III.12 Cryogenically Flexible, Low Permeability H_2 Delivery Hose

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- National Renewable Energy Laboratory, Golden, CO
- Swagelok, Solon, OH
- New England Wire Technologies, Inc., Lisbon, NH

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Overall Objectives

NanoSonic's overall objectives for hydrogen dispenser technologies mirror those of the Office of Energy Efficiency and Renewable Energy (EERE) Fuel Cell Technologies Office for hydrogen delivery to enable the widespread commercialization of hydrogen and fuel cell technologies. Outcomes of this project will include:

- A highly durable hose that can reliably perform at 875 bar (for H70 service, 70 MPa delivery) and over a temperature range of -50°C to +90°C
- A new Class D hydrogen dispensing hose, for use on station side applications, that is chemically engineered to survive 51,240 fills (70 fills/d, 2 yr) and meets the requirements outlined in American National Standards Institute (ANSI)/Canadian Standards Association (CSA) Hydrogen Gas Vehicle (HGV) 4.2-2013, with a dispenser compliant with SAE Technology Information Report J2601 and National Institute of Standards and Technology Handbook 44
- A state-of-the-art, metal-free hose based on a unique fiber reinforced, high performance, cryogenically flexible polymer to resist hydrogen embrittlement, that can survive the Joule-Thompson effect thermal cycles, perform consistently at pressures greater than 875 bar, and endure mechanical wear and fatigue at the pump
- The first U.S. supplier of hydrogen dispenser hoses qualified for H70 service

Fiscal Year (FY) 2016 Objectives

- Quantify the burst strength of the new hydrogen hose.
- Down-select a metal-free, fiber reinforced hose.
- Optimize the durability via pressure cycle testing.
- Demonstrate environmental durability and delivery of fuel cell grade hydrogen with total impurities <100,000 ppb.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section (3.2.5) of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(I) Other Fueling Site/Termination Operations

Technical Targets

The goals of this project mirror those of EERE to advance hydrogen delivery system technologies toward the DOE hydrogen delivery 2017 delivery targets [1]. NanoSonic has reduced the cryogenic flexibility of our hydrogen delivery hose by decreasing the glass transition temperature (T_g) to -100°C, and increasing upper thermal stability to 350°C (5% weight loss via thermogravimetric analysis [TGA]). This will enable a significantly wider service use temperature range than the competitor's hose with a service temperature range of -40°C to +65°C. Burst strength has been increased from 2,000 psi to 9,000 psi during first quarter testing by crimping hose fittings in-house. The burst strength will be increased in 2015 to 51,000 psi, four times the maximum allowing working pressure of 12,690 psi by a modification of the fiber–polymer interface design, and through the use of a fitting rated for >5,000 psi. Compression strength has been increased from 10 kN to >50 kN (>11,200 lb) through the use of a novel ceramer enhancement. Solvent and abrasion resistance are being tested per the targets outlined in ANSI/CSA HGV 4.2-2013; and evolved gas analysis and quality are being tested per the targets outlined in SAE J-2719 and International Organization for Standardization PDTS 14687-2. Current cost projections based on materials for 300 m of hose are two times less than the current technology. Cost savings based on durability; normalized for lifetime, predict a 4x savings. NanoSonic's planned scale-up method predicts an 8x cost savings normalized for lifetime and 600 m hose, per targets given in Table 1.

TABLE 1. Progress towards Meeting Technical Targets for Durable Hydrogen Hose for Fuel Cell Vehicles

Characteristic	Units	2017 Targets	NanoSonic
Tg for Cryogenic Service Temperature	°C	-50	meets
TGA 5% Weight Loss for Upper Service Temperature	°C	90	meets
Burst Strength	psi	51,000	>16,500
Cycle Pressure Test	cycles	50,000 cycles at MAWP at -40 °C and 50,000 cycles at 85 °C	in progress
Compression Strength	psi	12,690	>11,200
Hose Cost	$/m	< 200	<60

MAWP - maximum allowable working pressure

FY 2016 Accomplishments

- Developed low T_g (-100°C) hose with 5% weight loss at 350°C with ultra-low hydrogen permeance after 180° bending, three times in a -50°C chamber.
- Kevlar and carbon fiber reinforced hoses approached burst pressure of metal wrap.
- Innovative ceramer coupling agent enhances crimp survivability.
- Ceramer coupling agent developed for enhanced crimp survivability and increased compression strength, which exhibits compression strength >11,200 psi.
- Reduced cost to $300/m via scale-up.
- Collaborating with gas distribution original equipment manufacturers, fittings manufacturers, national laboratories, and safety standards groups to qualify the hose for H70 service.

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INTRODUCTION

NanoSonic is developing and manufacturing a cost effective new hose to offer reliable delivery of hydrogen for fuel cell vehicles as a safe, reliable, and cost competitive replacement for gasoline per EERE Fuel Cell Technologies Office for hydrogen delivery goals. This American made hose will meet EERE technical targets to enable the hydrogen economy through enhanced safety and durability. There is a need for a highly durable hose that can reliably perform at 875 bar (for H70 service, 70 MPa delivery) and over a temperature range of -50°C to +90°C.

NanoSonic has worked during this DOE Small Business Innovative Research program to produce a new Class D hydrogen dispensing hose, for use on station side applications. NanoSonic's hose was systematically and chemically engineered to survive 51,240 fills, or 70 fills/d for a period of at least two years. Our 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, and endure mechanical wear and fatigue at the pump. Currently, there is only one hydrogen dispenser hose that qualified for H70 service. This non-U.S., German made hose from Spir Star, is rated for a working pressure of 875 bar, though it does not meet the service requirement of 25,550 fills/yr, nor does its price allow for a cost of $2–4 gallon of gas equivalent.

APPROACH

The new hydrogen hose involves an all polymer material approach in contrast to the currently qualified hose that utilizes steel as its reinforcing agent. The unique polymer fiber reinforcement design shall meet the current burst strength requirements, and surpass the durability of steel based hoses which are susceptible to weakening and catastrophic failure via hydrogen embrittlement. NanoSonic's 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 (for H70 service, or 700 bar with a safety overpressure), and endure mechanical wear and fatigue at the pump. The polymer core is based on an ultra-low T_g backbone for cryogenic flexibility and modified for adhesion to the fiber reinforcing agents and ceramer inclusions for enhanced compression strength.

NanoSonic's manufacturing approach towards cost savings and enhanced durability is three-fold. First, a unique three-dimensional mold allows for tailored designs from the inner high pressure stable core to the fiber reinforced placement, and the outermost abrasion and solvent resistant jacket. Second, NanoSonic has two large scale reactors that allow for the cost effective production of 55-gal and 200-gal drum batches of our nanocomposite resins. Finally, NanoSonic has invested in a crimper to integrate the end connection fittings directly onto our hoses. This allows for enhanced adhesion and mechanical fit between the fitting and the hose. Crimping in-house also yields a product with complete fit and finish for qualification and distribution.

RESULTS

NanoSonic's major focus during FY 2016 is on unique fiber reinforcement designs and fittings to our hoses for hydrostatic strength and pressure cycle testing. The 2016 hoses are shown in Figure 1. Previously, NanoSonic delivered hoses to Swagelok for crimping. The low modulus hoses pulled out of the fitting during hydrostatic strength tests at CSA Group per Clause 2.4 in the hydraulic burst chamber, per the set up shown in Figure 2. The pressurization rate was set for 14,500 psi per minute. Failure pressure ranged between 200 psig to 2,100 psig, whereas the target value is four times (51,000 psi) the maximum allowable working pressure of 12,700 psi (875 bar) for H70 (70 MPa) service. Our Phase II fittings partner at Swagelok recommended that NanoSonic consider doing the fittings installation in house due to time constraints on their end. NanoSonic purchased a crimping machine from the recommended supplier. The crimper allows for installation of various dies for diameters down to 4 mm. NanoSonic owns crimping dies #12, 14, and 16 for an outer diameter (OD) crimping range of 12 mm to >19 mm.

NanoSonic produced hoses fitted with end connectors that were 15 in in length, as determined by the bend radii or as specified by the evaluating experiment scheduled at CSA laboratory. CSA was contracted to perform the two rounds of pressure evaluations on NanoSonic's high pressure hoses. The scheduled tests were (a) hydrostatic strength and (b) pressure cycle test. The description of each test is described below.

a. 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 times the manufacturers specified MAWP. Up to a 10,000 psi MAWP hose assembly. Two production assembly samples of each model at 12-in length are required.

b. 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 MAWP (assuming 10,000 psi) at 85°C followed by compliance testing to Leakage (Section 2.2a) and Electrical Conductivity (Section 2.5). Two production assembly samples of each model hose length of "π(minimum bend radius) + 2(hose OD)" are required.

FIGURE 2. NanoSonic hose in hydrostatic burst strength test configuration

CSA Group evaluated a new series of hoses given in Table 2 for hydrostatic burst strength, as a function of fitting as shown in Figure 3. The hydrostatic burst results here demonstrate that the ceramer is a beneficial additive in all cases as a coupling agent between the fittings and hoses (both NanoSonic and Spir Star), and with each type of fitting, as shown in Figure 4. The Swagelok fitting survived >50,000 psi with the Spir Star hose, though the DHH fitting did not. In future deliverables, NanoSonic shall continue with

FIGURE 1. NanoSonic's hydrogen delivery hoses demonstrating cryogenic flexibility

TABLE 2. CSA Group Hydrostatic Burst Pressure Data

Test ID	Hose Material	Length (inch)	Fitting Manufacturer	Fitting O.D. (mm)	Ceramer in Hose	Ceramer at Fitting	Burst Pressure (psi)
WH208-8A	NanoSonic	17	Swagelok	15.9	NO	YES	7,081
WH208-8B	NanoSonic	17	DHH	15.9	NO	YES	8,306
WH208-8C	NanoSonic	17	Swagelok	15.9	YES	NO	6,446
WH208-8D	NanoSonic	17	DHH	15.9	YES	NO	4,304
WH208-8E	NanoSonic	17	Swagelok	15.9	YES	YES	8,334
WH208-8F	NanoSonic	17	DHH	15.9	YES	YES	7,016
WH208-9A	Spir Star	17	Swagelok	15.9	NA	NO	52,959
WH208-9B	Spir Star	17	DHH	15.9	NA	NO	9,635
WH208-9C	Spir Star	17	Swagelok	15.9	NA	YES	58,449
WH208-9D	Spir Star	17	DHH	15.9	NA	YES	26,136

FIGURE 3. NanoSonic hydrogen hoses with varied fittings

the Swagelok fittings. Additionally, the ceramer fill within the entire hose did not enhance the compression strength, but rather weakened the polymer matrix due as potentially anticipated. Finally, the hose formulation was developed to survive extreme cold. Thus, the elastomeric matrix has a very low T_g, of ~ -100°C. This will need to be increased in the next deliverable set as the material does not exhibit the toughness required to survive >50,000 psi.

NanoSonic revised our metal-free hose design to include a series of materials with unique fibers. While the specific designs are proprietary, the data is given in Table 3. It was found that our weaves exhibits double the burst strength relative to wraps, and that our X layer system yields 80% burst strength of metal wrap having eight layers. Additionally, two of our weaves at X mm thick yields ~50% strength of metal wrap with a 1.25 mm thickness.

FIGURE 4. NanoSonic hydrogen hose with ceramer technology

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions derived from the work in FY 2016 are:

- NanoSonic is currently testing our hose with fittings against the Spir Star hose for hydrostatic burst strength and pressure cycling.
- We will also be testing our hose against emerging potential commercial competitors, such as Yokohama Rubber and Iwatani Industrial Gases, ContiTech, and Togawa Rubber. Yokohama's hose is rated for 70 MPa

TABLE 3. CSA Group Hydrostatic Burst Pressure Data

Sample	Failure Pressure (psig)	Comments
Nano4A	16700	Hose Rupture
Nano5A	1510	Hose assembly pulled out of end connections
Nano2B	9100	Hose assembly pulled out of end connections
Nano4B	11030	Hose Burst
SpirStar	21200	Hose assembly pulled out of end connections

and the Togawa hose is rated for 35 MPa. There are few details given for ContiTech products.

- Environmental robustness and fuel quality is being established through testing with CSA and National Renewable Energy Laboratory.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. Jennifer Lalli, "Cryogenically Flexible, Low Permeability H_2 Delivery Hose," *DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting, 2016.*