Cryogenically Flexible, Low Permeability Hydrogen Delivery Hose

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Subcontractors:

- National Renewable Energy Laboratory, Golden, CO
- Pacific Northwest National Laboratory, Pasco, WA
- Cardinal Rubber & Seal, Roanoke, VA
- LifeGuard Technologies, Springfield, PA

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Project End Date: October 2020

Overall Objectives

NanoSonic's overall objectives for hydrogen dispenser technologies mirror those of DOE's Fuel Cell Technologies Office hydrogen delivery goals to realize hydrogen as a safe, reliable, and cost-competitive replacement for gasoline. Outcomes of this project will include:

- A highly durable hose with fittings 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 hydrogen dispensing hose for use on station side applications that is chemically engineered to survive 51,240 fills (70 fills per day for 2 years) 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 International TIR J2601 and National Institute of Standards and Technology (NIST) 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, 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 hydrogen dispenser hose that is currently qualified for H70 service, though it does not meet the service requirement of 25,550 fills per year nor allow for a cost of $2–$4 per gasoline gallon equivalent.

Fiscal Year (FY) 2019 Objectives

- Demonstrate a new fitting for H70 service with NanoSonic's hydrogen hose.
- Model and down-select a metal-free, fiber-reinforced hose as a function of fiber material, angle, and filament wind design.
- Quantify the burst strength of the new hydrogen 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 of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan[1]:

- (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.

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

Technical Targets

The goals of this project mirror those of the DOE Office of Energy Efficiency and Renewable Energy to advance hydrogen delivery system technologies toward DOE's 2017 hydrogen delivery targets [1]. NanoSonic has enhanced the cryogenic flexibility of our hydrogen 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 31,000 psi to ~36,000 psi during second quarter testing on hoses with new custom fittings crimped in-house. A 20% increase in burst strength was realized with the new design regardless of core and fiber. The burst strength will be increased in 2019 to 51,000 psi, four times the maximum allowing working pressure of 12,690 psi, by modifying the fitting and the application methodology. As failure continues to be due to slippage, a second modification to the fitting design is being implemented. 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 ISO/PDTS 14687-2. Current cost projections based on materials for 300 meters of hose are two times less than that of the competitor. Cost savings based on durability and normalized for lifetime predict a four times savings. NanoSonic can produce 16 metal-free hydrogen hoses, each 3 meters in length, in an 8-hour work shift. NanoSonic's planned scale-up method predicts an eight times cost savings normalized for lifetime and 600 m hose, per targets given in Table 1.

FY 2019 Accomplishments

- Modeled, produced, and tested a new custom metal fitting for installation at NanoSonic for sale and distribution from NanoSonic.
- Modeled, produced, and down-selected a metal-free filament wound hose.
- Demonstrated H35 service with new fitting and hose combination.
- Demonstrated hydrostatic burst strength ~36,000 psi for three types of nonmetal fiber filament wound composite hoses.
- Demonstrated 25% weight reduction for composite hydrogen hose relative to metal-reinforced hose.
- Demonstrated enhanced flexibility for composite hose relative to metal-reinforced hose for increased durability and enhanced consumer experience.
- Crimped fittings onto metal-free composite hose and demonstrated burst strengths ~36,000 psi; failure was 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%.
- Demonstrated ceramer coupling agent with enhanced crimp survivability and increased compression strength >11,200 psi.
- Reduced cost to $200/m via scale-up.
- Collaborated with gas distribution original equipment manufacturers (OEMs), fittings manufacturers, national laboratories, and safety standards groups to qualify the hose for H70 service.

Table 1. Progress toward Meeting Technical Targets for Durable Hydrogen Hose for Fuel Cell Vehicles

Characteristic	Units	2019 Targets	NanoSonic
Tg for Cryogenic Service Temperature	°C	-50	meets
TGA 5% Weiht Loss for Upper Service Temperature	°C	90	meets
Burst Strength	psi	51,000	>36,000 failure due to fitting slippage rather than burst
Cycle Pressure Test	Cycles	50,000 cycles at MAWP at -40°	meets
Cycle Pressure Test	Cycles	50,000 cycles at MAWP at 85°	>1,900
Compression Strength	psi	12,690	meets
Hose Cost	$/m	<200	<60

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 DOE's Fuel Cell Technologies Office hydrogen delivery goals. This American-made hose will meet the DOE 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 (SBIR) 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 2 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 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 per year nor does its price allow for a cost of $2–$4 per gasoline gallon 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 toward cost savings and enhanced durability is threefold. 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-gallon and 200-gallon drum batches of our low T_g and low hydrogen permeable nanocomposite resins. Finally, NanoSonic has invested in a crimper to integrate the end connection fittings directly onto our hoses, and we have partnered with a hose assembly company to assist with swaged fittings. This 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 2019 was on demonstrating high burst strength and pressure cycle survivability for filament wound composite hoses with new fibers. Our 2019 metal-free composite hose is shown in Figure 1.

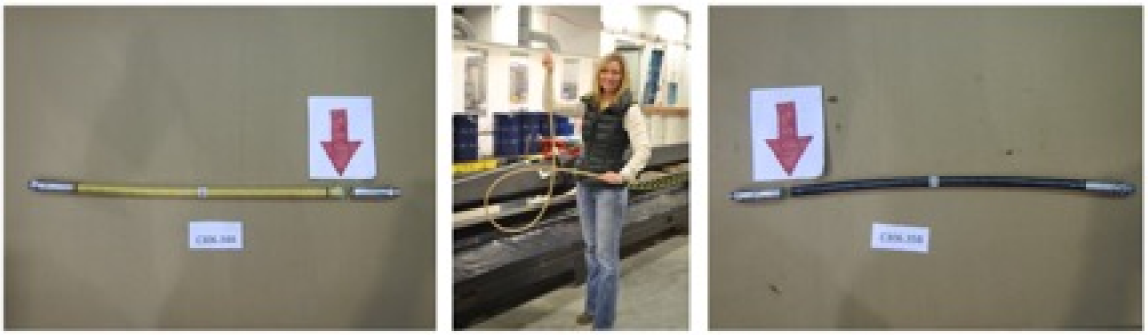

Figure 1. NanoSonic's hydrogen delivery hoses demonstrating cryogenic flexibility

NanoSonic produced hoses >3 meters in length, as shown in Figure 2, and fitted 15-in. long sections with end connectors in-house for hydrostatic burst strength testing. Hoses, 5 ft in length as determined by their 9-in. bend radius, were produced for pressure cycle testing at a 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 below.

Figure 2. NanoSonic 3-m length hoses for dispenser integration and 15-in. length for testing

A. Hydrostatic Strength (Section 2.4), ANSI/CSA HGV 4.2-2013, Hoses for Compressed Hydrogen Fuel Stations, Dispensers, and Vehicle Fuel Systems. Requires a 1-minute hold without burst or visible loss of fluid at a hydrostatic pressure of four times the manufacturers specified maximum allowable working pressure (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), ANSI/CSA HGV 4.2-2013, 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 of "π (minimum bend radius) + 2 (hose O.D.)" are required and are shown in Figure 3.

First, NanoSonic developed two new sets of custom fittings and applied our ceramer coupling agent to enhance the bond strength between the hose and the fitting. It was found that a proprietary modification to the custom fittings led to a 20% increase in burst (leak) strength. All results are given in Table 2 and Table 3 without proprietary details.

Table 2. NanoSonic Core A with New Fittings and Effect on Hose Burst Strength

Hose ID	Fiber	Ceramer	Fitting	I.D. (in)	Length (in)	Burst (lbs/in^2)
C306.31.A	A	Yes	1	~¼	15.4	22,594
C306.31.B	A	Yes	1	~¼	15.1	27,664
C306.31.C	A	Yes	2	~¼	15	25,279
C306.31.D	A	Yes	2	~¼	15.3	15,024
C306.33.A	B	Yes	1	~¼	14.8	22,001
C306.33.B	B	Yes	1	~¼	14.5	24,358
C306.33.C	B	Yes	2	~¼	14.4	19,900
C306.33.D	B	Yes	2	~¼	14.3	16,850

Table 3. NanoSonic Core B with New Fittings and Effect on Hose Burst Strength

Hose ID	Fiber	Ceramer	Fitting	I.D. (in)	Length (in)	Burst (lbs/in^2)
C306.34.A	A	Yes	1	~¼	19.25	35,680
C306.34.B	A	Yes	1	~¼	20.75	35,286
C306.34.C	A	Yes	2	~¼	20.75	28,751
C306.34.D	A	Yes	2	~¼	21	34,213
C306.35.A	B	Yes	1	~¼	19.9	32,338
C306.35.B	B	Yes	1	~¼	19.75	36,175
C306.35.C	B	Yes	2	~¼	19.9	32,002
C306.35.D	B	Yes	2	~¼	19.6	35,777

To gain further insight on the fittings design for proper mating with our hoses, NanoSonic worked with Pacific Northwest National Laboratory (PNNL) through our H2@Scale cooperative research and development agreement project to characterize the fitting/hose interface via digital image correlation (DIC) and X-ray analysis. DIC and X-ray provides noncontact shape and deformation measurements over a continuous surface to analyze strain development over time (Figure 3 and Figure 4). A colorant is applied to the area of interest to produce a random speckle pattern of contrasting colors. A pair of cameras is then focused on the surface and used to collect synchronized images of the specimen. In the DIC and X-ray analysis below, we can clearly see a small amount of strain (~3.4% at 25,000 psi) but no leakage at the fitting/hose interface, rather at the fitting connector interface at PNNL. Repeated experiments were conducted up to 36,000 psi.

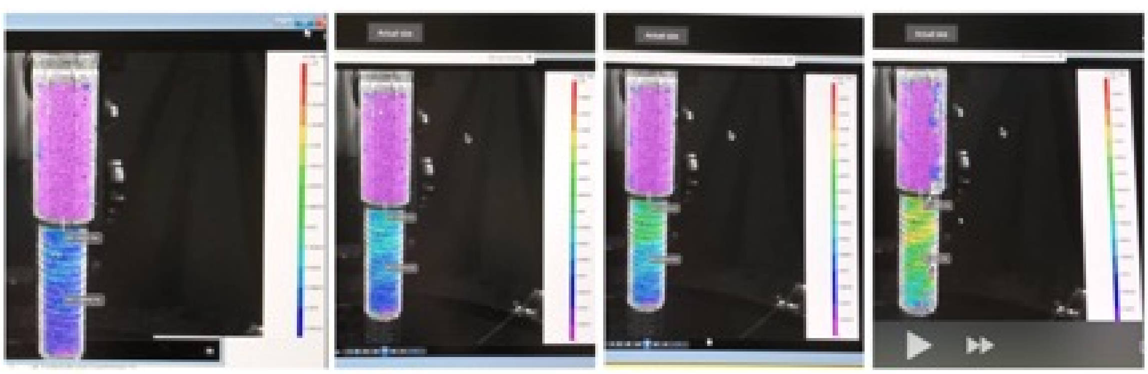

Figure 3. DIC data collected during pressurized leak testing at PNNL

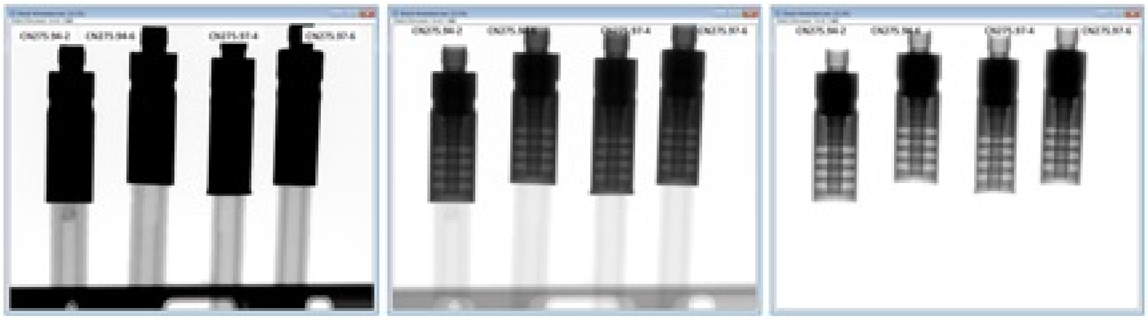

Figure 4. X-ray of hoses with fittings at PNNL

CONCLUSIONS AND UPCOMING ACTIVITIES

Conclusions derived from the work in FY 2019 are:

- NanoSonic's hydrogen hoses meet burst strength values for H35 service with multiple fibers and are expected to meet H70 service with the appropriate fittings.
- NanoSonic's ceramer results in increased hydrostatic burst strength.
- Fitting crimp recipe and type influences burst strength.
- NanoSonic's metal-free hydrogen hose exhibits hydrostatic strength values ~36,000 psi and fails due to fitting slippage rather than burst.
- NanoSonic's metal-free hydrogen 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 is 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, Techsburg, and LifeGuard Technologies.
- Benchmark testing against emerging potential commercial competitors, such as Yokohama Rubber/Iwatani Industrial Gases, ContiTech, and Togawa Rubber, will commence in the next quarter. 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 are being established through testing with CSA, PNNL, and the National Renewable Energy Laboratory.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Jennifer Lalli, "Cryogenically Flexible, Low Permeability H_2 Delivery Hose." DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, 2019.

REFERENCES

1. U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Fuel Cell Technologies Office, *Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan*, http://energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22.