III.6 Cryogenically Flexible, Low Permeability H_2 Delivery Hose

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Contract Number: DE-SC0010162

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

Project Start Date: July 28, 2014
Project End Date: August 27, 2016

Overall Objectives

NanoSonic's overall objectives for Hydrogen Dispenser Technologies mirror those of the Department of Energy Office of Energy Efficiency & Renewable Energy (DOE-EERE), Fuel Cell Technologies Office (FCTO), and Hydrogen Delivery Program to realize hydrogen as a safe, reliable, and cost competitive replacement for gasoline. 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 per day, 2 years) and meets the requirements outlined in American National Standards Institute/Canadian Standards Institute (ANSI/CSA) Hydrogen Gas Vehicle (HGV) 4.2-2013, with a dispenser compliant with Society of Automotive Engineers (SAE) Technical Information Report (TIR) J2601 and National Institute of Standards and Technology Handbook 44.
- A state-of-the-art hose based on a unique fiber reinforced, high performance, cryogenically flexible polymer to resist hydrogen embrittlement, survive the Joule-Thompson effect of thermal cycles, perform consistently at pressures greater than 875 bar, and endure mechanical wear and fatigue at the pump.
- An alternative to the singular German-made hydrogen dispenser hose that is currently qualified for H70 service, though it does not meet the service requirement of 25,550 fills/year, nor allow for a dispensed hydrogen cost of $4 per gallon of gasoline equivalent (gge).

Fiscal Year (FY) 2015 Objectives

- Quantify the burst strength of the new hydrogen 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 barrier from the Hydrogen Delivery section (3.2.5) of the FCTO Multi-Year Research, Development, and Demonstration Plan:

(I) Other Fueling Site/Termination Operations

Technical Targets

The goals of this project mirror those of the DOE-EERE to advance hydrogen delivery system technologies toward the DOE Hydrogen Delivery Program's 2017 delivery targets [1]. NanoSonic has increased the cryogenic flexibility of our hydrogen delivery hose by decreasing the glass transition temperature (T_g) to -65°C, and increasing upper thermal stability to 350°C (5% weight loss via thermogravimetric analysis (TGA). These modifications 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 was 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 (ISO)/TS 14687-2. Current cost projections based on materials for 300 meters of hose are two times less than the competitor's price. Cost savings, normalized for lifetime, predict a 4x savings. NanoSonic's planned scale-up method predicts an

8x cost savings, assuming batch production of 600 m of hose and normalizing for the hose life.

The NanoSonic hose is being designed to meet or exceed the requirements of ANSI/CSA HGV 4.2-2012 for Class D hoses for 700-bar dispensing. Table 1 describes NanoSonic's hose performance.

TABLE 1. Technical Performance of Durable Hydrogen Hose for Fuel Cell Vehicles

Characteristic	Units	NanoSonic
T_g	°C	-60
Upper Service Temperature (Corresponding to Weight Loss of 5%)	°C	350
Burst Strength	psi	>9,000 (24,730 expected)
Cycle Pressure Test	cycles	in progress
Cost	$/m	<60

FY 2015 Accomplishments

- Developed low T_g (60°C) hose with an upper service thermal stability of 350°C that demonstrates ultra-low hydrogen permeance after 180° bending, three times in a -50°C chamber
- Fiber-reinforced hose has a predicted burst pressure of 1,705 bar
- Developed unique ceramer coupling agent for enhanced crimp survivability and increased compression strength, >11,200 psi
- Reduced cost to $60/m via scale-up
- Collaborating with gas distribution original equipment manufacturers, fittings manufacturers, national laboratories, and safety standards groups to qualify the hose and bring it to market 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 the FCTO Hydrogen Delivery goals. This American-made hose will meet the DOE-EERE's FCTO 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 Innovation 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 per day 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 is qualified for H70 service. This hose is not manufactured in the United States and does not meet the service requirement of 25,550 fills/yr or enable a dispensed hydrogen cost of $4/gge.

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 that 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 gallon and 200 gallon drum batches of our nanocomposite resins. Finally, NanoSonic has invested in a crimper to integrate the end connection fittings directly onto our hoses. This design 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 2015 is on fittings' attachment to our hoses for hydrostatic strength and pressure cycle testing. The 2015 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 Section 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 200–2,100 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 crimping range of 12 mm to >19 mm.

NanoSonic purchased several types of materials to begin crimping with, including Swagelok fittings and carbon steel pipe. Our local distributor representative from Dibert Valve and Fittings recommended we begin with Swagelok compression tube fittings, end tub stub, and compressed natural gas hose ends with dimensions to accommodate our initial design. NanoSonic also purchased carbon steel pipe with similar dimensions as inexpensive option to begin with. Our partners at Swagelok conducted the initial crimping, and NanoSonic followed suit, though with our own crimp procedure, to yield a series of varied crimped dimensions, as shown in Table 2.

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

Pull-out tests were conducted on NanoSonic's crimpled hoses using our benchtop loadframe. The texture analyzer has an upper load limit of 50 kg (110 lb). It was found that significant crimping results in increased stress on the low modulus polymer. In this case, the materials failed prior to pull-out. An optimized crimp could not be pulled from the hose just beyond the maximum force of the loadframe at 120 lb. NanoSonic also owns an Instron with an upper load limit of 50 kN, although the grips are not wide enough to accommodate the hoses. We have ordered two sets to allow for pull-out and pulley-style tensile testing.

NanoSonic developed a unique ceramer for use as an adhesive between the fitting and hose to offer additional

FIGURE 2. NanoSonic hose in hydrostatic burst strength test configuration

TABLE 2. Dimensions before and after Crimping

Crimper	Material	OD 1 (mm)	OD 2 (mm)	WT 1 (mm)	WT 2 (mm)	ID 1 (mm)	ID 2 (mm)
Swagelok	Swagelok SS	20	18	1.5	1.61	16.3	16.2
NanoSonic	Swagelok SS	20	16	1.5	1.64	16.3	13.6
NanoSonic	CS Pipe	22.3	15, 16, 17, 18, 19	3.1	3.2–4.7	16	8.9–6.7
NanoSonic	CS Pipe		19.4		3.5		12.4

SS – stainless steel; CS – carbon steel; ID – inside diameter; OD – outside diameter; WT – wall thickness chemical strength beyond the mechanical strength of crimping alone. The adhesive-ceramer is a viable candidate as it also exhibits a wide service temperature range, with a low T_g of -60°C and exhibits 5% weight loss beyond 320°C.

Compression testing was conducted on NanoSonic's down-selected hose polymer and the proposed adhesive-ceramer material to establish feasibility for the high pressure testing. NanoSonic has designed a testing procedure in accordance with ASTM D 695: Standard Test Method for Compressive Properties of Rigid Plastics for materials greater than 3.2 mm thick. This testing was completed on NanoSonic's Instron load frame that has a 50 kN load cell, in conjunction with extensometer/compressometer. The exact cross-sectional area of all specimens was measured prior to testing, to ensure an accurate strength calculation. After the cross section of each specimen is measured, the samples are then be placed between two flat steel plates that are attached to the clamps of the Instron load frame. The cross-head is then moved at a constant rate of 1.3 mm/min until the compressive load begins to drop off. Three specimens for each sample set are tested. Data is given in Table 3, and materials are shown in Figure 3.

NanoSonic fabricated and delivered several hoses to Swagelok for fitting with end connectors. The down-selected prototype hydrogen dispensing hoses were of made using two different copolymers. These copolymer compositions are proprietary and the composition has proved to be influential on the flexibility and toughness of prototype hoses as well as the measured hydrogen permeability.

The hoses fitted with end connectors were 15 inches 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 4.2-201 Standard for hoses for compressed hydrogen fuel stations, dispensers and vehicle fuel systems requires the following.

TABLE 3. Compression Testing on NanoSonic Hose and Adhesive with Ceramer

Material	Thickness (mm)	Displacement at Peak Load (mm)	Peak Load (kN)
Hose Control 1	6.14	-6.39	11.67
1-X % Ceramer	6.81	-6.87	22.02
1-Y % Ceramer	5.89	-5.97	2.73
1-Z % Ceramer	4.85	-4.86	23.54
Hose Control 2	5.43	-5.53	47.12
2-X % Ceramer	7.28	-6.89	52.50
2-Y % Ceramer	6.53	-5.86	51.38
2-Z % Ceramer	5.18	-3.85	52.50

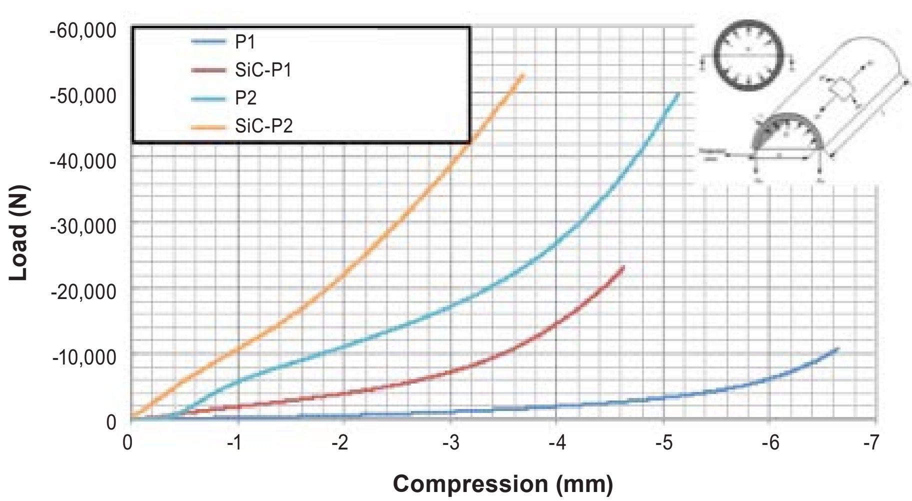

FIGURE 3. Compression strength for NanoSonic's ceramer enhanced hydrogen hoses

- A 1 min hold without burst or visible loss of fluid at a hydrostatic pressure of four times the manufacturer's specified MAWP
- Up to a 10,000 psi MAWP hose assembly
- Two production assembly samples of each model at 12-in length

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 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 production assembly samples of each model hose length of "π(minimum bend radius) + 2(hose OD)" are required.

During the initial round of CSA testing, the outfitted hoses failed at the connector ends. The mode of failure was not rupture or bursting but slippage of the hose from the stainless steel hardware. There is no apparent damage to either the detached hose or the end connector. Post-test analysis of the hoses prompted discussions on how to prevent this failure mode in the future.

Crimping in house was conducted on the second set of hoses delivered to CSA for hydrostatic burst strength measurements. In this second set of tests, the hose burst strength was increased to >9,000 psi. A third set of hoses is under development with NanoSonic's ceramer technology, as the ceramer enables a significant increase in compression strength, as shown in Figure 4. NanoSonic is currently seeking fittings that exceed 5,000 psi to complement our new hoses.

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions derived from the work in FY 2015 are:

- NanoSonic is currently testing our hose with fittings against the Spir Star hose for hydrostatic burst strength and pressure cycling.

FIGURE 4. NanoSonic hydrogen hose with ceramer technology

- We will also be testing our hose against emerging potential commercial competitors, such as: Yokohama Rubber/Iwatani Industrial Gases, ContiTech, and Togawa Rubber. Yokohama's hose is rated for 70 MPa and the Togawa hose is rated for 35 MPa. There are few details given for ContiTech products.
- Environmental robustness and impact on fuel quality are being established through testing with CSA and the National Renewable Energy Laboratory.

FY 2015 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, 2015.*