IV.F.4 Synergistically Enhanced Materials and Design Parameters for Reducing the Cost of Hydrogen Storage Tanks

Kevin L. Simmons

Pacific Northwest National Laboratory (PNNL) PO Box 999, MSIN K2-44 Richland, WA 99352 Phone: (509) 376-3651 Email: kevin.simmons@pnnl.gov

DOE Managers

Ned Stetson Phone: (202) 586-9995 Email: Ned.Stetson@ee.doe.gov 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, 2015

Overall Objectives

- Reduce carbon fiber (CF) usage and associated compressed hydrogen tank cost through a series of combined material and design approaches for a cumulative 37% cost savings.
- Improve the tank cost performance using the following techniques in a holistic design approach: (A) resin matrix modifications and alternatives, (B) load translational efficiency improvements by CF surface modification, (C) alternate fiber placement and materials, and (D) enhanced operating conditions to increase the energy density.
- Demonstrate the combined costs reductions through modeling, materials, and burst testing.

Fiscal Year (FY) 2013 Objectives

- Develop a feasible pathway to achieve at least a 10% (\$1.5/kWh) cost reduction, compared to a 2010 projected high-volume baseline cost of \$15/kWh for 70-MPa Type IV pressure vessels
- Conduct material testing of resin modifications with higher filler concentrations

- Evaluate tank dormancy for cold gas storage
- Establish tank modeling for resizing of cold gas storage
- Complete tooling for producing liners for baseline tanks
- Fabricate baseline sub-scale prototype tank
- Accomplish burst testing of baseline sub-scale tank

Technical Barrier

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 Hydrogen Storage 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 H_{2 stored}).

TABLE 1. Progress towards Meeting Technical Targets for Onboard Hydrogen

 Storage for Light-Duty Fuel Cell Vehicles

Technical System Targets: Onboard Hydrogen Storage for Light-Duty Fuel Cell Vehicles			
Storage Parameter	Units	2017 Targets	PNNL 2013 Status
System Gravimetric Capacity	kg H ₂ /kg system	0.055	0.051
System Volumetric Capacity	kg H ₂ /L system	0.040	.027
Storage System Cost	\$/kWh net	12	15.37

FY 2013 Accomplishments

• Developed and validated simplified estimator model for predicting tank parameters within +/- 5% of existing tank hardware.

- Completed extensive cost estimating comparison with Argonne National Laboratory and Strategic Analysis, resulting in consistent values.
- Identified 15% tank cost reduction opportunities and projected path toward a 37% target reduction.
- Accomplished modeling and material testing to identify the following potential cost savings:
 - Low cost resins (4% cost reduction)
 - Resin additive/modification improvements (5% cost reduction)
 - Alternative fiber placement and fiber types (6% cost reduction)
- Total savings after cost model analysis is 15%.

 $\diamond \quad \diamond \quad \diamond \quad \diamond \quad \diamond$

INTRODUCTION

The ultimate DOE goal of this research is to reduce the cost of compressed hydrogen storage vessels by at least 50% from the current high volume projections of \$17/kWh for commercialization in early-market and light-duty hydrogen fuel cell vehicles. The cost and performance baseline comparisons are the current 70-MPa , high-pressure storage vessels primarily constructed of standard-modulus, high-strength CF in an epoxy matrix that is overwrapped on a high density polyethylene liner (Type IV pressure vessel). The high-strength CF composite can account for nearly70-80% of the overall tank costs.

Since the composite is the dominate cost, the objective of this research is to reduce CF usage and associated tank cost through a series of combined material and design improvements that are estimated to total nearly 37% in overall cost savings. The project has identified, through modeling a series of material design requirements and experiments, the cost savings necessary to achieve the project goal. It is probable that these cost savings, combined with future reductions in CF cost, could lead to the 50% ultimate DOE target.

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 CF 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 project milestone, "to develop a feasible pathway to achieve at least a 10% (\$1.5/kWh) cost reduction, compared to a 2010 projected high-volume baseline cost of \$15/kWh for 70-MPa Type IV pressure vessels through detailed cost modeling and specific individual technical approaches," has been exceeded with an estimated 15% cost reduction in the first year based on detailed cost modeling and specific individual approaches to cost reductions. A thorough baseline performance and cost analysis was shown to compare within 5% of existing tank hardware predictions and 10% of tank costs estimated by two other independent cost models. The waterfall diagram in Figure 1 illustrates the progress of the individual technical approaches (described in the following) with estimates of future savings of nearly 40%. Each of the cost saving measures described are cumulative.



FIGURE 1. Waterfall Plot of Costs Savings

Low-Cost Resin Systems

When changing resin chemistry, the most critical element in composites is the interfacial adhesion. Fiber surface chemistries must be compatible with the resin system in use or the results will be poor-performing composite properties. The results of poor fiber wetting from incompatible surfaces of CF can be dry fiber bundles, low interfacial shear strength, and low translational efficiency in the tank windings.

Toray has developed several surface treatments for T700 fibers that have been tested with four AOC resin systems. The AOC vinyl-ester resins are lower in cost than the standard epoxies used in filament winding. Short-beam shear tests were performed to confirm that interfacial adhesion between the AOC resins and Toray fibers is similar to short-beam shear performance of the current epoxy resin system. Toray fabricated and tested short-beam shear specimens, with Ford testing a second set to confirm the test results. The tests identified fiber surface treatments that exceeded the shear strength of the CF epoxy baseline materials which confirmed vinyl-ester as a low resin replacement resulting in 4% lower tank cost.

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 nano-additives 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 strength can be achieved to an increased burst pressure of approximately 8%. This is equivalent to an 8% reduction in CF usage. Because this is direct modification of the resin matrix properties and not the fiber, we expect additional strength improvement with the CF modification for a combined savings. Figure 2 illustrates the various morphologies being under evaluation and Figure 3 is the results of the various morphologies in the low-cost resin.

Composite Layup Optimization Study

A modeling study was conducted to evaluate alternative fibers, fiber combinations, and alternative laminate designs in the construction of 70-MPa all-composite pressure vessels. The primary and secondary evaluation parameters were vessel cost and mass, respectively. A finite element model was constructed of an axisymmetric cylindrical vessel wall. The model was loaded with pressure on the inner radius and axially with the appropriate closed end axial load.

The single fiber design comparison demonstrated that the industry standard T700 fiber provides the best strength vs. cost price point of the fibers that were evaluated. The hybrid combinations of the currently available commercial fibers did not show a significant cost reduction, however, several layup combinations did show a significant reduction in the tank mass. In particular, the combination of 51% T720 inside and 49% T700 outside predicted a mass reduction of 23% without impacting the tank cost.

Altering the typical layup design approach for wind angle and sequencing showed the most significant potential for reducing both tank cost and mass. In addition, the benefit of these alternate layup designs would apply to any fiber and they are not limited to the T700 fiber used for the study. Tailoring the wind angles has the potential to reduce cost



FIGURE 2. Scanning Electron Microscope Images of Nano-Scale Material Morphology



Ultimate Tensile Strength [MPa]



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. Therefore, a low- to mid-range composite cost savings of 6% was assumed in the FY 2013 cost analysis. Detailed tank design analysis and testing will be performed during the ongoing tasks of this project to validate and likely increase this number.

CONCLUSIONS AND FUTURE DIRECTIONS

The conclusions from FY 2013 have demonstrated that there are several routes in cost reduction through combined material improvements and design. The work in FY 2013 has exceeded the target of a 10% cost savings by nearly 5% through material improvements. It is expected that future work will demonstrate these improvements in tank design and through the use of alternative materials and their improved properties.

FY 2014 FUTURE WORK

- Perform thermal and cost modeling to show the feasibility of 20% cost savings using tank insulation concepts for cold gas enhanced operation.
- Fabricate and burst test prototype baseline T700S CF 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 CF and epoxy composite used in the baseline prototype tank.
- Fabricate and burst test prototype 50-MPa prototype tanks using the standard T700S CF 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

1. K.L. Simmons. 2013. "Enhanced Materials and Design Parameters for Reducing the Cost of Hydrogen Storage Tanks." Project ID# ST101. DOE Fuel Cells Office Annual Merit Review, May 13-17, 2013, Arlington, VA. Pacific Northwest National Laboratory, Richland, WA.