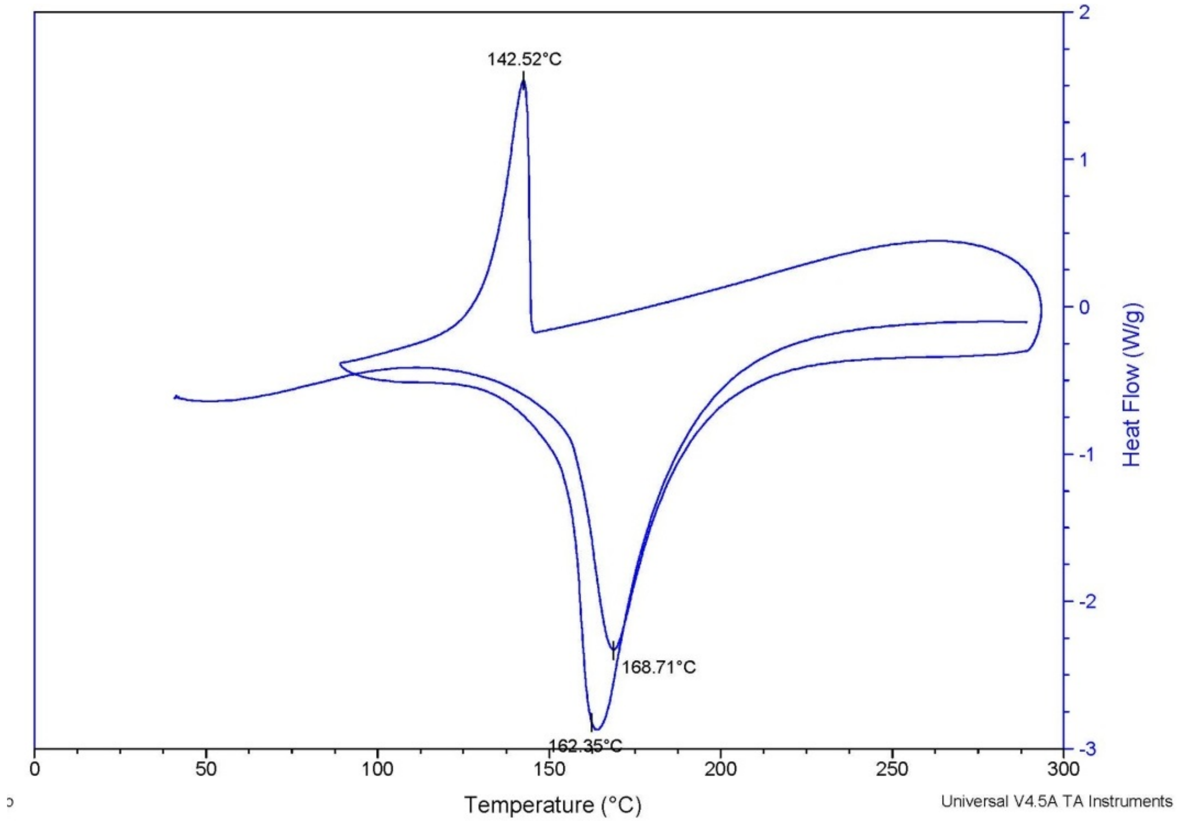
TGA = Thermogravimetric Analyzer (thermal analysis method that accurately monitors mass changes of materials during controlled temperature profiles)

Technical Accomplishments – DSC – Heat flow cycling in inert gas

This analysis will be used to show physical property changes of the material between the pre- and post-cycle testing of the inner hose material

$M_{p1/2}$ = [#1] 169^{o}C, [#2] 162^{o}C

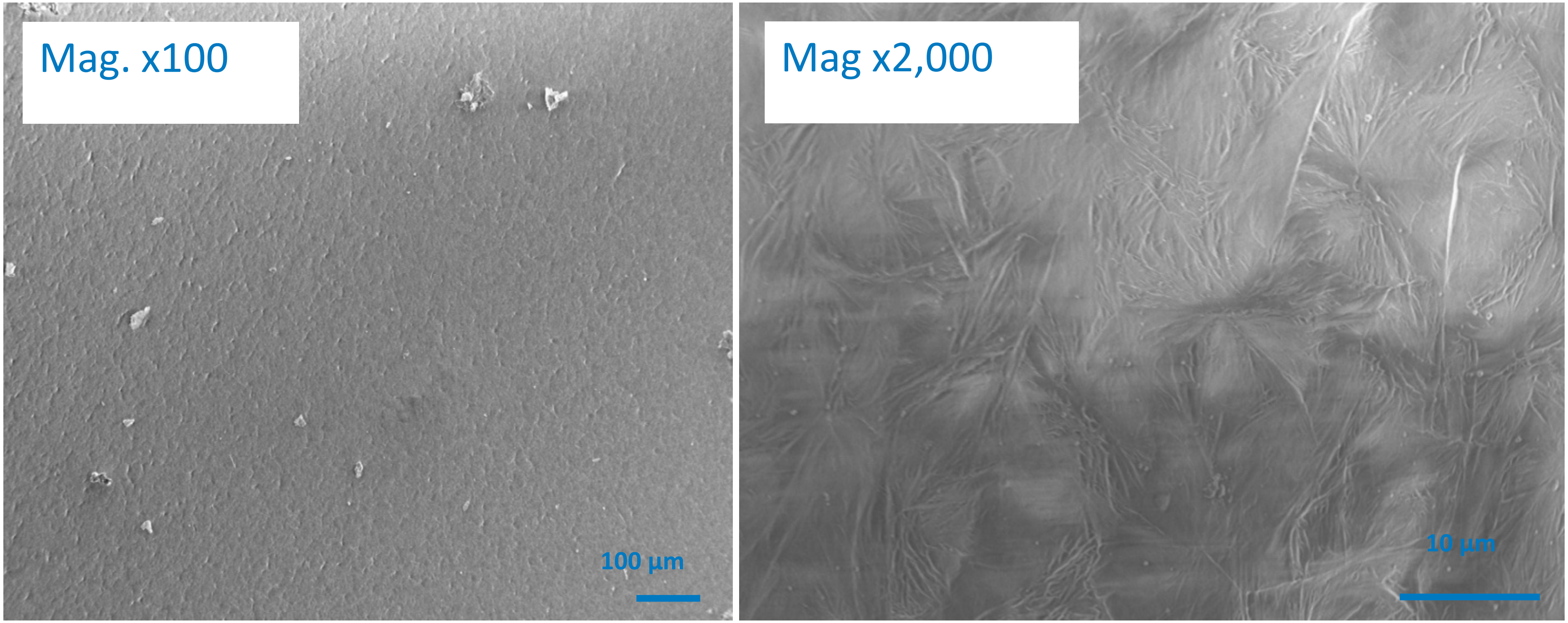
Recrystallization = 143 ^{o}C



DSC = differential scanning calorimeter (Thermal analysis method that accurately monitors changes of heat flow in/out of a material to identify physical transformations)

Technical Accomplishments – Morphology: SEM analysis

This analysis will be used to show changes in the material morphology between the pre- and post-cycle testing of the inner hose material



Technical Accomplishments – Elemental Composition: EDX and XPS analysis

Energy Dispersive X-Ray spectroscopy (EDX):

Bulk elemental composition, at%

	new	new
	inside	outside
Carbon	60.6	63.7
Oxygen	**39.4**	**36.3**

X-ray Photoelectron Spectroscopy (XPS):

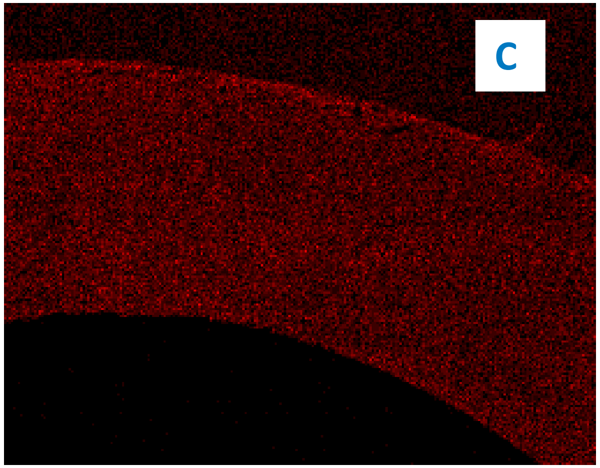
Surface elemental composition, at %

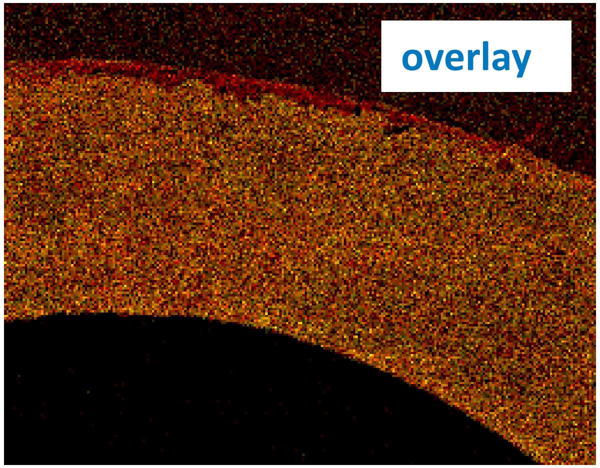
(~7-10 nm of surface)

	new	new
	inside	outside
Carbon	77.9	77.2
Oxygen	**19.6**	**22.6**
Nitrogen	2.4	0.3
other elements		Ca, Si

- **Inner hose material consists of carbon and oxygen**
- **EDX and XPS show difference between inside and outside surfaces**
- **EDX mapping allows elemental mapping, which can be useful for**
  - **plane view analysis (not shown)**
  - **cross-sectional analysis (shown)**

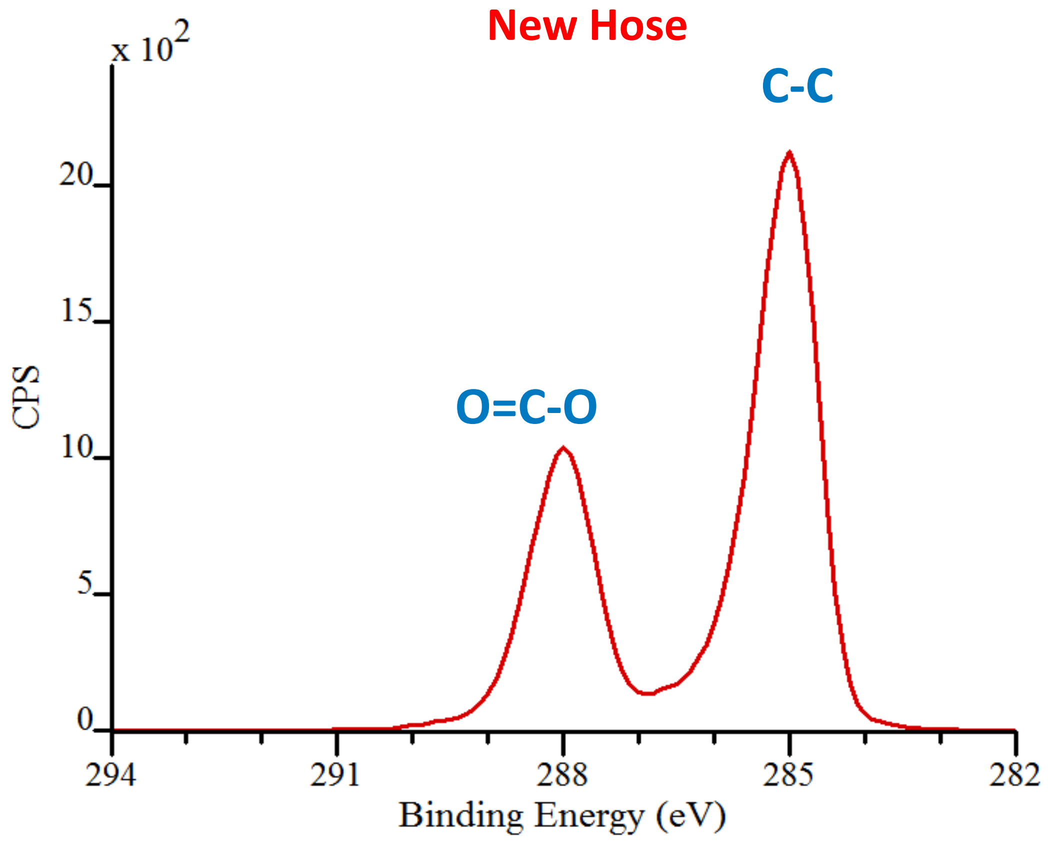
This analysis will be used to show changes in material chemical composition between the pre- and post-cycle testing of the inner hose material





Technical Accomplishments – Chemical composition: XPS analysis

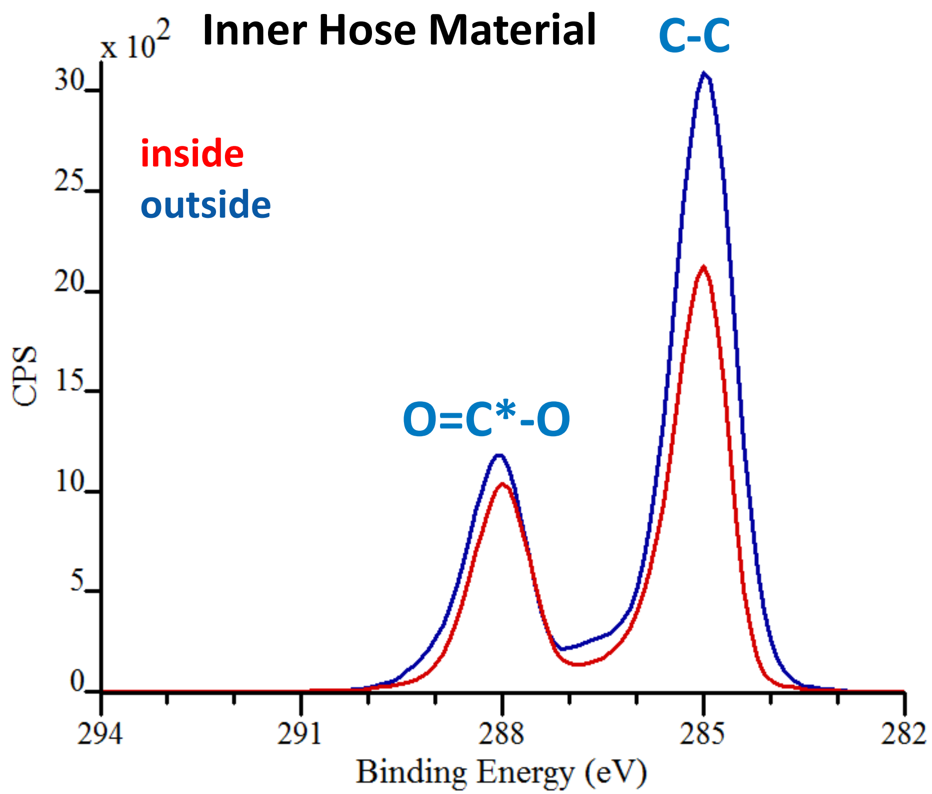
- High-resolution C1s spectra allow to identify carbon species, i.e. allow to differentiate C-C, C-O, C=O, O-C=O, ect../
- C-C or CH-CH bonds are located at binding energy of 285 eV
- Inner hose material consists of carbon-carbon and carbon-oxygen bonds



Technical Accomplishments – Chemical composition: XPS analysis

High-resolution C1s spectra:

- Inside and outside surfaces have some structural differences, mainly higher amount of C-C bonds.
- The difference between inside and outside is more pronounced in the cycled sample

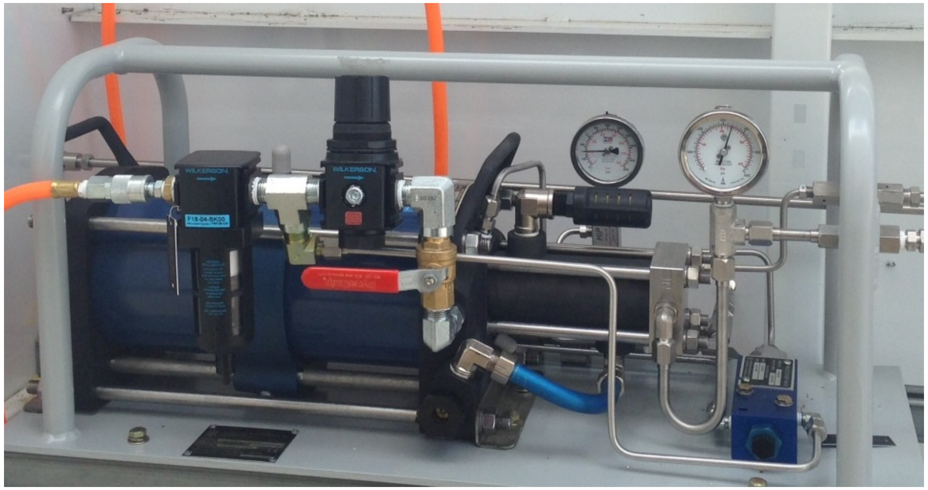


Collaborations

- **Spir Star**
  - To date, provided three hose assemblies
  - Provided spare hose material from same batch of for pre-cycling analysis
- **Sandia National Laboratory**
  - Burst testing hose
- **NanoSonic**
  - SBIR Phase I, "*Cryogenically Flexible, Low Permeability Thoraeus Rubber™ Hydrogen Dispenser Hose*"
  - If successful in securing Phase II, hoses will be tested at NREL
- **NREL Chemists & Hydrogen Sensor Group**
  - Conducted chemical analysis of pre-cycled hose material
  - Calibrated hydrogen sensors at altitude
- **Colorado School of Mines**
  - SEM-EDX, XPS

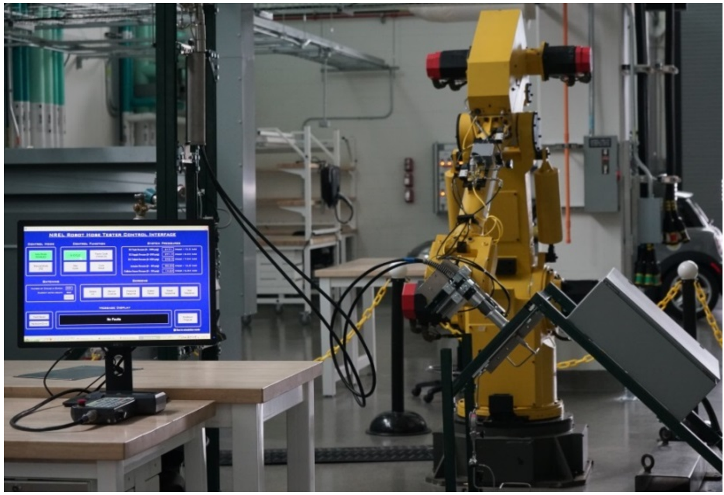
Remaining Challenges & Barriers

- **NREL's experience with air-driven gas boosters used for compressions, so far, has shown about 200 hours between rebuilds**
  - The high cost of diaphragm and hydraulic compressors is a barrier
- **The NREL-funded 700 bar refueling station has had vendor contractual delays that may impact the expected hose cycling that is planned in September 2014**



Future work – Full Operations and Testing

- **Major Systems Integrations and Commissioning**
  - July – August 2014
  - Production, compression, chiller and storage
  - New automation inside High Pressure Test Bay at ESIF
- **Automated high pressure, low temperature hose cycling – 9/14**
- **Post material analysis after cycling – 12/14**
- **Test hoses from other manufacturers – FY15-16**



Summary

Relevance: To characterize and improve upon 700 bar refueling hose reliability under mature market conditions

Approach: By working closely with Spir Star, NREL has designed a test system that unifies the four stresses (Pressure, Temperature, Mechanical and Time) in one high-cycling autonomous test apparatus is expected 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 approach includes performing physical and chemical analysis on hose material before and after testing to understand the relative changes in its bulk and surface properties and material degradation mechanism.

Technical Accomplishments:

- Automated cycling exceeded milestone by 10 times goal
  - Lessons learned being transferred to 700 bar system hardware
- **These tests are aimed at revealing material changes of the same hose material before and after cycling**
- Down-selected chemical and physical material analysis
- Burst test completed and hose failed at 58,800 psig; above the specification (50,800, ±5% psig) from Spir Star
- Using FTIR, new hose material was found to be consistent with Polyoxymethylene [POM]
- Thermogravimetric analysis (TGA) resulted in and 100% material loss in 2 concurrent steps
- Differential scanning calorimeter (DSC) shows melting temperature in the range of 162 – 169°C
- Scanning electron microscopy (SEM) shows structure resembling wrinkles/folds
- XPS analysis reveals inner hose material consists of carbon-carbon and carbon-oxygen bonds

Collaborations:

- Spir Star, Sandia National Laboratory, NanoSonic, NREL Chemists and Sensor Group, Colorado School of Mines

Future Work:

- Major Systems Integration and Operation
- Automated cycling at 700 bar (nominal) pressure and -40 temperature
- Post material analysis of inner hose polymer

Technical Back-Up Slides

Dynamic Mechanical Analysis [DMA]

Additional recommended rheology experimentation.

DMA

- Measure of viscoelasticity
- Variables include Force, Temperature, Frequency… Stress/Strain
- Calculate and compare material modulus [storage, Young's or other]
- Small amount of material required

Typical DMA setup

Common method of determining differences in physcial properties of polymers.