# IV.D.1 Enhanced Materials and Design Parameters for Reducing the Cost of Hydrogen Storage Tanks

David W. Gotthold
Pacific Northwest National Laboratory
P.O. Box 999, MSIN
Richland, WA 99352
Phone: (509) 375-2073
Email: David.Gotthold@pnnl.gov

DOE Manager: Grace Ordaz
Phone: (202) 586-8350
Email: Grace.Ordaz@ee.doe.gov

Subcontractors:

- Hexagon Lincoln, Lincoln, NE
- Ford Motor Company, Dearborn, MI
- Toray Composites America, Decatur, AL
- AOC, LLC, Collierville, TN

Project Start Date: January 18, 2012
Project End Date: September 30, 2016

## Overall Objectives

- Reduce carbon fiber (CF) usage and hydrogen tank cost through a series of combined material and design approaches for a cumulative 37% cost savings.
- Reduce tank cost by reducing composite mass through: (1) resin matrix modifications and alternatives, (2) CF surface properties that increase load translational efficiency, (3) alternate CF placement and materials, and (4) enhanced operating conditions to increase the energy density vs. pressure.
- Demonstrate the combined cost reductions through modeling, materials, and burst testing.

## Fiscal Year (FY) 2016 Objectives

- Acquire and test physical insulations for cold gas storage.
- Complete low temperature materials compatibility testing.
- Complete impact and fatigue testing of vinyl ester resin tanks.
- Assess tank burst performance at cold gas operating temperatures.

## Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

(A) System Weight and Volume

(B) System Cost

(G) Materials of Construction

(J) Thermal Management

(L) Lack of Tank Performance Data and Understanding of Failure Mechanisms

## Technical Targets

This project contributes to achieving the following DOE milestone from the Manufacturing R&D section of the Fuel Cell Technologies Office Multi-Year Research, Development and Demonstration Plan.

- By 2020, develop and verify onboard automotive hydrogen storage systems achieving 1.8 kWh/kg system (5.5 wt% $H_2$) and 1.3 kWh/L system (0.040 kg $H_2$/L) at a cost of $10/kWh ($333/kg $H_{2\ stored}$). The progress toward targets is shown in Table 1. The gravimetric and volumetric capacities decrease slightly, due to the required insulation weight and volume. The storage system cost decreases 22% from the 2012 cost, due to the reduced carbon fiber composite in the 500 bar tank vs. the 700 bar tank.

**TABLE 1.** Progress toward Meeting Technical Targets for Onboard Hydrogen Storage for Light-Duty Fuel Cell Vehicles

| Storage Parameter | Units | 2020 Targets | 2012 Project Start, 700 bar, T = 293K | 2016 PNNL Status, 500 bar, T = 200K |
|---|---|---|---|---|
| System Gravimetric Capacity | kg $H_2$/kg system | 0.055 | 0.042 | 0.039 |
| System Volumetric Capacity | kg $H_2$/L system | 0.040 | 0.025 | 0.024 |
| Storage System Cost | $/kWh net | 10 | 17.00 | 13.30 |

T – Temperature; PNNL – Pacific Northwest National Laboratory

## FY 2016 Accomplishments

- Eleven sets of six tanks were built and burst tested to evaluate previous theoretical design improvements with statistically significant sample sizes. This included testing of tanks with varying wind patterns, nanoparticle reinforced resins, and the alternate vinyl ester resin. The results of each is described below.
- Low cost resin alternative developed and tested with equivalent or better performance than existing epoxy resin that, based on analysis by Strategic Analysis, will reduce the storage system cost by $0.59/kWh compared to DOE's 2013 baseline of $16.8/kWh.
- Optimized nanoparticulate materials and processing selected and scaled to tens of gallons of modified resin to enable production of 70-L batches of modified resins. The modified resins did not show increases in burst pressure and caused increased manufacturing variations. Nanoparticles did not increase the strength or stiffness of the resin enough to significantly increase the composite lamina strength or stiffness. In addition, clumping of nanoparticles led to defects that may be connected to increased performance variation.
- Alternate winding patterns were tested. An improved failure model that accounts for high shear stresses more accurately explains the lower burst pressures observed in tank winding patterns with higher interlaminar shear stress. The trade-off between fiber tensile failure and interlaminar shear failure demonstrates that the existing winding pattern is near optimal for the selected tank dimensions and manufacturing processes.
- Advanced physical insulation materials (vacuum insulated panel [VIP] and aerogel batting) were procured and tested to estimate dormancy performance at cold gas operating conditions. The measured insulation R-values of VIP (R-25/in) and aerogel batting (R8.5/in) were about 12% and 4% as effective (respectively) as multi-layer vacuum insulation (approximately R-215 equivalent).
- Multiple nonmetallic component materials were evaluated at cold temperatures (-129°C to 23°C) to determine feasibility for cold gas operation expected to be at approximately -73°C.
- Cold gas burst tests were done on 250 bar standard test and evaluation bottle (STEB) poly(vinyl ester) (PVE) tanks precooled to 200 K. Average burst pressure was 714 bar, which exceeds the target room temperature burst of ~625 bar.

## INTRODUCTION

The goal of this research was to reduce the cost of compressed hydrogen storage vessels by at least 37% from the current high volume projections of $17/kWh to $11/kWh for commercialization in early-market and light-duty hydrogen fuel cell vehicles. The cost and performance baseline was the current 70 MPa Type IV pressure vessel (high-strength, standard modulus carbon fiber in an epoxy matrix filament wound on a high density polyethylene liner). The high-strength carbon fiber composite can account for nearly 70%–80% of the overall tank costs. Therefore, the team's research objective is to reduce carbon fiber usage and associated tank cost through a series of combined material and design improvements that were estimated to total nearly 37% of the project initial baseline tank cost. The project identified through modeling a series of material design optimizations and experiments that were expected to achieve the cost savings goal. It was initially estimated that these cost savings, combined with future reductions in CF cost, could lead to the 50% cost reduction toward the ultimate DOE target.

## APPROACH

The project took a holistic approach to improve performance by lowering the required gas pressure at lower operating temperature, refining the tank composite design with local reinforcement and hybrid layups, plus increasing the composite translation efficiency with material modifications at the composite constituent level. The project team includes industry experts in each of the following focus areas of improvement: enhanced operating conditions to improve energy density/pressure ratios, load translational efficiency improvements by CF surface modification, resin matrix modifications and alternatives, and alternate fiber placement and materials. The team expects these savings approaches to be compatible and additive.

## RESULTS

The key work for 2016 was to validate the performance of the improved resins and the ability to operate tanks with cold gas. This included measuring the impact and fatigue performance of full vinyl ester resin tanks, burst testing of the nano-particle reinforced resin tanks, plus low temperature testing of tank materials, insulations and full tanks. Additional work was done on updating the cost estimates for tank manufacturing both for ambient temperatures and enhanced operating conditions.

### Improved and Modified Resins

Based on the FY 2015 work showing improved performance of the vinyl ester (VE) tanks, a series of additional impact and fatigue tests were performed on a second batch of VE tanks to understand the suitability for

transition to manufacturing. A series of 250 bar STEB tanks were made with both VE and epoxy resins. The tanks were then subjected to a calibrated impact and then burst tested after either 0, 5,000, or 10,000 cycles. The results are shown in Table 2. For the unimpacted tanks, the relative performace of the VE and epoxy resins was as expected based on the initial results. The initial burst was slightly improved and the fatigue testing was within expected variations. In the initial round of impact tests, one VE tank failed early in the pressure cycling (the one marked "Did Not Finish" in Table 2), with a clear damage pattern from the impact point shown in Figure 1. In a repeat of the testing, the VE tanks actually outperformed the epoxy tanks for all three test conditions. Note that while the vinyl ester tanks demonstrated equivalent or better structural performance, challenges remain with managing the styrene vapors (approximately 30% by weight) during the winding and curing processes. This is managed in the fiberglass industry with the use of industrial fume hoods and air handling design.

In FY 2016, testing was performed on tanks with carbon and silica nano-particle resins. Previous work had been on measuring mechanical performance of resin-only samples and scaling up the mixing process to enable full tank testing. Multiple tanks were built and burst tested with generally poor results. With the carbon nanoparticles, the best tank had a burst strength of only 98.7% of the reference tank. More importantly, the tank-to-tank variation was extremely high, with a variation of +/-14% which is well above the typical variation of less than 4% and unacceptable for production. The silica nano-particle tanks showed similar results, with the best tank at only 96.9% of the baseline burst pressure and a tank-to-tank variation +/-8.1%. With none of the tanks achieving improved performance, it was determined that at least within the materials scope of this program that the reinforced resins were not going to provide any potential improvement. To confirm this, the team did a brief study using a commercially available nano-particle reinforced epoxy resin. While the tank-to-tank variation was better, it was still higher than the standard process and there was no improvement in overall burst pressure. Impact and fatigue testing also showed no significant improvement. The nanoparticle additives did not increase the strength or stiffness of the resin enough to significantly increase the composite lamina strength or stiffness. In addition, the increased variation in burst pressure was attributed to the non-uniform distribution and clumping of particles, which was observed in composite samples from the ruptured tanks, as well as electron microscopy analysis.

**TABLE 2.** Summary of Measured Burst Results after Impact and Pressure Cycling

| | | Epoxy | Vinyl Ester |
|---|---|---|---|
| | **Test Type** | **Relative Burst** | **Relative Burst** |
| **No Impact** | Burst | 105% | 111% |
| | Cycle A | 100% | 103% |
| | Cycle B | 99% | 95% |
| | | | |
| **Impact Test Round 1** | Burst | 57% | 55% |
| | Cycle A | 67% | Did Not Finish |
| | Cycle B | 58% | 63% |
| | | | |
| **Impact Test Round 2** | Burst | 70% | 82% |
| | Cycle A | 55% | 74% |
| | Cycle B | 62% | 67% |

**FIGURE 1.** Image of burst tank made with vinyl ester resin after impact testing

## Enhanced Operating Conditions

### Burst Tests

Low temperature burst tests of full VE resin tanks were carried out to evaluate enhanced operating condition performance. Testing was performed by Cimarron

Composites using 250 bar STEB tanks precooled to 200 K. The average burst pressure was 714 bar with a 6% variation. The burst pressure exceeds the room temperature performance (target burst ~625 bar) and the variation, while slightly higher than room temperature, is still acceptable.

## Materials Cold Performance Testing

In FY 2016, the team completed the cold material testing for the enhanced operating conditions. Testing was done in an MTS environmental chamber mounted on a 20 kip MTS mechanical testing frame. The chamber was cooled using a dewar of liquid nitrogen controlled by a solenoid valve to achieve the desired temperature. The temperature was verified with thermocouples inside the chamber to monitor the environment as well as a thermocouple on or near the sample to verify sample temperature.

Tensile tests were performed at seven temperatures ranging from room temperature (23°C) down to -129°C in 30°C increments. Tensile specimens were made from sheets of high-density polyethylene, low-density polyethylene, nylon, polytetrafluoroethylene, and ultra-high-molecular-weight polyethylene using the specimen dimensions from the ASTM D638 Standard Test Method for Tensile Properties of Plastics. Load and displacement data was gathered and used to calculate the ultimate tensile strength, yield strength, ultimate strain, and modulus of elasticity.

Flexural tests were performed according to ASTM Standard D6272 using a four-point bend fixture. The samples were approximately 1/8-in thick and 1-in wide so they were much better suited for flexural testing than tensile because of their brittle nature. Testing was performed with a support span of 2 in and a loading span of 1 in. Samples were cooled and tested at temperatures from room temperature to -129°C and data was collected to calculate the flexural strength, flexural strain, and modulus of elasticity.

Short beam strength testing (Figure 2) was performed according to ASTM D2344 Short Beam Strength of Polymer Matrix Composite Materials. Samples were made of two cured resins designated L047 and L046. L047 is the baseline epoxy resin material and L046 is VE resin. Samples chosen for testing were the most uniform samples available from the cured resin panels that were provided. This was done to minimize adverse effects of stress concentrations due to irregularities in the sample microstructure. Testing was performed using a short beam strength fixture conforming to ASTM standards and three tests were done at each of the standard temperatures that the other tests were performed at.

Data for the short beam shear as a function of temperature is shown in Figure 2. Here one can readily observe that while both the epoxy (L047) and the PVE (L046) generally increase in strength with decreasing temperature, it appears that the PVE peaks at 100°C. This may indicate that the sweet spot for the PVE resin is between -70°C and -100°C, which aligns well with the enhanced operating conditions expected.

Most of the materials tested, including the previously developed vinyl ester resin, were found to be suitable for use at the enhanced operating conditions. Nylon was found to be unsuitable for temperatures below approximately -40°C.

## Physical Insulation Testing

Samples of VIP insulation were procured and tested at dry ice temperature to compare their measured insulating properties for cold gas operation with the available literature values. The results of the testing of three different VIP panels are shown in Table 3.

The insulation R-values achieved in the tests were estimated by comparing the measured temperature histories with the steady state and transient temperatures from a finite element model that varied the R-value. In each case, the

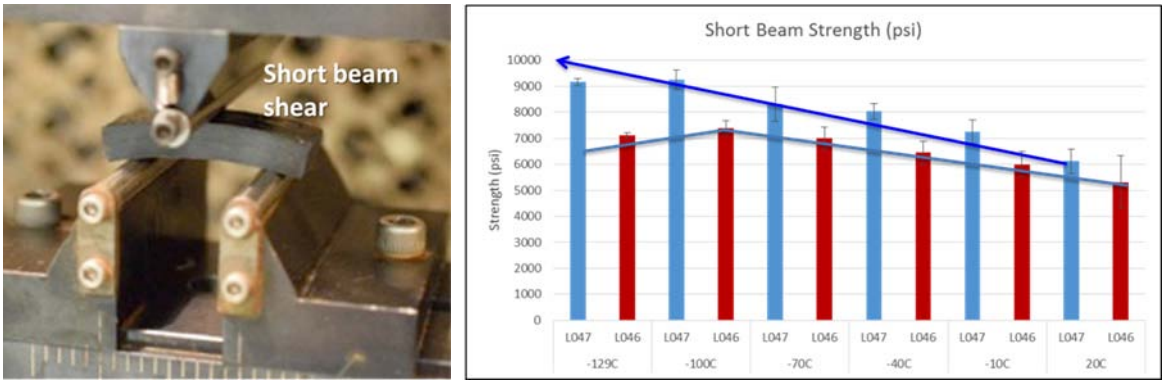


**FIGURE 2.** (left) Photograph of a short beam shear test of a portion of an ASTM ring made by Hexagon Lincoln. (right) The strength of both the epoxy (L047) and the PVE (L046) increases generally with decreasing temperature. Interestingly, the PVE strength appears to peak at approximately -100°C.

**TABLE 3.** Reported and Observed Insulation Values

| | | | Reported | Reported | Observed | Observed |
|---|---|---|---|---|---|---|
| **Test Designation** | **Brand Name** | **Thickness (mm)** | **Conductivity (W/mK)** | **R/inch** | **Conductivity (W/mK)** | **R/inch** |
| VIP 1 | Kevothermal, VIP-AM | 19 | 0.004 (website) | 36 (website) | 0.0053 | 27 |
| VIP 2 | Kevothermal, VIP | 13 | 0.004 (website) | 36 (website) | 0.0044 | 33 |
| VIP 3 | Promat (SlimVac), VIP-AM | 16 | 0.0042 (brochure) | 34.3 (website) | 0.0058 | 25 |

observed insulation values were similar but somewhat less than the reported values.

Dormancy tests were also conducted with a sub-scale composite tank capable of containing 1 kg of hydrogen at 50 MPa and 200 K. Unpressurized tests were performed by adding sand to replace the thermal mass of the hydrogen. Models that matched the measured temperature rise estimate that the VIP panels as configured provided about half the insulation value of the single panel tests. It is expected that the most significant factor in this reduced performance is heat loss through the joints between the panels used to construct the rectangular insulation boxes for the tests.

Finally, the transient thermal performance of tanks insulated with 1-in R30, 2-in R30, and multi-layer vacuum insulation was simulated to estimate when hydrogen venting would be required and how much hydrogen would be lost as the tank warmed to 300 K. The initial vent (62.5 MPa to 50 MPa) was estimated to occur at about 1.6, 3, and 12 days, and the second partial vent (62.5 MPa to 58.1 MPa) was estimated to occur at about 6.1, 11, and 36 days for the 1-in R30, 2-in R30, and multi-layer vacuum insulations, respectively. However, this study demonstrates that hydrogen loss from pressure relief could be eliminated if 10% of the tank capacity could be used efficiently (i.e., through driving, active cooling, battery charging, etc.) before the first vent time, followed by an additional 3.2% usage before the second vent time. Thus, usage cycles are significant in determining the required insulation for cold hydrogen storage options.

## CONCLUSIONS AND FUTURE DIRECTIONS

Research completed in FY 2016 has demonstrated that the VE resin has performance and cost benefits that are encouraging for transition to manufacturing scales. However, this will require significant additional testing plus addressing the safety and environmental issues around the styrene content of the uncured resin. The materials compatibility testing for enhanced operating conditions reveals no critical issues. Testing of currently available physical insulations revealed that they are not yet capable of providing the long dormancy times targeted for cold gas storage.

### FY 2016 Future Work

- Identify future development efforts around production, delivery, and storage of cold hydrogen.

## FY 2016 PUBLICATIONS/PRESENTATIONS

**1.** D.W. Gotthold et al. 2015. "Enhanced Materials and Design Parameters for Reducing the Cost of Hydrogen Storage Tanks." Project ID# ST101. DOE Hydrogen and Fuel Cells Program Annual Merit Review, June 6–10, 2016, Washington, D.C., Pacific Northwest National Laboratory, Richland, WA.