IV.F.3 Synergistically Enhanced Materials and Design Parameters for Reducing the Cost of Hydrogen Storage Tanks

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• 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, 2015

Overall Objectives

• Reduce carbon fiber 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: (A) resin matrix modifications and alternatives, (B) carbon fiber surface properties that increase load translational efficiency, (C) alternate carbon fiber placement and materials, and (D) enhanced operating conditions to increase the energy density vs. pressure.

• Demonstrate the combined carbon fiber as well as cost reductions through modeling, materials, and burst testing.

Fiscal Year (FY) 2014 Objectives

• Develop a feasible pathway through cold gas enhanced operating conditions to achieve at least an additional 20% ($3.4/Kwh) (mass reduction of 18.7 kg composite or 13.3 kg carbon fiber) cost reduction for compressed hydrogen storage tank above the 15% (13.5 kg composite, 9.6 kg carbon fiber) accomplished in FY 2013 through resin modification and fiber placement. This will be demonstrated through thermal and cost modeling of low-cost thermal insulating approaches. Percent improvements are based on a 2013 projected high-volume baseline (composite mass 93.6 kg, carbon fiber mass 66.3 kg) cost of $17/kWh for 70-MPa compressed hydrogen storage tanks.

• Conduct material testing of resin modifications with higher filler concentrations.

• Complete modeling of tank dormancy for cold gas storage.

• Model tank to redesign for cold gas storage.

• Complete tooling for baseline tank fabrication.

• Fabricate baseline sub-scale prototype tank.

• Accomplish burst testing of baseline sub-scale tank.

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  
(H) Balance-of-Plant (BOP) Components

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 2017, develop and verify onboard automotive hydrogen storage systems achieving 1.8 kWh/kg system (5.5 wt% hydrogen) and 1.3 kWh/L system (0.040 kg hydrogen/L) at a cost of $12/kWh ($400/kg H2 stored). Progress toward targets is shown in Table 1.

<table>
<thead>
<tr>
<th>Storage Parameter</th>
<th>Units</th>
<th>2017 Targets</th>
<th>PNLL 2014 Status</th>
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</thead>
<tbody>
<tr>
<td>System Gravimetric Capacity</td>
<td>kg H2/kg system</td>
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<td>0.051</td>
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<tr>
<td>System Volumetric Capacity</td>
<td>kg H2/L system</td>
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<td>0.027</td>
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<tr>
<td>Storage System Cost</td>
<td>$/kWh net</td>
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<td>15.37</td>
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TABLE 1. Progress toward Meeting Technical Targets for Onboard Hydrogen Storage for Light-Duty Fuel Cell Vehicles
FY 2014 Accomplishments

- Completed testing of material modification enhancements with higher concentrations of nanofillers.
- Fabricated tanks with baseline geometry with alternate fiber placement and several fiber types.
- Fabricated baseline tank geometry with material property enhancements.
- Completed matrix of burst tests.
- Identified additional 38% tank composite mass reduction through lower pressure cold gas storage, which is greater than the required Go/No-Go of 20% additional reduction. Total mass reduction of all design enhancements is 52% of the baseline.
- Identified a path to 30% tank cost reduction with combined efficiencies of 1) lower cost resins, 2) improved nanofilled resins, 3) alternative fibers and winding patterns, and 4) cold gas storage.

Approach

The project takes 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 carbon fiber surface modification, resin matrix modifications and alternatives, and alternate fiber placement and materials. We expect these savings approaches to be compatible and additive.

Results

The following Go/No-Go Milestone was specified for FY 2014:

“PNNL, along with partner Ford, will demonstrate a feasible path to reduce the overall carbon fiber composite weight by 20% (composite savings of 18.7 kg from the 2013 baseline estimate of 93.6 kg) of a composite overwrapped pressure vessel through modeling of cold gas (200 K) enhanced operation.”

The waterfall plot in Figure 1 shows the progressive savings of the composite material and tank design improvements studied in this project. These results were calculated using the tank mass and cost model developed by Ford and PNNL during the first year. For the baseline 145-liter Type IV composite pressure vessel (5.8 kg of total hydrogen at 288 K (15°C) and 70 MPa), this model predicts a tank composite mass of 93.6 kg compared to 91 kg estimated by the DOE model by Strategic Analysis, Inc (3% difference). In the first year, the engineering cost analysis estimated that 12% of the $3,171 tank cost (and 14% of the 93.6 kg composite mass) could be saved with low cost reinforced resins combined with improved fiber placement and winding efficiencies. Analysis of the reduced pressure, cold-gas operating condition in the second year estimated that the tank mass could be further reduced by 38% (52% total mass reduction) with a total cost reduction including insulation of 30% from the baseline. The additional 38% mass savings is significantly greater than the 20% composite mass reduction required by the Go/No-Go Milestone.

The net cost of the tank at cold-gas conditions must include the insulation system required to maintain cold-gas dormancy. Comparing the estimated 37% cost reduction with the 30% project goal leaves 7% or $222 for the insulation system. PNNL performed thermal analysis of the vacuum insulation system used by Lawrence Livermore National Laboratory on their cryo-compressed hydrogen tank. The model was validated against the measured thermal
performance and then used to estimate the dormancy time of a similar vacuum vessel at the cold-gas conditions. The analysis estimated that 18 days of dormancy could be achieved before the 50-MPa rated pressure increased to the 125% maximum operating pressure (62.5 MPa). Published cost analysis of the cryo-compressed tank [1] estimated the vacuum vessel cost to be about $290, which is similar to our $222 insulation margin. Reducing the tank volume to 141 L at cold conditions (vs. the 151-L cryo-compressed tank) and designing for a shorter dormancy (i.e., 7 days) may reduce the insulation system cost. High-performance physical insulations will also be tested in the coming year to compare cost and thermal performance with vacuum insulation.

Resin Matrix Modifications

Resin fillers or additives can improve load translation in the composite by increasing the resin modulus and strength to be more compatible with the fiber transverse modulus, as well as some improvement in matrix elongation at break. Detailed finite element calculations, including elastic/plastic matrix deformation with damage, were performed for a composite tank cylinder to estimate the effect of nanoadditives on composite strength and burst pressure. Tensile test models of the matrix alone agreed within 5% of particle strengthening effects reported in the literature. Based on these calculations, we estimate that a 15% improvement in matrix modulus with an accompanying 12% increase in material strength can achieve to an increased burst pressure of approximately 8%. This is equivalent to an 8% reduction in carbon fiber usage. Because this is direct modification of the resin matrix properties and not the fiber, we expect additional strength improvement with the carbon fiber modification for a combined savings.

Based on expected cost and performance to date, we have down-selected to two very different nanofiller morphologies: 1) a silica nanofiber (SNF) with very high aspect ratio, and a nanoscale graphite material (N307 by Asbury) similar to graphene platelets (Figure 2). Here we report findings of the relative tensile properties of the T015 system doped with SNF. Figure 3 shows the tensile strength and modulus data taken from samples machined from neat and nanofilled resin panels. The addition of the SNF improved the modulus of the resin as compared to the T015, but resulted in a simultaneous drop in strength. Since both parameters are important to improving tank burst pressure, we have been working on addressing improvements in strength of the nanofilled resin. Issues can arise in nanofilled systems due to either poor dispersion or poor interfacial adhesion with the nanomaterial and the resin. Poor dispersion was indicated by the presence of clumping in scanning electron microscope images of the fractured edges of the SNF containing resins. To correct this we modify the SNF fiber surface using silane (3-(Trimethoxysilyl)propyl methacrylate) to improve wetting, dispersion, and interfacial adhesion; and we used ultrasonic mixing to improve dispersion.

Figures 3 shows both the sonication and surface modification have increased the strength and modulus of the nanofilled resins. In fact, the strength of the surface modified nanofilled resin is nearly that of the neat resin, while the modulus is significantly improved. It is likely that additional sonication (up to a point) will further increase properties as dispersion is improved. Beyond a certain point the sonication will start to break up the nanofibers and the properties will again decrease. It is likely that the two combined effects will result in a resin that exceeds both the strength and modulus of the neat resin. In the next phase of work, we will continue to improve the dispersion and interfacial adhesion...
by optimizing the sonication for surface modified SNF resins and in the new resin systems with the new peroxide. In addition, we will adopt the same approach for the N307 material.

**Composite Layup Optimization Study**

From the modeling study in FY 2013, a series of prototype tanks have been wound for experimental validation. The study includes alternative fibers, fiber combinations, and alternate laminate designs in the construction of 70-MPa all-composite pressure vessels. Vessel cost and mass are the primary and secondary evaluation parameters. A finite element model of an axisymmetric cylinder wall was used to guide the tank design selection. There are over 60 pressure vessel tanks currently being evaluated.

The tanks being wound include a single fiber design comparison of T700, T720, and T800 fibers. Hybrid combinations of the currently available commercial fibers are also included. Although these did not show a significant cost reduction, several layup combinations showed a significant reduction in the tank mass. Most notable was the combination of 51% T720 inside and 49% T700 outside with a 23% predicted mass reduction without impacting the tank cost.

Other tank experiments include altering the typical layup design approach for wind angle and sequencing. The modeling study showed that tailoring the wind angles has the potential to reduce cost and mass by 3% to 14%. Increasing the stresses in the low angle helical (near axial) fibers could potentially reduce cost and mass by 7% to 16%. Implementing these alternate layup designs will require more detailed composites analysis of the tank, including the need for local reinforcement in the dome. Wind angle tailoring has higher risk with processing challenges that will be assessed through our experimental validation.

**Conclusions and Future Directions**

Research during FY 2014 has demonstrated cost reductions totaling 30% (including insulation for cold-gas) through combined material improvements, composite layup design, and cold-gas operation. The model also estimates that cold-gas operation will save an additional 38% composite mass by shifting from 70 MPa at room temperature to 50 MPa at 200 K. This is nearly double the 20% mass savings required by the Go/No-Go.

Work in the next year will focus on demonstrating these improvements through burst testing of prototype tanks with alternative resins and reduced carbon fiber mass. High-performance physical insulations will also be tested to compare cost, formability, and thermal performance.

**FUTURE WORK**

- Fabricate and burst test prototype baseline T700S carbon fiber plus epoxy tanks rated for 50 MPa and 70 MPa.
• Perform material testing of T700S fiber treatments and alternate filled resins at room temperature and cold-gas operating temperature for comparison with T700S carbon fiber and epoxy composite used in the baseline prototype tank.

• High-performance physical insulations will also be tested to compare cost, formability and thermal performance.

• Fabricate and burst test 50-MPa prototype tanks using the standard T700S carbon fiber plus AOC alternate resins reinforced with nano-particle additives.

• Report project results of modeling, material testing, and tank fabrication and burst testing.

FY 2013 PUBLICATIONS/PRESENTATIONS


REFERENCES