III.8 Cryogenically Flexible, Low Permeability H_2 Delivery Hose

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Contract Number: DE-SC0010162

Subcontractors:
- National Renewable Energy Laboratory, Golden, CO
- Cardinal Rubber & Seal, Roanoke, VA
- LifeGuard Technologies, Springfield, PA

Project Start Date: April 30, 2016
Project End Date: April 29, 2017

Overall Objectives

NanoSonic's overall objectives for hydrogen dispenser technologies mirror those of the Hydrogen Delivery program within the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy Fuel Cell Technologies Office (FCTO). These technologies aim to help realize hydrogen as a safe, reliable, and cost competitive energy carrier. 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 -40°C to 85°C.
- A new Class D H_2 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 of relevant industry standards outlined in American National Standards Institute (ANSI)/Canadian Standards Association (CSA) hydrogen gas vehicle (HGV) 4.2-2013, with a dispenser compliant with SAE International Technical 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 H_2 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.
- An alternative to the German made H_2 dispenser hose that is currently qualified for H70 service, though it does not meet the service requirement of 25,550 fills/yr, nor allow for a cost of $2–4 gallon of gas equivalent (gge).

Fiscal Year (FY) 2017 Objectives

- Demonstrate a new fitting for H70 service with NanoSonic's H_2 hose.
- Model and down-select a metal-free, fiber reinforced hose as a functions of fiber material, angle, and filament wind design.
- Quantify the burst strength of the new H_2 hose with the new fitting.
- Demonstrate durability via pressure cycle testing.
- Verify durability, purity, and consumer ease of use at dispensing stations.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery section (3.2.5) of the FCTO Multi-Year Research, Development, and Demonstration Plan.

(A) Lack of Hydrogen/Carrier and Infrastructure Options Analysis

(C) Reliability and Costs of Liquid Hydrogen Pumping

(E) Gaseous Hydrogen Storage and Tube Trailer Delivery Costs

(I) Other Fueling Site/Termination Operations

Technical Targets

The goals of this project mirror those of the Office of Energy Efficiency and Renewable Energy to advance hydrogen delivery system technologies toward the FCTO Hydrogen Delivery Program's 2020 delivery targets [1]. NanoSonic has reduced the cryogenic flexibility of our H_2 hose by decreasing the glass transition temperature (T_g) to -100°C, and increasing upper thermal stability to 350°C to enable a wide service use temperature range of -50°C to 90°C. Burst strength has been increased from 9,000 psi to >31,000 psi during first quarter testing on hoses with fittings crimped in-house. The burst strength will be increased in 2018 to 51,000 psi, four times the maximum allowable working pressure (MAWP) of 12,690 psi, by modifying the fitting and the application methodology. NanoSonic modeled, produced, and down-selected a filament wound hose that survived 50,000 cryogenic cycles at (-40°C) conducted at a working pressure of 12,000 psi. This same hose also survived nearly 2,000 cycles (at 85°C) prior to failure due to fitting slippage rather than burst. The new fitting is expected to survive 100,000 combined pressure and thermal cycles over -40°C to 85°C. A novel ceramer coupling agent with a T_g of -65°C was developed and demonstrated an increase of 25% burst strength with all fittings. 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 publication PDTS 14687-2. Current cost projections based on materials for 300 meters of hose are two times less than the competitor. Cost savings based on durability and normalized for lifetime, predict a 4x savings. NanoSonic can produce 16 metal-free H_2 hoses, each three meters in length, in an 8-hr work shift. NanoSonic's planned scale-up method predicts an 8x cost savings normalized for lifetime and 600 meters of hose, per targets given in Table 1.

FY 2017 Accomplishments

- Modeled, produced, and down-selected a metal-free filament wound hose.
- Demonstrated 25% weight reduction for composite H_2 hose relative to metal reinforced hose.
- Demonstrated enhanced flexibility for composite hose relative to metal reinforced hose for increased durability and an enhanced consumer experience.
- Crimped fittings onto metal-free composite hose and demonstrated burst strengths >31,000 psi; failure due to fitting slippage rather than burst.
- Demonstrated a metal-free composite hose that survives 50,000 cycles at 12,000 psi at -40°C.
- Demonstrated an additional >1,900 cycles at 12,000 psi at 85°C.
- Developed low T_g ceramer coupling agent that enhances crimp survivability by >25%.
- Ceramer coupling agent for enhanced crimp survivability and increased compression strength, 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 dispensing hose to enable cost-effective, reliable delivery of H_2 to fuel cell vehicles. This American made hose will meet FCTO's goals to enable domestic competitiveness and energy dominance through hydrogen technologies. Performance of dispensing hoses today is challenged by the operating conditions they experience during a hydrogen fill: repeated cycling at 875 bar (for H70 service, 70 MPa delivery), and over a temperature range of -50°C to +90°C. Hoses in use at stations today are, moreover, manufactured primarily outside of the United States.

NanoSonic has worked during this DOE Small Business Innovative Research program to produce a new Class D H_2 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 2 yr. Our state-of-the-art hose is based on a unique fiber reinforced high performance, cryogenically flexible polymer to resist H_2 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. Currently, there are only a couple of H_2 dispenser hoses that are qualified for H70 service. These hoses are not made in the United States, do not meet the service requirement of 25,550 fills/yr, and are not priced at a point that will allow hydrogen to cost $2–4 gge at the pump.

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

Characteristic	Units	2018 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	> 31,000, failure due to fitting slippage rather than burst
Cycle Pressure Test	cycles	50,000 cycles at MAWP at -40 ° C	meets
Cycle Pressure Test	cycles	50,000 cycles at MAWP at 85 ° C	> 1900
Compression Strength	psi	12,690	meets
Hose Cost	$/m	<200	<60

TGA – thermogravimetric analysis

APPROACH

The new H_2 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 H_2 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 of thermal cycles, perform consistently at pressures greater than 875 bar (for H70 service), 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 filament winding additive manufacturing technique allows for rapid, reproducible, and reliable production of composite hoses with tailored angular designs. Second, NanoSonic has two large scale reactors that allow for the cost effective production of 55 gal and 200 gal drum batches of our low T_g and low H_2 permeable nanocomposite resins. Finally, NanoSonic has invested in a crimper to integrate the end connection fittings directly onto our hoses, and has partnered with a hose assembly company to assist with swaged fittings. The combination of swaging and crimping allows for enhanced adhesion and mechanical fit between the fitting and the hose. Crimping in-house and with our local partners also yields a product with complete fit and finish for qualification and distribution.

RESULTS

NanoSonic's major focus during FY 2017 was on demonstrating high burst strength and pressure cycle survivability for filament wound composite hoses. Our 2017 metal-free composite hose is shown in Figure 1. NanoSonic produced hoses fitted with end connectors in-house that were 15 in. in length for hydrostatic burst strength testing, and 5 ft in length, as determined by their 9 in bend radius, as specified by the pressure cycle experiment 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.

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.

FIGURE 1. NanoSonic's H_2 delivery hoses demonstrating cryogenic flexibility

Two production assembly samples of each model at 12 in 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 MAWP (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 are required. The length of each hose is defined by:

Hose Length = π * (minimum bend radius) + 2 * (hose outer diameter)

First, NanoSonic developed a ceramer coupling agent to enhance the bond strength between the hose and the fitting. The ceramer was initially evaluated on a commercial hose and two types of commercial hose fittings. Experimentation showed that NanoSonic's ceramer increased the burst strength of each hose by 10–50% for each hose (Table 2).

NanoSonic subsequently infused their own hoses with the ceramer described above, and then tested these metal-free, carbon fiber reinforced hoses on a filament winder, wherein they exhibited hydrostatic burst strength values >31,000 psi (Table 3). Hose failure occurred for each of these hoses at the end near the fitting. The fitting crimp recipe was found to influence the burst strength. The NanoSonic hoses with highest burst strength of 31,421 psi failed due to fitting slippage (Figure 2). The commercial hoses, however, failed from burst. Also of importance; NanoSonic's hoses weigh 25% less than commercial hoses, each with fittings.

NanoSonic submitted six composites (three types, two of each) for pressure cycle testing at CSA Group (Figure 3). Each of these specimens were 5 ft in length and the architecture consisted of a low H_2 permeable core with a carbon fiber wound overwrap infused with our low T_g polymer matrix resin. Each filament wound architecture varies as a function of the overwrap angle. Pressure Cycle

TABLE 2. NanoSonic Ceramer Coupling Agent Effect on Hose Burst Strength

Hose Type	Hose ID	Fitting	Fitting OD (mm)	Ceramer	Burst Strength (psi)	Failure Mode
commercial	41A	A	16.1	yes	21,191	Burst
commercial	41B	A	16.1	no	10,096	Burst
commercial	WH208-9C20893	A	15.9	yes	58,449	Burst
commercial	WH208-9A20891	A	15.9	no	52,959	Burst
commercial	WH208-9D20894	B	15.9	yes	26,136	Burst
commercial	WH208-9B20892	B	15.9	no	9,635	Burst

ID – inner diameter; OD – outer diameter

TABLE 3. NanoSonic and Commercial H_2 Hose Crimp Recipes, Weight, and Hydrostatic Burst Strength Values

Hose Type	Hose ID	Fitting Type	Fitting OD (mm)	Ceramer	Burst Strength (psi)	Length (in)	Average Weight (g)
NanoSonic	7-1	A	14.9	yes	19,237	15	**200**
	7-2	A	15.3	yes	26,614	15	
	7-3	A	15.8	yes	25,380	15	
	8A-1	A	16.1	yes	31,421	15	
	8A-2	A	16.5	yes	30,475	15	
	8A-3	A	17.0	yes	16,357	15	
	8B-1	A	15.2	yes	22,591	15	
	8B-2	A	15.2	yes	30,576	15	
	8B-3	A	16.1	yes	28,063	15	
	13-1	A	15.6	yes	24,916	15	
	13-2	A	16.0	yes	24,273	15	
	13-3	A	16.4	yes	23,522	15	
Commercial	41A	A	16.1	yes	21,191	15	**250**
	41B	A	16.1	no	10,096	15	
	WH208-9A20891	A	15.9	yes	52,959	15	
	WH208-9B20892	B	15.9	no	9,635	15	
	WH208-9C20893	A	15.9	yes	58,449	15	
	WH208-9D20894	B	15.9	no	26,136	15	

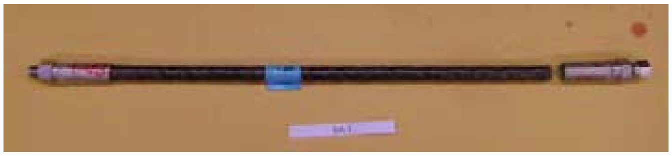

FIGURE 2. NanoSonic hose post hydrostatic burst strength, failure due to fitting slippage

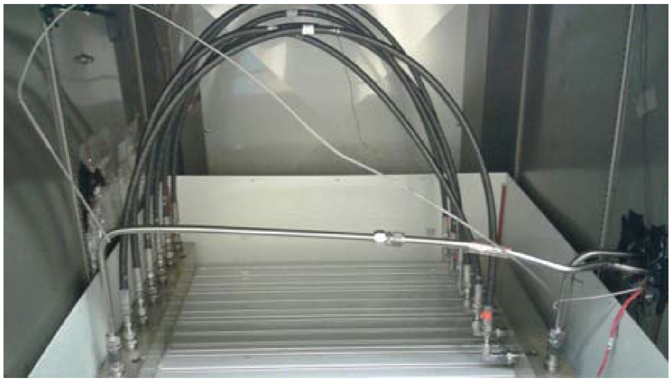

FIGURE 3. NanoSonic H_2 hoses in pressure cycle testing system

Test (Section 2.17) of ANSI/CSA HGV 4.2-2013 was conducted per the following schedule:

- 50,000 cycles at 12,000 psi (827 bar) at -40°C.
- 50,000 cycles at 12,000 psi (827 bar) at 85°C.

Our down-selected material design survived:

- 50,000 cryogenic cycles at (-40°C) conducted at 12,000 psi.
- This same specimen also survived nearly 2,000 cycles (at 85°C) prior to failure due to the fitting slipping off.
- Failure occurred at the 1,988th cycle.
- Failure mode was fitting slippage (Figure 4).

CONCLUSIONS AND UPCOMING ACTIVITIES

Conclusions derived from the work in FY 2017 are:

- NanoSonic's ceramer results in increased hydrostatic burst strength.
- Fitting crimp recipe and type influences burst strength.

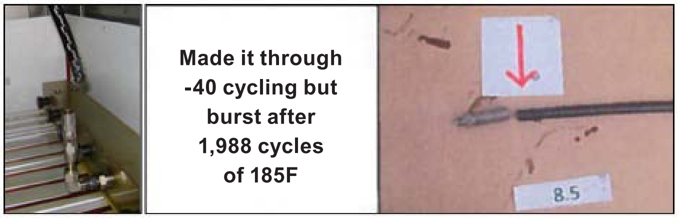

FIGURE 4. NanoSonic H_2 hose post pressure cycle testing at 12,000 psi after 50,000 cycles at -40°C and ~1,988 cycles at 85°C; failure shown due to fitting slippage

- NanoSonic's metal-free H_2 hose exhibits hydrostatic strength values >31,000 psi and fails due to fitting slippage rather than burst.
- NanoSonic's metal-free H_2 hose survives >51,900 pressure cycles at 12,000 psi per 50,000 impulses at -40°C, and >1,900 impulses at 85°C; failure due to fitting slippage rather than burst.
- NanoSonic is currently testing our hose with new fittings produced locally per internal designs with Cardinal Rubber & Seal, Shenandoah Machine, and LifeGuard Technologies.
- Benchmark testing against emerging potential commercial competitors will commence in the next quarter, 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 fuel quality is being established through testing with CSA and National Renewable Energy Laboratory.