NanoSonic, Inc.

2014 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office
Annual Merit Review and Peer Evaluation Meeting

Cryogenically Flexible, Low Permeability H_2 700 Bar Delivery Hose

P. I.: Dr. Jennifer Lalli, President

Presenter: Mr. Keith Hill, PM, Mech. Engr.

NanoSonic, Inc.

6/17/2014

Project ID # **PD101**

Overview

Timeline
- **Project Start Date: 6/10/2013**
- **Project End Date: 5/23/2014**

Budget
- **FY13 DOE Funding: $150,000**
- **Planned FY14 DOE Funding: $1,000,000**
- **Total DOE Project Value: $1,150,000**

Barriers
- **Lack of H_2 / Carrier and Infrastructure Options**
- **Reliability and Costs of Gaseous H_2 Compression**
- **Reliability and Costs of Liquid H_2 Pumping**

Partners
- CSA Group
- NREL
- Fittings Partner
- WEH USA
- **Giles County Government**

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Relevance:
Develop a H_2 Hose Dispenser for Fuel Cell Vehicles

Flexhose Objectives:

Develop: a flexhose that dispenses H_2 for < $4 gge

Verify: flexhose reliability at -40 °C, under 860 bar H_2 for H70 fill, and Joule-Thompson cycle

Optimize: cost, safety, and maintenance of flexhose for 70 fills / day (25,550 fills / year)

Qualify: per ANSI/CSA HGV 4.2-2012 for class D hoses

Dispenser Compliance: with SAE TIR J2601 and NIST Handbook 44



NanoSonic Approach:

Combine: NanoSonic's Thoraeus Rubber™ technology with Advanced Low T_g Resins

Produce: an Anti-Static, Low H_2 Permeability Flexhose that can Store H_2 under Cryogenic Conditions, and Resist H_2 Embrittlement under High Pressures and Flexing During Use

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Approach:
Develop a H_2 Hose Dispenser for Fuel Cell Vehicles

<u>Combine:</u> NanoSonic's Thoraeus Rubber™ technology with Advanced Low T_g Resins

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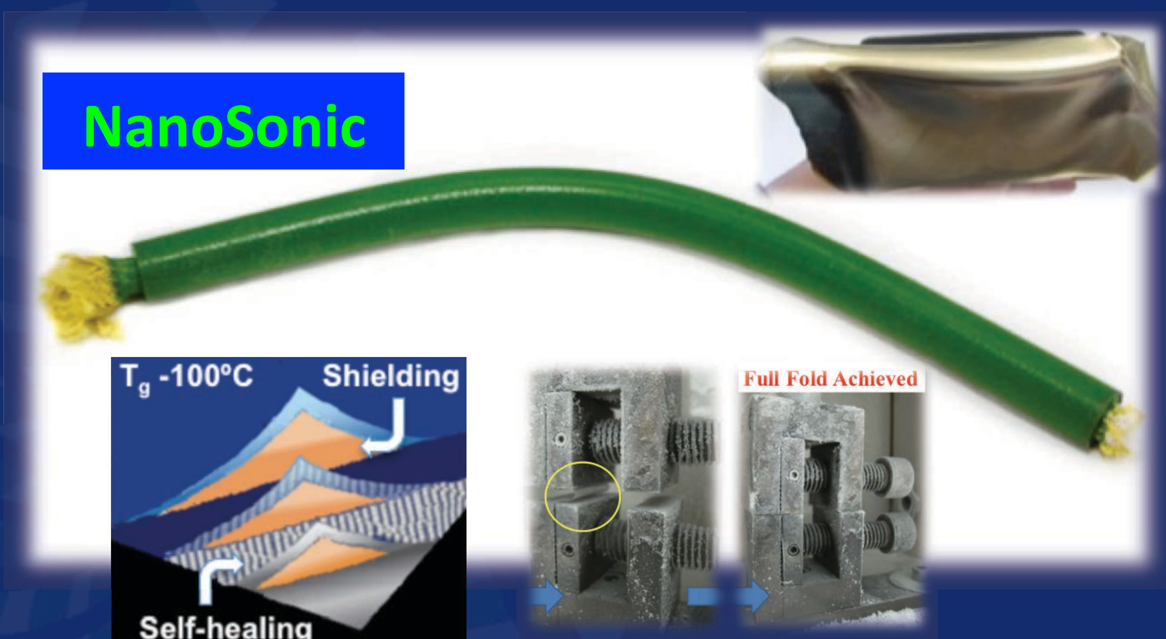
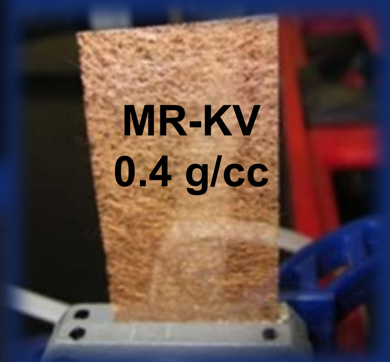
GO / NO GOs

1. Low Temperature Flexibility for -40 °C Dispensing Requirement
2. Fiber Reinforced to Prevent H_2 Induced Cracking (HIC) and Meet High Pressure (875 Bar)
3. Cycling Requirements (25,550 annually) and Compete with Spir Star



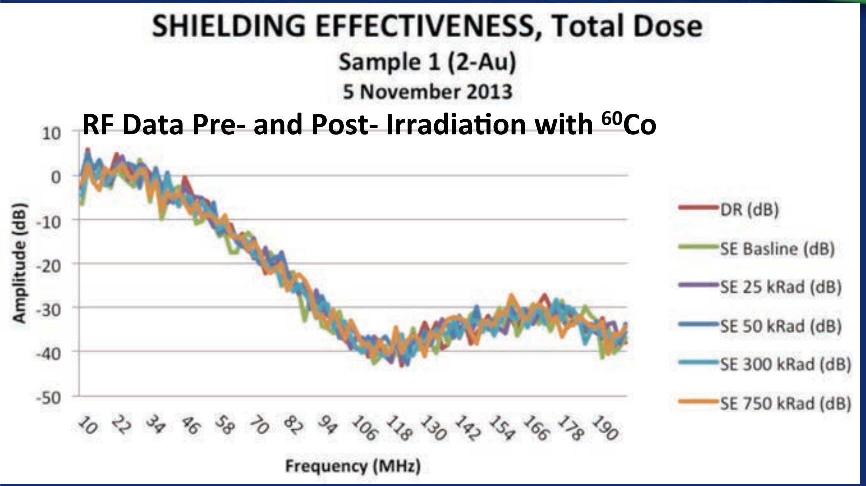
Metal Rubber™
Flexible ESD Protective Materials



- Electrostatic Dissipation
- EMI/Radiation Shielding
- Lightweight/Flexible
- Textile Reinforcement
- Shielding for Hose Grounding Applications

Lightweight EMI and Radiation Shielding Material with Improved Quality & Reproducibility

RF Data
-106 dB
Mass Density
0.58 g/cc



Highly uniform, high transmission loss over every 2” square cut from 12” x 12” composites

ID	Metal	Weight (g)	Width (cm)	Length (cm)	Thickness (cm)	plies	Mass Density (g/cc)	Transmission Loss (dB)
MH-202-35A	Au	0.9	5.08	5.08	0.045	2	0.79	-63
MH-177-182	Au	1.23	5.08	5.08	0.070	4	0.68	-101
MH-202-35B	Au	1.54	5.08	5.08	0.113	6	0.53	-101
MH-202-21A	Au	0.71	5.08	5.08	0.037	2	0.75	-50
MH-202-21B	Au	0.88	5.08	5.08	0.061	4	0.56	-76
MH-202-21C	Au	1.32	5.08	5.08	0.088	6	0.58	-106
MH-202-26A	Ag	0.80	5.08	5.08	0.048	2	0.65	-71
MH-202-26B	Ag	1.53	5.08	5.08	0.086	4	0.69	-97
MH-202-26C	Ag	1.96	5.08	5.08	0.126	6	0.60	-102
MH-202-30A	Ag	0.62	5.08	5.08	0.038	2	0.63	-73
MH-202-30B	Ag	0.89	5.08	5.08	0.072	4	0.48	-100
MH-202-30C	Ag	1.31	5.08	5.08	0.103	6	0.49	-100

Multiple Formats for Widespread Hose and Conduit Products

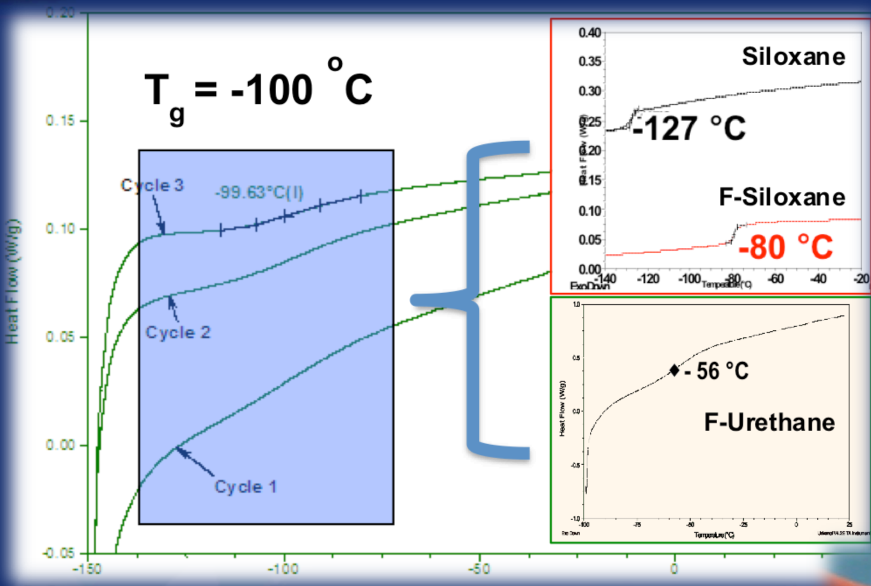
Noble
Metal
Au
Nanoparticles

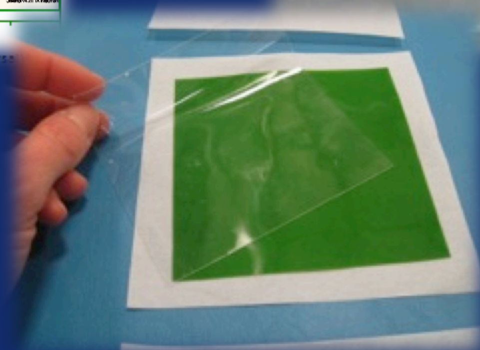
50' x 12"
Scale-up
For Cost
Reduction

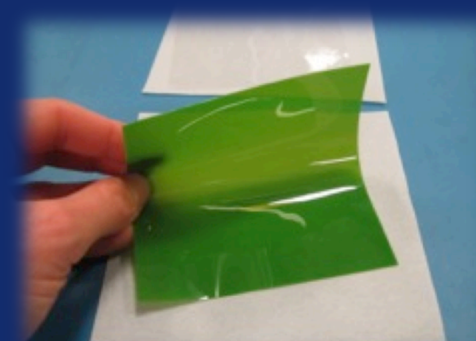
Filled
Rigid & Flex
Grounding
Hoses

High Pressure
Flexible H_2
Delivery
Hose

Low T_g Polymer Matrix Resins and Films for Cryogenic Flex Testing Followed by H_2 Permeance







(6) 5” x 5” Films per H_2 Test Permeance
per ASTM D 1434
at Polyhedron Laboratories®

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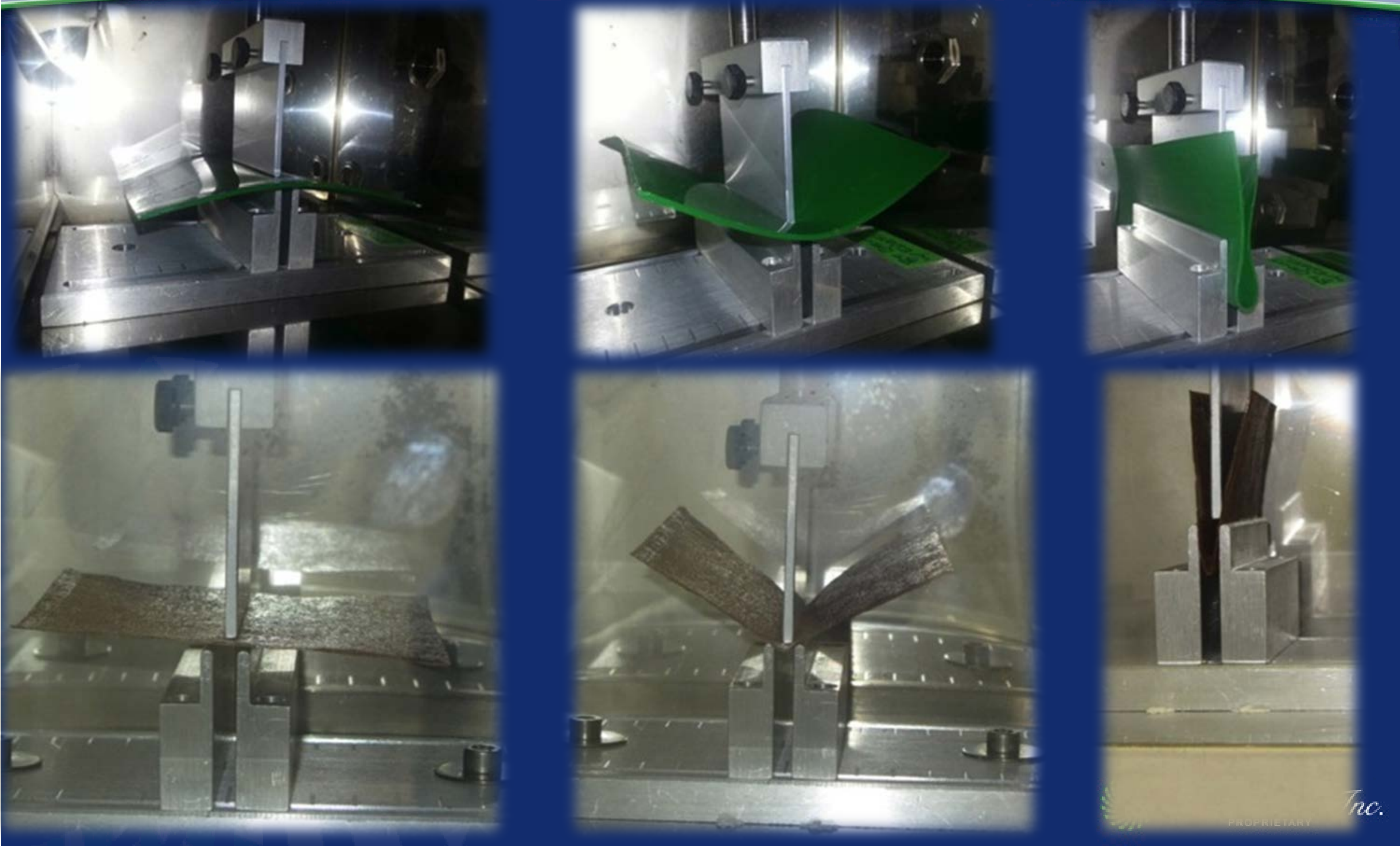
NanoSonic Triple Cold Flex Test for H_2 Permeance Specimens at -50 °C on Hose Materials: Shown Flat, Mid-Way, and at 180 ° Fold



Accomplishments in Measurements

Air and H_2 Permeance Pre- and Post -50 °C Triple Fold Flex Test

A study by Savannah River National Laboratory concluded there was no mechanism for degradation and/or embrittlement of several polymers by hydrogen gas alone

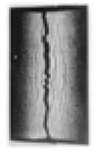
Air Permeance by ASTM D 1434

Sample No.	Thickness (in)	Air Permeance (cc/ 100in^2·Atm·day)
Set 4 - Lot # LB199-119		
AIR - 10A, 10B, 10C	0.01110	0.11 0.00 0.01 AV = 0.04 ± 0.06
AIR COLD - 10A, 10B, 10C	0.01110	0.12 0.09 0.11 AV = 0.11 ± 0.01

Hydrogen Permeance by ASTM D 1434

Sample No.	Thickness (in)	Hydrogen Permeance (cc/ 100in^2·Atm·day)
Set 4 - Lot # LB199-119		
Hydrogen - 10A, 10B, 10C	0.01060	0.29 0.22 0.20 AV = 0.24 ± 0.04
Hydrogen Cold - 10A, 10B, 10C	0.01100	0.36 0.35 0.20 AV = 0.31 ± 0.09

High-strength SS becomes brittle and fractures upon exposure to H_2



Lone hydrogen atoms diffuse through the metal, recombine in the matrix voids to form H_2, and create a pressure increase that leads to reduced ductility and tensile strength causing the metal to crack

Ferrosilicates are used to treat metals. NanoSonic uses a polymer fiber reinforced (rather than SS) low H_2 permeance HybridSil polymer matrix resin as the hose

Tests: ASTM F1459-06 and G142-98

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Accomplishments in Design

Ideal Burst Pressure of Composite H_2 Hose Based on Fiber Braid Alone

Inner Braid | **Outer Braid** | **Middle Braid** | **Inner and Outer Braids**

Barlow's formula:

$$P = 2\, s\, t / (d_o\, SF)$$

where

P = max. working pressure (psig)

s = material strength (psi) = 10.2×10^6 (Aramid fiber)

– yield strength = 522,000 psi

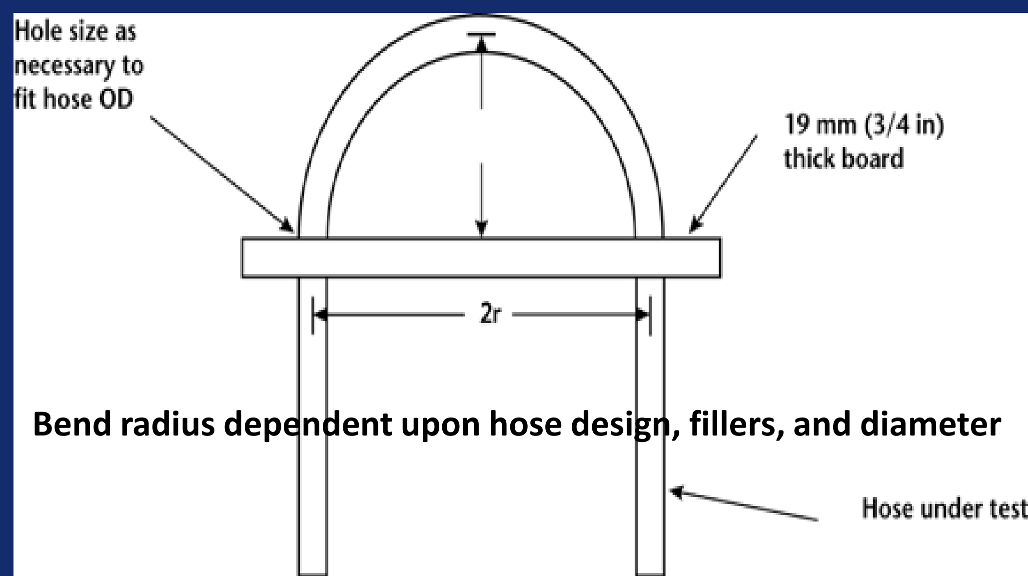
t = wall thickness (in) = 0.02” (Braid thickness)

d_o = outside diameter (in) = 0.563” (9/16”)

SF = safety factor (in general 1.5 to 10) = 1

Calculated maximum working Pressure 724000psi

37,129 psi (2560 Bar or 256 MPa)

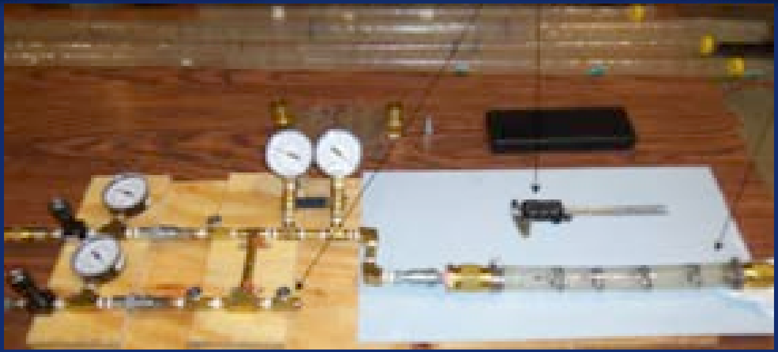


Bend radius dependent upon hose design, fillers, and diameter

Accomplishments in Production

Fiber Reinforced Hoses for In-House and 3rd Party Testing

Future Work
Inflation Testing in-House and at CSA



Hydrostatic Strength (section 2.4) of ANSI/CSA HGV 4.2-2013
Standard for hoses for compressed hydrogen fuel stations, dispensers and vehicle fuel systems
Requires a 1 min hold without burst or visible loss of fluid at a hydrostatic pressure of four (4) times the manufacturers specified maximum allowable working pressure (MAWP). Up to a 10,000 PSI MAWP hose assembly. Two (2) production assembly samples of each model at 12-inches length are required.

Pressure Cycle Test (section 2.17) of ANSI/CSA HGV 4.2-2013
Standard for hoses for compressed hydrogen fuel stations, dispensers and vehicle fuel systems
Requires 50,000 cycles with maximum allowable working pressure (assuming 10,000 PSI) at - 40°C and 50,000 cycles with maximum allowable working pressure (assuming 10,000 PSI) at 85°C followed by compliance testing to Leakage (section 2.2a) and Electrical Conductivity (section 2.5). Two (2) production assembly samples of each model hose length of "π(minimum bend radius) + 2(hose O.D.)" are required.

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Remaining Challenges and Barriers
Lifetime Prediction Testing via DMA Q800

Dual & Single Cantilever

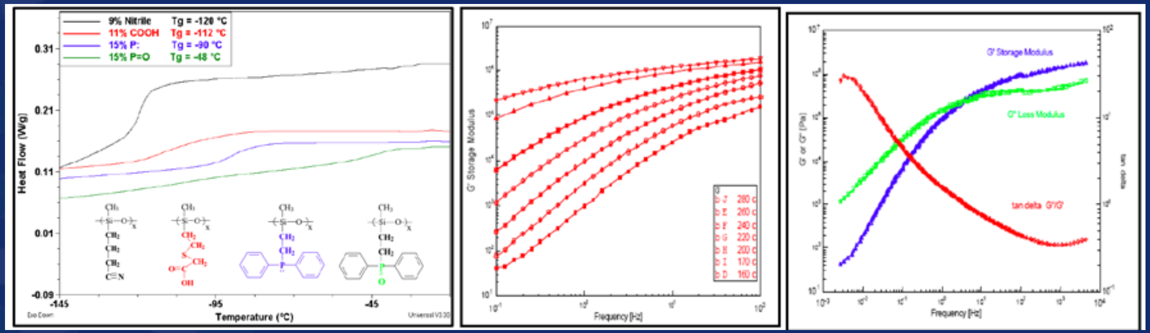
Viscoelastic properties measured dynamically over:

- Wide temperature (T) range
- Modest frequency (t) range

Modulus data is shifted to make master curves using:

- Arrhenius Equation
- Williams, Landel, Ferry (WLF) Equation

Film & Fiber Tension



3-point bend

Compression

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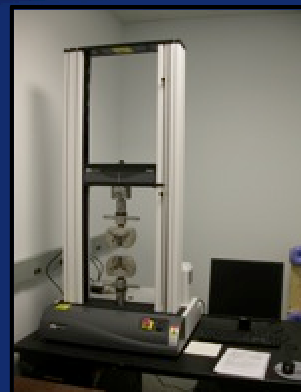
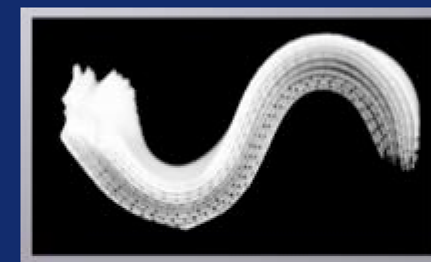
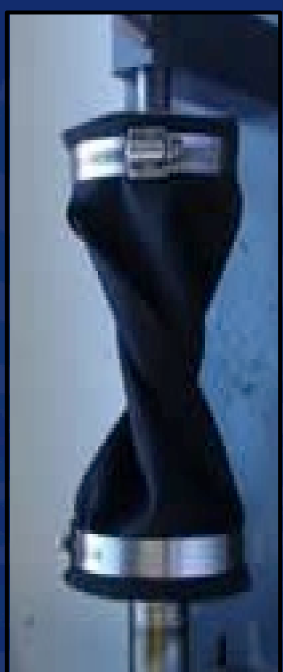
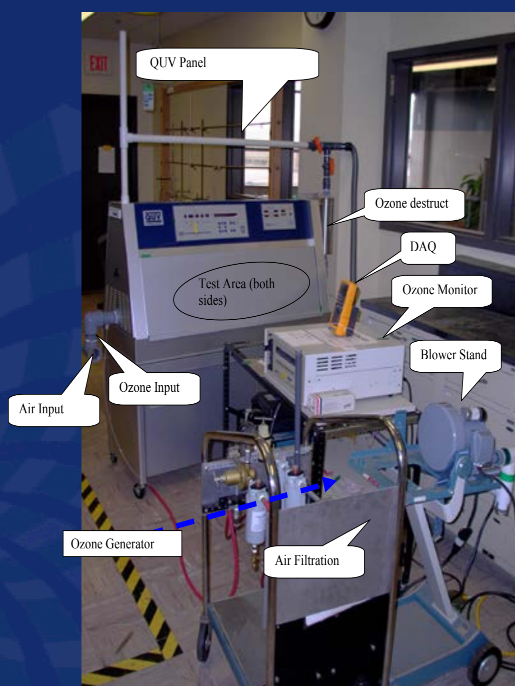
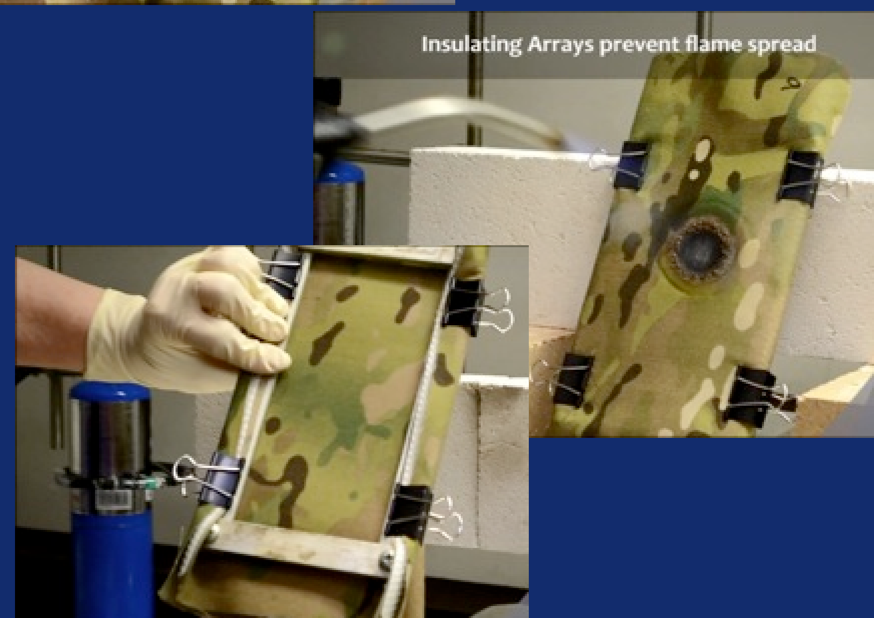
Mechanical and Environmental Testing & Fire Resistant Composites











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Extrude Flexhose at NanoSonic and with Partners

Collaborations and Cost Sharing

- CSA Group – Integrations Test Partner
- NREL – Qualification Test Partner
- Swagelok – Industrial Fittings Partner
- WEH USA – Integrator and Producer of Breakaway and H_2 Fueling Dispensers
- H_2 Stations in CA (60 current, visited several)
- Giles County Government – Manufacturing Facility Support
- Lockheed Martin – Dual-use Commercialization Needs for High Pressure Conduits

Funding Type	Source	Type	Amount	Years	Covers
Phase I SBIR	DOE	Cash	$100,000	2013	R & D, Prototype Design & Production
Phase II SBIR	DOE	Cash	$1,000,000	2014-2016	Product Engineering, Qualification
Phase III IDIQ	DOE & H2 Fueling Stations	Cash	$1,500,000	2017-2020	Purchase Order and Installation
Company Contribution	NanoSonic	Cash	$600,000	$200k annual	Commercialization and Marketing
Alliance Agreement	Lockheed Martin				
Partner Contribution	Hose Parts Partners				
County Contribution	Giles County	In-kind	$1,100,000	2010-2016	Manufacturing and Shipping
County Infrastructure	Giles County	In-kind	$7,500,000	2010	Infrastructure

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Project Summary

- Relevance: Need for durable and cost effective H_2 delivery hose that resists H_2 embrittlement, survives 25,550 fills for H70 service, cycled at pressures > than 875 bar over a range of -50 °C to 90 °C. A single competing hose exists on the market, though it does not meet the service requirements or allow for a cost of $2-4 gallon of gas equivalent.

- Approach: NanoSonic is developing a new class D hydrogen dispensing hose, for use on station side applications, systematically and chemically engineered to survive 51,240 fills (70 fills/day, 2 years). This state-of-the-art hose is based on a unique fiber reinforced, high performance, cryogenically flexible polymer to resist hydrogen embrittlement, survive the Joule-Thompson effect thermal cycles, perform consistently at pressures greater than 875-bar (H70 service, 700-bar and safety overpressure), and endure mechanical wear and fatigue at the pump.

- Technical Accomplishments: Developed a superior class of low T_g polymers that survived the harsh, triple fold cold flexure test. Down-selected materials for hose construction, which exhibited an ultra-low hydrogen permeance after severe 180° bending, three times in a -50°C chamber. This non-electrically conductive polymer was reinforced with an engineered fiber design and formed into hoses with a predicted burst pressure of 2560-bar, and an innovative path to dissipate static electricity.

- Proposed Future Research: During Phase II, a series of advanced, fiber reinforced, low temperature flexible and low hydrogen permeable hoses shall be evaluated per ANSI/CSA HGV 4.2-2013 for class D hoses to verify the safety, compatibility for hydrogen service, and weatherability. A hose shall be down-selected, transitioned from a Technology Readiness Level of 5–8, and presented to hydrogen hose partners (California dispensing stations and fittings/breakaway/fueling nozzle manufacturers) with a detailed integration design plan and cost analysis. The fully integrated hydrogen dispensing hose system, rated for H70 service, shall be demonstrated as compliant with SAE TIR J2601 and NIST Handbook 44, as a durable and competitive alternative to gasoline.

Scale-up of High Performance Polymer Resins, Composites and Hoses

50 and 200 gallon batches

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Questions and Acknowledgements

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DOE-EERE DOE Fuel Cell Technologies Office:
Grace Ordaz, Sunita Satyapal, Charles James, and Erika Sutherland (TPOC)

Phase II Integrators and Testing Facilities

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Outline

I. NanoSonic Background
   i. *Our Company*
   ii. *DOE Program*

II. H_2 Hose Production
   i. *Overview*
   ii. *Relevance*
   iii. *Approach - Materials Development*
   iv. *Accomplishments – Materials Testing and Hose Production*
   v. *Future Work - Test Plan*
   vi. *Collaborators*

III. Summary

METALRUBBER™

Our Company

HybridSil®

Metal Rubber™ and HybridSil®

Multifunctional Durable Materials

- Polymer and Small Molecule Synthesis
- Pilot-Scale Manufacturing
- Protective Coatings
- Sheet Stock Production
- Advanced Textiles
- Appliques
- RF Testing

Sustainability

- LEED Green Building
- Green Engineering
- Non-Toxic Products
- Community

Cost Effective H_2 Delivery

NanoSonic's Contribution: Flexible, Durable, Safe, H_2 Hose

DoE Topic 6 – HYDROGEN DISPENSER TECHNOLOGIES

Subtopic a – Dispenser Hose Assemblies

Goal for 2020: Develop a hose that enables H_2 delivery at < $4 per gallon of gas equivalent (gge) to promote fuel cell vehicles as an affordable alternative

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