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

David W. Gotthold (Primary Contact)
Pacific Northwest National Laboratory (PNNL)
PO 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: June 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 costs reductions through modeling, materials, and burst testing

Fiscal Year (FY) 2015 Objectives

- Fabricate set of six test tanks for each identified design improvement: (1) resin matrix modifications and alternatives, (2) CF surface properties that increase load translational efficiency, and (3) alternate CF placement and materials.
- Complete burst testing of all tank sets to validate design improvements
- Develop scalable process for resin modification with nanoparticulates and evaluate performance with test tanks

Technical Barriers

This project addresses the following technical barriers from the Manufacturing R&D section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration (MYRDD) 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 MYRDD Plan:

- By 2020, the project will 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 $10/kWh ($333/kg $H_{2\ stored}$). Progress toward targets shown in Table 1.

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

Storage Parameter	Units	2020 Targets	PNNL 2015 Status
System Gravimetric Capacity	kg H_2/kg system	0.055	0.051
System Volumetric Capacity	kg H_2/L system	0.040	0.027
Storage System Cost	$/kWh net	10	15.37

FY 2015 Accomplishments

- 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
- Optimized nanoparticulate materials and processing selected and scaled to tens of gallons of modified resin to enable production of 70l batches of modified resins. The modified resins did not show increases in burst pressure and caused increased manufacturing variations

- Alternate winding patterns tested, improved high shear failure model developed that more accurately represents high shear layers and determined that existing winding pattern is near optimal for the selected tank dimensions and manufacturing processes
- Eleven sets of six tanks built and burst tested to evaluate previous theoretical design improvements with statistically significant sample sizes

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INTRODUCTION

The goal of this research is 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 comparisons are 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, our research objective is to reduce carbon fiber usage and associated tank cost through a series of combined material and design improvements that are estimated to total nearly 37% of the project initial baseline tank cost. The project has identified through modeling a series of material design optimizations and experiments that achieve the cost savings goal. It is probable 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 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 key work for FY 2015 was to validate the previously identified design and material improvements by fabricating and burst testing a set of six tanks with each design modification. In total 66 tanks were made and burst tested and the results are summarized in Table 2.

Improved and Modified Resins

Based on work in FY 2014, a low cost modifed vinyl ester resin was developed based on a commercially standard T015 vinyl ester resin. The new resin, XR-4079, was modified to have a reduced tackiness and optimized viscosity for nanoparticle integration. Tanks were made with both standard 24k tow carbon fiber with epoxy sizing and with 12k

TABLE 2. Summary of measured tank data for the 35.4 L test tanks. The burst data is all measured relative to the baseline tank. The rightmost column is the estimated total tank masses for a full-size 145 L tank.

									Tank Volume	
				Estimated Tank Masses at 100% Burst					35.4L	145L
		Actual		Estimated			Liner &	Total	Total Composite @ 1	
		Relative to Baseline		Mass** at	Carbon	Resin	Bosses	Mass	Test	Fullscale
Description		Mass	Burst	100% Burst	Fiber, kg	kg	kg	kg	Tank	Tank
	Baseline	100.0%	100.0%	100.0%	18.0	8.4	6.8	33.2	26.4	108.1
Low cost Resins										
	Baseline + Resin 1 Substitution	95.3%	100.0%	95.3%	18.0	6.9	6.8	31.6	24.8	101.7
	Baseline+Resin1+12kT700+Alt. Sizing	93.2%	101.2%	92.3%	17.7	6.1	6.8	30.7	23.9	97.7
Modified Resins										
	Baseline + Resin 1 + Nano Mod 1	96.1%	87.4%	107.0%	20.5	8.2	6.8	35.5	28.7	117.7
	Baseline + Resin 1 + Nano Mod 2	95.8%	89.9%	104.3%	20.0	7.8	6.8	34.6	27.8	113.9
Fiber Winding Patterns										
	Sorted HAHs, Interspersed with LAH	95.0%	91.0%	102.4%	18.5	8.7	6.8	34.0	27.2	111.4
	Sorted HAHs, No Interspersion	88.0%	83.0%	101.8%	18.4	8.6	6.8	33.8	27.0	110.6
	Baseline with 1 Adj Removed	96.0%	95.0%	100.0%	17.9	8.4	6.8	33.2	26.4	108.1
	Baseline with 2 Adj Removed	91.0%	88.0%	100.6%	18.1	8.5	6.8	33.4	26.6	109.0
Alternate Fibers										
	Baseline with T720 Substitution	96.2%	104.0%	93.3%	17.3	6.9	6.8	31.0	24.2	99.0
	Baseline with T800 Substitution	98.7%	112.6%	89.9%	15.9	7.1	6.8	29.9	23.1	94.5

tow carbon with sizing optimized for vinyl ester resins. Both fibers showed reduced mass compared to the baseline tanks.

For tanks made with the standard 24k tow T700 carbon fibers, the average burst pressure for these tanks was exactly the same as the baseline tank. The reduction in mass was due to the reduced viscosity of the resin leading to a high CF volume fraction in the final tank. This is reflected in the same CF mass (18 kg) as the baseline tank, and the reduced resin mass (6.9 kg vs. 8.4 kg). A full scale tank would weigh 101.7 kg vs. 108.1 kg for a baseline epoxy tank.

For the tanks made with the 12k T700 fiber with a sizing optimized for vinyl ester resins, the measured burst pressure was improved by 1.2% over the baseline tank due to improve adhesion between the resin matrix and the fibers. The improved performance is visible in the burst tank shown in Figure 1, where the broomstraw-like appearance is an indication of improved energy transfer. This improved burst pressure means that the carbon fiber content can be reduced from 18 kg to 17.7 kg and still achieve the same burst pressure as the baseline tank. When combined with the reduced resin cost (~50% of standard epoxy resins), this will lead to a 5%–7% cost reduction in the full sized tanks.

Alternative fiber placement

Despite initially promising model predictions, fiber placement resulted in lower burst pressures. Extensive work was done to understand the mismatch between the modeled and measured burst pressures for the alternate winding patterns. Hexagon Lincoln reviewed a range of different failure models and observed that burst performance correlated well with the Yamada-Sun combined stress (or strain) failure criteria [1]. The Yamada-Sun model combines both the uniaxial and shear stresses (or strains) to better predict failure when there is a high shear component.

$$\left[\frac{\sigma_1}{X_1}\right]^2 + \left[\frac{\tau_{12}}{S_{12}}\right]^2 = 1$$

FIGURE 1. Image of burst tank made with vinyl ester resin

The equation accounts for both the uniaxial stress (σ_1) and shear stress (τ_{12}) and scales both to the corresponding uniaxial failure strength (X_1) and shear failure strength (S_{12}). The Yamada-Sun failure criteria can also be expressed in terms of the ratios of the applied uniaxial and shear strains to the corresponding failure strains. With this new model, shown in Figure 2, we can now accurately predict failures for designs with higher interlaminar shear. However, this new understanding implies that the current designs are near at least a local optimum, as the most load is taken up by the purely tensile carbon fiber, not the lower strength matrix needed for shear. At this point, we continue to review the model to see if there are significant improvements to be made, but the likelihood of significant improvement is reduced.

Alternative fibers, T720 and T800, were also made into tanks to evaluate opportunities for fiber strength optimization. While significant weight reductions were observed—6.7% for the T720 and 10.1% for the T800 fibers—the increased cost of these fibers outweighs the potential savings from mass reductions.

Enhanced Operating Conditions

Initial materials testing has been initiated to validate the feasibility of low temperature gas storage. Initial tests have been completed for standard high density polyethylene (HDPE) at dry-ice temperatures. For the purposes of testing the HDPE, button head dog-bone type tensile samples were fabricated from standard HDPE rod stock. Samples were cooled for at least two hours in crushed dry-ice to ensure cold temperature saturation at -78.5°C. The dwell time was determined by monitoring a similar HDPE sample with a thermocouple implanted inside it.

The tensile tests clearly showed increased modulus and ultimate tensile strength (UTS) for the HDPE with decreasing temperature at both dry-ice and liquid nitrogen (LN_2) temperatures. No significant changes in ductility were observed within this temperature range. For example, the UTS was nearly 50% higher at dry-ice temperatures and 70% higher at LN_2 temperatures relative to room temperature. Likewise, the modulus was increased by 60% and 125% for dry-ice and LN_2 temperatures respectively as compared to room temperature. Elongation of at least 20% was observed at all temperatures.

CONCLUSIONS AND FUTURE DIRECTIONS

Research during FY 2015 has demonstrated the challenges between modeling and full scale test data, with better than expected results for the alternative resins, and worse than expected for the nanoparticle modified and alternate winding patterns.

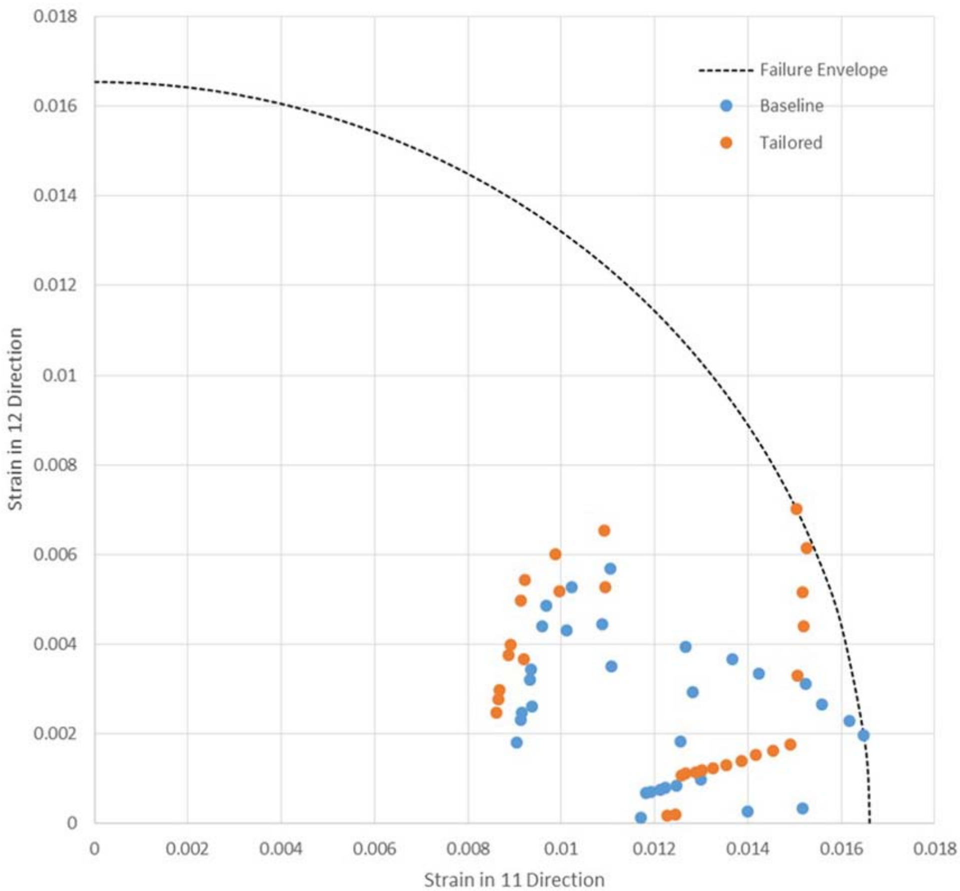

FIGURE 2. Tensile and shear strains for discrete lamina in both the baseline and tailored tank designs. The arc is the Yamada-Sun combine tensile-shear failure criteria, while the standard failure criteria only considers tensile strain (x-axis).

FY 2016 Future Work

- Fabricate and fatigue test impact damaged tanks to further validate the performance of the new vinyl ester resin for potential commercial usage
- Perform mechanical properties tests at low temperature enhanced operating conditions for key materials, including stability of all key structural materials and performance of insulation
- Coordinate vehicle-level enhanced operating conditions with the infrastructure and delivery model developed by Argonne National Laboratory
- Report project results of modeling, material testing, and tank fabrication and burst testing

FY 2015 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 Fuel Cells Office Annual Merit Review, June 8–12, 2015, Washington, DC. Pacific Northwest National Laboratory, Richland, WA.

REFERENCES

1. Yamada, S.E. and C.T. Sun, “Analysis of Laminate Strength and Its Distribution.” Journal of Composite Materials, 1978. **12**(JUL): p. 275–284.