# 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 2019


## Overall Objectives

NanoSonic's overall objectives for hydrogen dispenser technologies mirror those of the DOE Office of Energy Efficiency and Renewable Energy (DOE-EERE) Fuel Cell Technologies Office's 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 -40°–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/day, 2 years) and meets the requirements outlined in ANSI/CSA HGV 4.2-2013, with a dispenser compliant with SAE TIR J2601 and 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, although it does not meet the service requirement of 25,550 fills/year, nor allow for a cost of $2–$4 per gallon of gas equivalent.

## Fiscal Year (FY) 2018 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 functions 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] http://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 DOE-EERE to advance hydrogen delivery-system technologies toward the DOE hydrogen delivery program's 2017 delivery targets. NanoSonic has reduced 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 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 FY 2019 to 51,000 psi, which is 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 it 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 J2719 and ISO/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 hydrogen hoses, each 3 meters in length, in an 8-hour work shift. NanoSonic's planned scale-up method predicts an 8x cost savings normalized for lifetime and 600 m hose, per targets given in Table 1.

## FY 2018 Accomplishments

- Modeled, produced, and down-selected a metal-free filament-wound hose.
- Demonstrated hydrostatic burst strength ~36,000 psi for three types of non-metal 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 an enhanced consumer experience.
- Crimped fittings onto metal-free composite hose and demonstrated burst strengths ~36,000 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% 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.

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% Weight 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 °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 |

## 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-EERE hydrogen delivery goals. This American-made hose will meet DOE-EERE's technical targets to enable the hydrogen economy through enhanced safety and durability. There is 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/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 is qualified for H70 service. This non-U.S., German-made hose from Spir Star is rated for a working pressure of 875 bar, although it does not meet the service requirement of 25,550 fills/year, nor does its price allow for a cost of $2–$4 per gallon of gas equivalent.

## APPROACH

The new hydrogen hose involves an all-polymer material approach, in contrast to the currently qualified hose that uses steel as its reinforcing agent. The unique polymer-fiber reinforcement design will 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 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-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 2018 was on demonstrating high burst strength and pressure-cycle survivability for filament-wound composite hoses with new fibers. Our 2018 metal-free composite hose is shown in Figure 1. NanoSonic produced hoses >3 meters in length, as shown in Figure 2, and fitted 15"-long sections with end connectors in-house for hydrostatic burst-strength testing, and 5' in length, as determined by their 9" bend radius, for pressure-cycle testing at CSA's 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. Each test is described below.


Figure 1. NanoSonic's hydrogen delivery hoses demonstrating cryogenic flexibility at the National Renewable Energy Laboratory

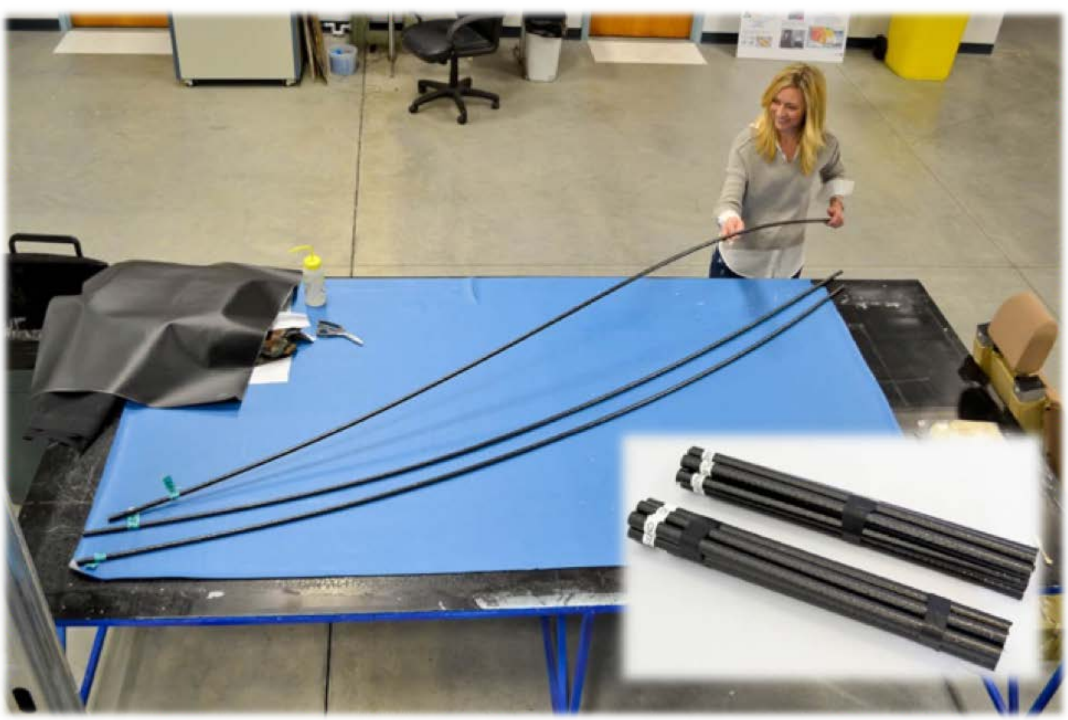

Figure 2. NanoSonic 3-m-length hoses for dispenser integration and 15-in.-length for testing

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 4 times the manufacturer's specified maximum allowable working pressure (MAWP), up to a 10,000 psi MAWP hose assembly. Two production-assembly samples of each model at 12-inches 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 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.

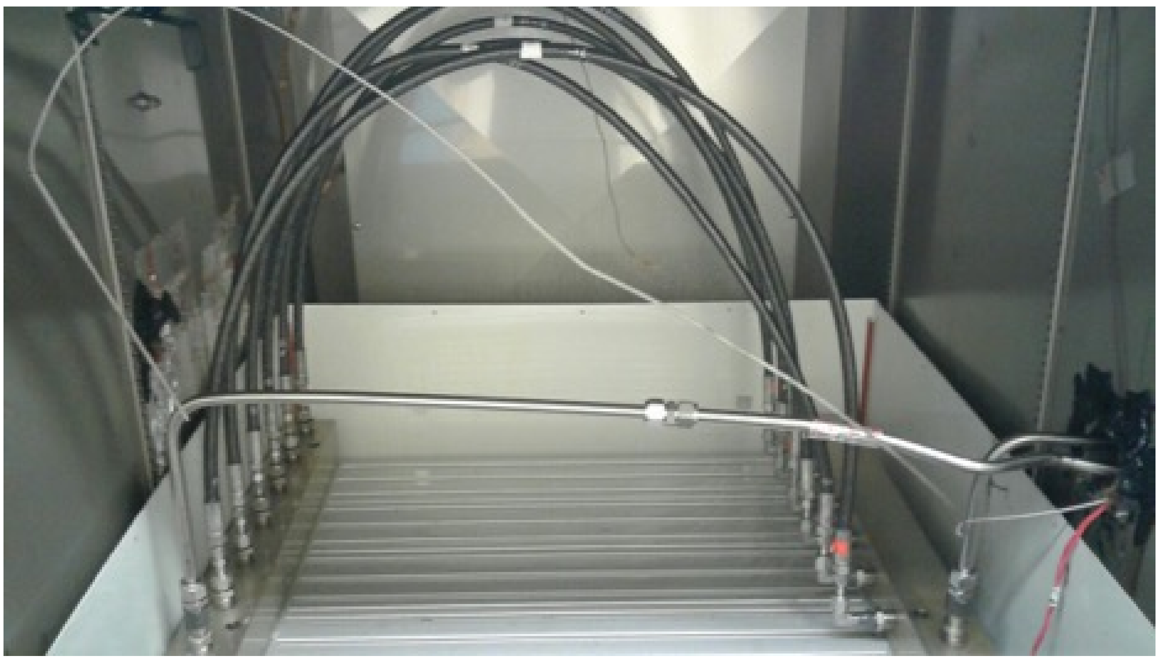

Figure 3. NanoSonic hydrogen hoses in pressure-cycle testing system

First, NanoSonic developed a ceramer coupling agent to enhance the bond strength between the hose and the fitting. It was first demonstrated with a commercial hose and two types of commercial hose fittings. NanoSonic's ceramer resulted in increased burst strengths that ranged from 10%–50% for each hose (Table 2).

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 |

NanoSonic used our ceramer with all NanoSonic hydrogen hoses based on the burst-strength enhancements documented with commercial hoses. In 2018, NanoSonic produced a series of metal-free, carbon, and two additional fiber-reinforced hoses on our filament winder that exhibited hydrostatic burst-strength values consistent with H35 service (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, and NanoSonic hoses with highest burst strength of 35,981 psi failed due to fitting slippage (Figure 4). It was also found that the failure mechanism of commercial hoses was burst. Also of importance, NanoSonic's hoses weigh 25% less than commercial hoses, each with fittings.

Table 3. NanoSonic Hydrostatic Burst-Strength Values for H35 Hoses

| Hose ID | Fiber | Ceramer | Fitting | I.D. (in) | Length (in) | Burst (lbs/in$^2$) |
|---|---|---|---|---|---|---|
| 2 | C | yes | A | ¼ | 14 | 26,418 |
| 3 | C | yes | A | ¼ | 14 | 25,242 |
| 4 | C | yes | A | ¼ | 14 | 25,228 |
| 5 | C | yes | A | ¼ | 14 | 30,515 |
| 6 | C | yes | A | ¼ | 14 | 28,715 |
| 7 | C | yes | A | ¼ | 14 | 30,224 |
| 8 | C | yes | A | ¼ | 14 | 31,776 |
| 10 | C | yes | A | ¼ | 14 | 30,609 |
| 11 | C | yes | A | ¼ | 14 | 35,295 |
| 12 | C | yes | A | ¼ | 14 | 35,981 |
| 13 | D | yes | A | ¼ | 14 | 26,259 |
| 21 | E | yes | A | ¼ | 14 | 31,790 |
| 23 | E | yes | A | ¼ | 14 | 29,052 |
| 24 | E | yes | A | ¼ | 14 | 29,641 |

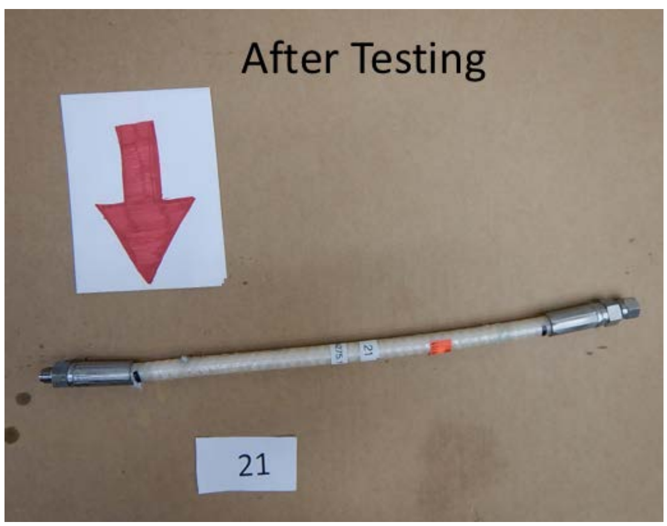


Figure 4. NanoSonic H35 hose with fitting failure

NanoSonic submitted six composites (three types, two of each) for pressure-cycle testing at CSA Group (Figure 3). Each of these specimens was 5' in length, and the architecture consisted of a low-hydrogen-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. The Pressure Cycle 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 the following:

- 50,000 cryogenic cycles at (-40°C) conducted at 12,000 psi.
- This same specimen also survived nearly 2,000 cycles (at 185°F) prior to failure due to the fitting slipping off.
- Failure occurred at the 1,988$^{th}$ cycle.
- Failure mode was fitting slippage (Figure 4).

## CONCLUSIONS AND UPCOMING ACTIVITIES

Conclusions derived from the work in FY 2018 are the following:

- 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 influence burst strength.
- NanoSonic's metal-free hydrogen hose exhibits values of hydrostatic strength of ~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 was 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 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 are being established through testing with CSA, Pacific Northwest National Laboratory and the National Renewable Energy Laboratory.

## FY 2018 PUBLICATIONS/PRESENTATIONS

1. J. Lalli, "Cryogenically Flexible, Low Permeability $H_2$ Delivery Hose," DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting (2018).