2016 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office
Annual Merit Review and Peer Evaluation Meeting

Cryogenically Flexible, Low Permeability H_2 Delivery Hose

P. I.: Dr. Jennifer Lalli, President
NanoSonic, Inc.
6/9/2016

Project ID # **PD101**

Overview

Timeline
- Project Start Date: 7/28/2014
- Project End Date: 7/27/2016

Barriers
- Lack of H_2 / Carrier and Infrastructure Options
- Reliability and Cost of Gaseous H_2 Compression
- Reliability and Cost of Liquid H_2 Pumping
- Eliminate H_2 Embrittlement, Increase Durability

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

Partners
- CSA Group
- NREL
- Swagelok and Lillbacka
- New England Wire Technologies
- Shell and WEH USA
- Giles County Government

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Relevance:
Develop a H_2 Hose Dispenser for Fuel Cell Vehicles

Objectives:

- Develop: Flexible dispensing hose to enable H_2 delivery < $2/gge
- Demonstrate: Reliability at -50 °C and 875 bar for H70 service
- Optimize: Ruggedness, cost, and safety, 70 fills/day, > 2 years

Impact in April 2015 – April 2016:

- Produced: Low T_g, Low H_2 Permeability, Fiber Reinforced Hose with High Pressure Fittings
- Verified: Mechanical and Solvent Durability for H_2 Dispensing Stations

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Approach:

Develop Advanced Metal-free H_2 Hose Dispenser for Fuel Cell Vehicles

- **Technical**: Low T_g Hose Matrix Resin for Cryogenic, High Pressure Flexhose Service
- **Safety**: Low H_2 Permeability, Zero VOCs, and No Residual Monomer for EGA
- **Durability:** Fiber Reinforced to Eliminate H_2 Embrittlement and Optimize Burst Strength
- **Manufacturing**: Ceramer Crimping Agent to Match CTE/Modulus of Hose and Fitting
- **Cost:** lifetime against: Spir Star, Yokohama, ContiTech, Togawa, Aeroflex

Spir Star	Yokohama Rubber / Iwanti IG	Togawa Rubber	ContiTech	AeroFlex Hose & Engineering
6mmHydrogen -40 °C to 65 °C Steel H70	ibar HG_{70} H70	H35	Metal Corrugated core	750 bar H_2

Approach:
Project Phases and Selected Milestones

Define and Evaluate FY14 – FY15 Q2
critical performance metrics, components, partners, materials, and deployable design

Test Prototype FY15 Q2-Q3
hose/fittings with H_2 under service Pressure, temperature, and mechanical

Qualify FY15 Q4 – FY16 Q3
H70/H35 hose with OEM dispenser/nozzle for safety and environmental durability

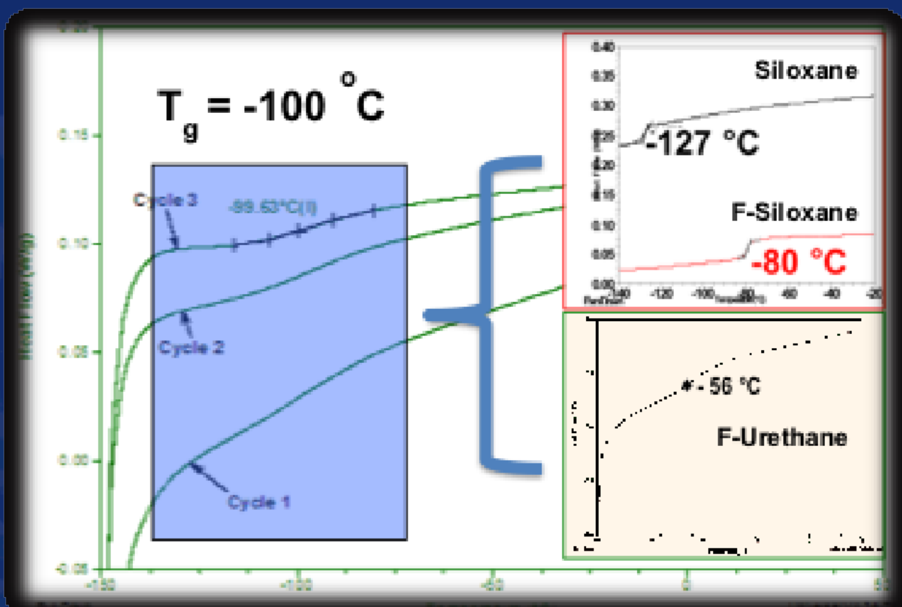
Deploy FY16 Q4
H70/H35 hose at H_2 stations

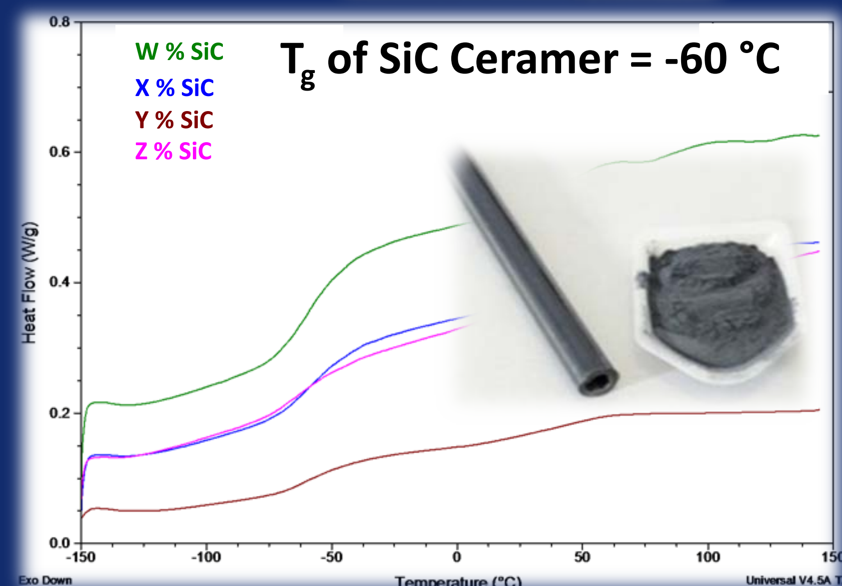
Critical Criteria

- Low T_g for expected -50 °C dispensing
- Surpass 875 Bar hydrostatic strength and pressure cycle testing
- No contaminant leaching
- Competitive cost, mechanical durability, and environmental lifetime

Accomplishments in Cryogenic Service

1. siloxane backbone – low T_g for cryogenic flexibility
2. urethane component – amine bonding to reinforments
3. fluorinated siloxane – UV, ozone, and atomic oxygen
4. tailored molecular weight (M_n) - extrusion manufacturing
5. Low T_g ceramer - durable polymer / fitting connection





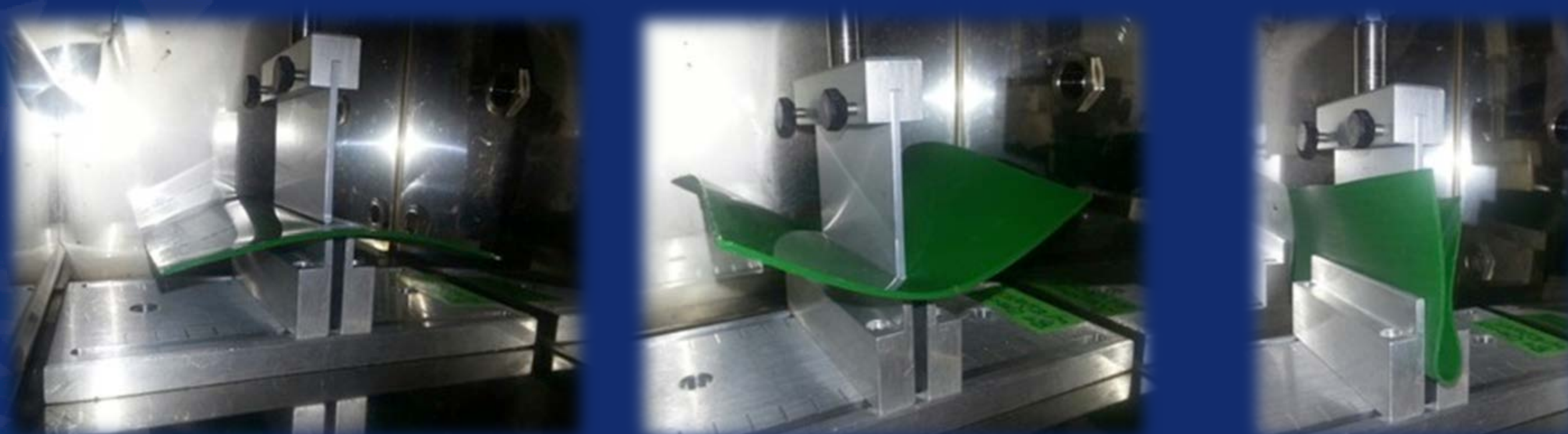
Low T_g polymer matrix resin and ceramer with verified low off-gassing has been engineered, and tested for long-term use as the flexible hose material and coupling agent

Accomplishments in Low H_2 Permeance

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

H_2 Test Permeance, ASTM D 1434, Polyhedron Laboratories®

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



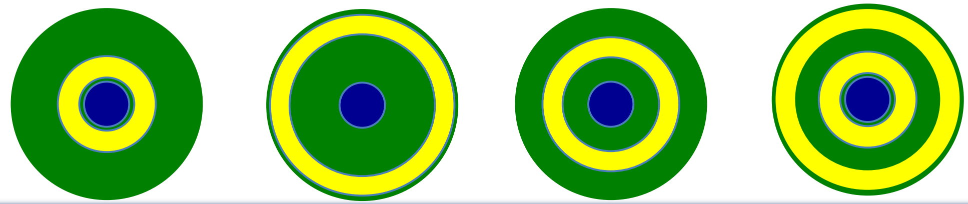
The hose material exhibits ultra low H_2 permeance before and after being subjected to the harsh 180 ° triple fold, cold flex test, conducted at -50 °C

Accomplishments in Mechanical Durability:

Fiber Reinforcement : $P = 2\ s\ t\ /\ (d_o\ SF) = 1705$ bar or 24,725 psi

	Polymer 1 - Kevlar	Polymer 1 - Spectra	Polymer 1	Down-Select Fiber & Design
	IB	IB	down-select fiber and design	Polymer 2
Clause 2.4	OB	OB		Polymer 3
	MB	MB		Polymer 2 + fill
	I/OB	I/OB		Polymer 3 + fill

	Down-Selected Polymer & Fiber
	IB
Clause 2.17	OB
	MB
	I/OB



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

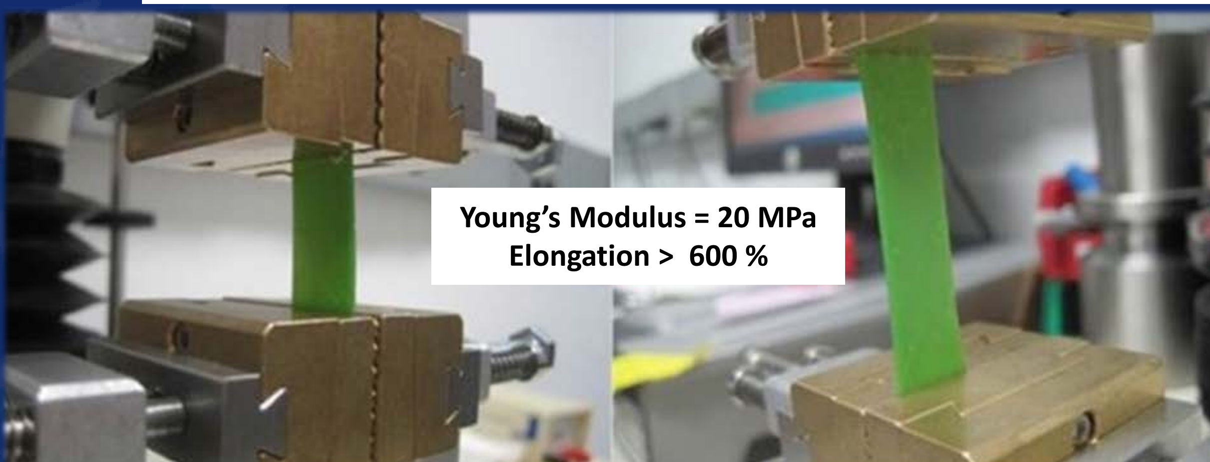
NanoSonic's all-polymer, fiber reinforced hose survives the triple cold flex test and has a predicted burst strength of 1705 bar. The design will be selected per pressure testing.

Challenges in Manufacturing

<u>ANSI/CSA HGV 4.2-2013: Clause 2.4 Hydrostatic Strength</u>

- NanoSonic hose Swagelok ¼-inch compression tube fitting
- Fixtured in the Hydraulic Burst Chamber
- Pressurization rate was set for 14500 psi/min
- Pressure Transducer (CSA asset Z00001141 – Viatran transmitter)
- Pressure Gauge (CSA asset PG-74 – Astragauge analog)

Sample:	Failure Pressure (PSIG):	Comments:
LB199-157-2	2,073	hose assembly pulled out of end connections
LB199-157-3	1,082	hose assembly pulled out of end connections
LB199-159-1	985	hose assembly leakage past end connections
LB199-164-2B	223	hose assembly pulled out of end connections



Young's Modulus = 20 MPa
Elongation > 600 %

The tough low T_g, low modulus hose posed a crimping challenge that is being addressed though chemistry, hose/fiber design, and crimping techniques

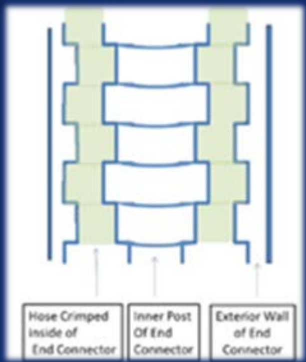
Accomplishments in Manufacturing: Reinforced with Ceramer Coupling Agent

SiC Ceramer adhesion promoter
for crimped fitting

Test ID	Hose	Length (inch)	Fitting Manufacturer	Fitting OD	Ceramer in Hose	Ceramer at Fitting	Burst Pressure (psi)
WH208-8C	A	17	1	proprietary	x		6446
WH208-8D	A	17	1	proprietary	x	x	8334
WH208-8E	A	17	2	proprietary	x		4304
WH208-8F	A	17	2	proprietary	x	x	7016
WH208-9A	B	17	1	proprietary			52959
WH208-9B	B	17	1	proprietary		x	58440
WH208-9C	B	17	2	proprietary			9635
WH208-9D	B	17	2	proprietary		x	26136

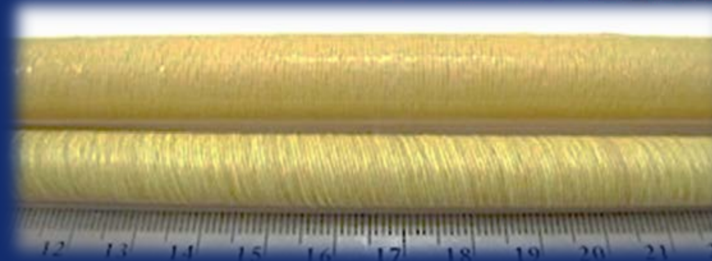
Ceramer significantly increases burst strength as a coupling agent with the fitting

New Challenges in Manufacturing



Bonding /crimping in-house yields a complete product, but challenges in procuring optimal fitting.

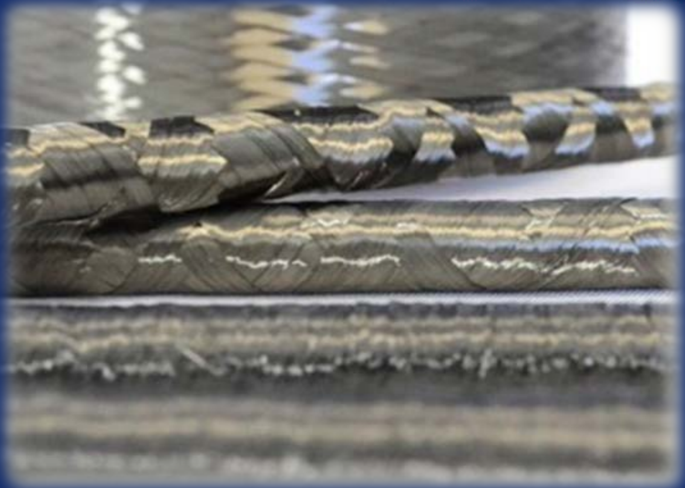
Accomplishments in Fiber Reinforcements



Sample:	Failure Pressure (PSIG)	Comments:
POMKWrap-1	10300	Hose assembly pulled out of end connections
POMKWrap-3	7200	Hose assembly pulled out of end connections
POMKWrap-7	8100	Hose Rupture
POMKWrap+Spectra	16700	Hose Rupture
POMWeave	15100	Hose assembly pulled out of end connections
SpirStar	21200	Hose assembly pulled out of end connections

Kevlar fiber weave doubles burst strength relative to wrap
Kevlar wrap (4 layers) yields 80% burst strength of metal wrap (8 layers)

Accomplishments in Carbon Fiber Reinforcements



Bob Norris in Carbon and Composites Group, ORNL and Craig A. Blue, CEO, IACMI-The Composites Institute, Knoxville, TN

Sample:	Failure Pressure (PSIG)	Comments:
POMCFWrap-32A	8300	Hose Burst
POMCFWrap-39A	9100	Hose assembly pulled out of end connections
POMCFWeave	9400	Hose Burst
POMCFWeave	11030	Hose Burst
SpirStar	21200	Hose assembly pulled out of end connections

Carbon fiber weave exhibits 20% greater burst strength relative to wrap
Carbon fiber weave (0.5 mm thick) yields ~ 50% strength of metal wrap (1.25 mm thick)

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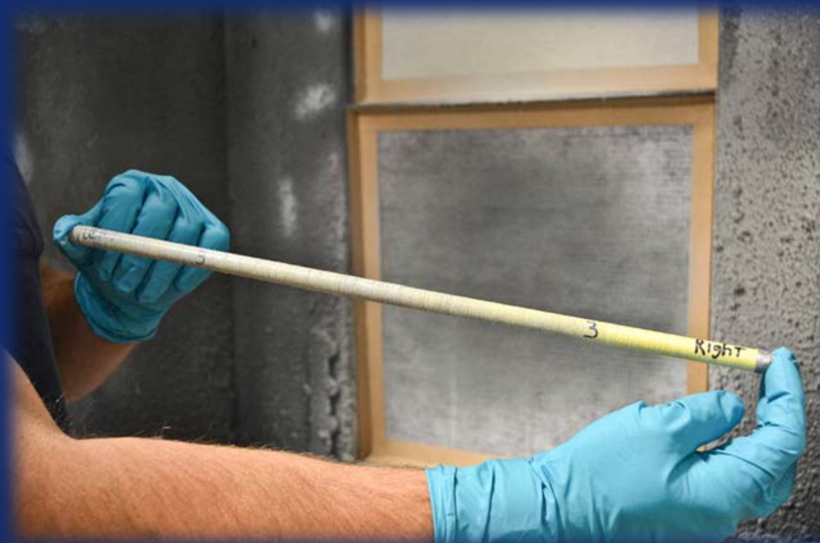
Technical Accomplishments: Cost

Innovative Approach and In-house Manufacturing Enables Competitive and Cost Advantage at Any Scale

- Current projected cost at 300 meter with fittings is 2x less than qualified German competitor
- Cost normalized for lifetime predicts a 4x savings
- Proprietary scale-up method for hose production length may lead to an 8x savings for 600 meter



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Collaborations and Cost Sharing

1. **CSA Group**
   - Testing – briefing at CSA on 11/6/14
2. **National Renewable Energy Laboratories (NREL)**
   - Prototype evaluation – subcontract executed on 11/4/14
3. **Swagelok**
   - Fittings - ongoing consulting on fittings and high pressure hoses
4. **Lillbacka**
   - Hose crimping – purchased crimper on 1/03/15
5. **WEH USA**
   - Integration – breakaway connector and H_2 fueling nozzle
6. **New England Wire Technologies**
   - Prototype manufacturing – subcontract executed on 10/29/14
7. **Giles County Government**
   - Local large scale manufacturing support and architecture for 100ksf building

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				Product Validation
Partner Contribution	Hose Parts Partners				Porduct Integration
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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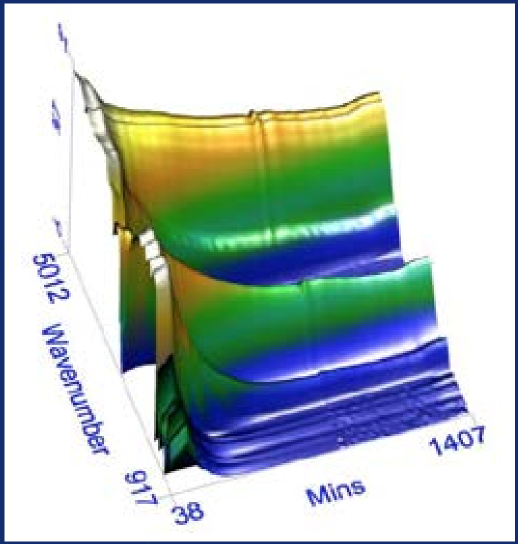
Future Work: Durability and Quality

ANSI/CSA HGV 4.2-2013: Hoses for Compressed H_2 Fuel Stations, Dispensers and Vehicle Fuel Systems

SAE J2719: H_2 Fuel Quality for Fuel Cell Vehicles

- **Mechanical**: Pull-Out Strength of Crimp/Hose and and pre- post- stress strain morphology at NREL
- **Hydrostatic Strength 2.4**: 1 min hold without burst at hydrostatic pressure of 4 times the maximum allowable working pressure (MAWP), up to 10,000 PSI MAWP
- **Pressure Cycle 2.17**: 50,000 cycles at MAWP at -40 °C and 50,000 cycles at 85 °C followed by compliance testing to Leakage and Electrical Conductivity
- **Hydraulic Pulse**: testing conducted up to 14,500 psig at 1Hz with a fluid temperature up to 150 °C
- **Evolved Gas Analysis**: and leak monitoring to ensure that the hose will not compromise H_2 quality per the SAE J-2719 and ISO/PDTS 14687-2 specs, where Minimum Fuel Cell Grade H_2 = 99.99%, total impurities < 100 ppmv, and total impurities < 100,000 ppb



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Future Work: Scale-up Resins in-House

NanoSonic has 50 and 200 gallon batch reactors to scale-up hose and ceramers for cost savings

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Remaining Challenges and Barriers: Hose Qualification & Deployment

- Challenge: Deployment date of FY16 Q4 because of delayed pressure testing due to fittings
- Resolution: Obtained fitting crimper and developed innovative ceramer technology
- Benefit: Ceramer inclusion may surpass durability of all current or future competitors
- Benefit: Investigating new non-metal reinforcing materials and designs

McCLEAN ANDERSON®

Filament Winder System

Improve Understanding
Of Crimping Techniques

Hydraulic Test Chamber

Pneumatic Test Chamber

Project Summary

- **Relevance**: Durable and cost effective H_2 delivery hose that resists H_2 embrittlement, survives 25,550 fills/year for H70 service, cycled at pressures > than 875 bar over a range of -50 °C to 90 °C. A single qualified hose exists.

- **Approach**: NanoSonic's all polymer new class D hydrogen dispensing hose, for use on H70 station side applications, is chemically engineered to survive 51,240 fills, resist H_2 embrittlement, survive Joule-Thompson effect, and endure mechanical fatigue at the pump. Innovative SiC ceramer adhesive is under development to enhance fitting durability

- **Technical Accomplishments**:
  - Developed low T_g hose that demonstrates ultra-low hydrogen permeance after 180° bending, three times in a -50°C chamber
  - Kevlar and carbon fiber reinforced hose approached burst pressure of metal wrap
  - Innovative ceramer coupling agent enhances crimp survivability
  - Reduced cost via scale-up

- **Proposed Future Research**: Evaluate new fiber wraps with multiple fittings. Present H_2 hose partners (dispensing stations and fittings/breakaway/fueling nozzle OEMs) with integration and cost. H70 hose compliant with SAE TIR J2601 and NIST Handbook 44, as a durable cost effective alternative to gasoline

Questions and Acknowledgements

This material is based upon work supported by the Department of Energy under Award No. DE-SC0010162

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Phase II Integrators and Testing Facilities