IV.D.11 Development of Improved Composite Pressure Vessels for Hydrogen Storage

Jon Knudsen (Primary Contact), Norm Newhouse, John Makinson
Lincoln Composites, Inc.
5117 NW 40th Street
Lincoln, NE 68524
Phone: (402) 470-5039
E-mail: jknudsen@lincolncomposites.com

DOE Managers
HQ: Ned Stetson
Phone: (202) 586-9995
E-mail: Ned.Stetson@ee.doe.gov
GO: Jesse Adams
Phone: (720) 356-1421
E-mail: Jesse.Adams@go.doe.gov

Contract Number: DE-FC36-09GO19004

Project Start Date: January 1, 2009
Project End Date: July 31, 2014

Fiscal Year (FY) 2011 Objectives

- To improve the performance characteristics, including weight, volumetric efficiency, and cost, of composite pressure vessels used to contain hydrogen in media such as metal hydrides, chemical hydrides, or adsorbents.
- To evaluate design, materials, or manufacturing process improvements necessary for containing metal hydrides, chemical hydrides, or adsorbents.
- To demonstrate these improvements in prototype systems through fabrication, testing, and evaluation.

Technical Barriers

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

(A) System Weight and Volume
(B) System Cost
(G) Materials of Construction

Technical Targets

This project is conducting fundamental studies for the development of improved composite pressure vessels for hydrogen storage. Insights gained from these studies will be applied toward the design and manufacturing of hydrogen storage vessels that meet the DOE 2010 hydrogen storage targets in Table 1.

TABLE 1. Hydrogen Storage Targets

	2010	2015
Gravimetric capacity:	>4.5%	>5.5%
Volumetric capacity:	>0.028 kg H_2/L	>0.040 kg H_2/L
Storage system cost:	TBD	TBD

TBD – to be determined

✧ ✧ ✧ ✧ ✧

Introduction

Lincoln Composites is conducting research to meet DOE 2010 and 2015 Hydrogen Storage Goals for a storage system by identifying appropriate materials and design approaches for the composite container. At the same time, continue to maintain durability, operability and safety characteristics that already meet DOE guidelines for 2010 and 2015. There is a continuation of work with Hydrogen Storage Engineering Center of Excellence (HSECoE) partners to identify pressure vessel characteristics and opportunities for performance improvement. Lincoln Composites is working to develop high pressure vessels as are required to enable hybrid tank approaches to meet weight and volume goals and to allow metal hydrides with slow charging kinetics to meet charging goals.

Approach

Lincoln Composites is establishing and documenting a baseline design as a means to compare and evaluate potential improvements in design, materials and process to achieve cylinder performance improvements for weight, volume and cost. Lincoln Composites will then down-select the most promising engineering concepts which will then be evaluated to meet Go/No-Go requirements for moving forward.

The following areas will be researched and documented:

- Evaluation of alternate fiber reinforcement
- Evaluation of boss materials and designs
- Evaluation of resin toughening agents
- Evaluation of alternate liner materials
- Evaluation of damage vs. impact
- Evaluation of stress rupture characteristics
- Evaluation of in situ non-destructive examination (NDE) methods to detect damage

Results

Lincoln Composites has completed the documentation of a baseline design as a means to compare and evaluate potential improvements in design, materials and process to achieve cylinder performance improvements for weight, volume and cost. Baseline characteristics, service conditions and nominal properties, are listed in Table 2.

Lincoln Composites has completed testing on alternate fibers relative to fiber strength and impact tolerance. Baseline fiber was selected as Toray T700. Five alternative carbon fibers were tested as part of the study. Vessels were constructed with each of the five fibers using same parameters on each: mandrel, wind patterns, tooling and processing. Tow count was adjusted, per fiber, to maintain consistent band cross sectional area. Testing was completed on all vessels including burst testing and drop/cycling. (See Table 3 showing a comparison of results of initial testing.) Two of the fibers indicated higher strength than baseline. Four fibers showed a potential lower cost per pound. The testing showed that these new fibers as received and tested did not meet expectations and strength versus cost showed no improvement compared with the baseline. Lincoln Composites worked directly with two of the fiber suppliers, Toho and Grafil, to obtain improved fiber strength. After making improvements to their fibers, additional vessels were fabricated and their fibers were found to match existing baseline fiber in strength during burst testing. A benefit is the fact that having alternate fibers could potentially reduce costs by 10-15% from suppliers. Three fibers now could be used interchangeably in the construction of composite pressure vessels.

Lincoln Composites has completed the testing of an alternative boss material as part of the project. Baseline material is 6061-T6 aluminum. Investigations have been completed to create bosses constructed with aluminum 7075-T73. Properties, of which, are difficult to acquire through entire thickness. Higher strength would allow reduction in boss size and allow aluminum use at high pressures. Proper heat treat is a challenge to get correct strength properties and to avoid embrittlement. Near net shaped bosses were machined from 7075-T6 aluminum with the following

TABLE 2. Service Conditions and Nominal Cylinder Properties

Service Pressure	5,000 psi (344.7 bar)
Gas Settling Temperature	59 °F (15 °C)
Maximum Fill Pressure	6,500 psi (448 bar)
Service Life	20 years
Gas Fill Temperature Limits	-40 to 149 °F (-40 to 65 °C)
Operating Temperature Limits	-40 to 180 °F (-40 to 82 °C)
Proof Test Pressure	7500 psi (517 bar)
Minimum Rupture Pressure	11,700 psi (807 bar)
Cylinder Diameter	21.4 inches (543.4 mm)
Cylinder Length (unpressurized)	63.0 inches (1600 mm)
Cylinder Length at Maximum Fill Pressure	63.34 inches (1609 mm)
Cylinder Empty Weight (excluding hardware)	231 lbs (105 kg)
Cylinder Volume	15,865 in^2 (260 L)
Cylinder Volume at Service Pressure	16,132 in^2 (264.4 L)
Cylinder interior diameter	19.2 inches (488 mm)

TABLE 3. Initial Results of Alternate Fiber Testing

	Performance			Construction	
Fiber	Virgin Burst (psi)	Burst after Drop/ Cycle (psi)	% Reduction	Tows of Carbon Fiber	Band Carbon Cross Section (in^2)
Toray T700 24K (Baseline)	13,415	-		3	0.00429
Toray T800 24K	16,009	14,599	-9%	5	0.00444
Toho J30743HP 24K	12,249	10,543	-14%	3	0.00433
Grafil TRH50 18K	13,542	12,837	-5%	5	0.00433
Grafil TRH50 60K	12,152	10,193	-16%	2	0.00548
Hexcel AS7 12K	11,721	9,841	-16%	6	0.00414

surface finishes: smooth machining, rough machining, sand blasted and chemical etching. These bosses were then heat treated to a T73 condition. Bosses were sectioned and tensile testing on the specimens has been completed. Testing has confirmed the proper heat treat on the aluminum. Yield strength is 2 times that of 6061-T6 aluminum or 316 SS. Cost of bosses could be same to 1.5 times that of 6061-T6 and 1/5 that of 316 SS. Next step is to incorporate 7075 aluminum into new designs.

Investigations into alternate resin compilation are underway to determine effects on the toughening properties of a full-scale vessel, and would support the reduction in safety factors required for the vessel. First phase was to research and perform testing on alternate hardeners that could be used with our current baseline resin. Several experiments were run with alternate hardeners with an end result that our current hardener performs best. Next step is to use this hardener to begin looking at different resin formulations. One task is to down-select based on screening of viscosity and T_g results. Further testing is planned to determine mechanical and environmental/chemical properties. Upon completion, a down-select activity will determine what resin formulations will be used to produce coupons for impact testing. The last activity will then be to build full-scale vessels with the alternate resin formulations and to perform further testing such as impact. Initial candidates for toughening agents have been selected. This task will be continued as composite coupons and full-scale vessels are built for further testing.

Studies are ongoing with respect to alternate materials to minimize the permeability of gas through the high-density polyethylene (HDPE) liners that Lincoln Composites currently uses. The evaluations of coatings and surface treatments have shown blistering following a hydrogen soak and blow down. Surface treatments have not shown to be effective. The first investigation into Nanoclay additives gave unsuccessful results. The molecular properties of HDPE did not promote dispersion. However, new material found from alternate vendor has shown some improvements, with a reduction of about 40% in permeation. HDPE with titanium dioxide has resulted in a 25% reduction in permeation. Lincoln Composites has also worked with the addition of ethylene vinyl alcohol (EVOH). We encountered problems with layered materials including the ability to weld. We looked at adding as an outside layer to keep the material away from the weld joint, however, have had issues with adhesion of the EVOH to the HDPE. Lincoln Composites is in the process of looking at EVOH that has been modified to increase ductility. The evaluation of nylon as a filler has also been targeted. The cost of nylon, when compared with HDPE, would generate a large cost increase. Liners have been built with the following conditions: HDPE (baseline), HDPE/standard nanoclay, HDPE/development nanoclay, and HDPE/titanium dioxide. These have been wound into short tanks and testing will then move forward on full-scale models. A permeation rate versus cost relative to HDPE is shown in Figure 1. HDPE is the baseline at 1:1. HDPE fillers show a 40% reduction with limited cost increase. Alternate materials show promise of significant permeation reduction while others are prohibitively expensive. Reduction of the liner thickness will increase internal volume, allowing storage of more hydrogen, and will reduce weight. This task will be continued as further means to reduce permeation are investigated.

Lincoln Composites is looking into an improved data base for stress rupture of carbon fiber that may allow for reduced safety factors. This will in turn maintain projected reliability and reduce cost, weight and increase volumetric efficiency with thinner walls. A stress rupture project presented at industry workshop to gain feedback and support was conducted. The project is currently being refined with some collaborators and funding identified. Additional collaboration and funding is being sought, however, this additional funding has not been committed. Stress rupture, fatigue and damage tolerance are all being considered in the study. Fiber stress rupture and cyclic fatigue are directly related to stress ratio and damage tolerance is affected. The reduction in safety factor from 2.25 to 2.00 is planned and studies indicate that high reliability is maintained. Field experience indicates safe operation as long as damage tolerance is addressed. It can be addressed by other designs and testing. The evaluation of damage vs. impact is being considered to characterize safety and ability to remain in service after damage. NDE as a means of monitoring the structural integrity is being considered which will allow for thinner laminates and removal from service before rupture. The benefits of a reduced safety factor include: carbon fiber cost reduction of 10%, potential for increased cylinder volume, and the potential for weight reduction. All factors must be balanced against cost, envelope, and weight of other means of damage

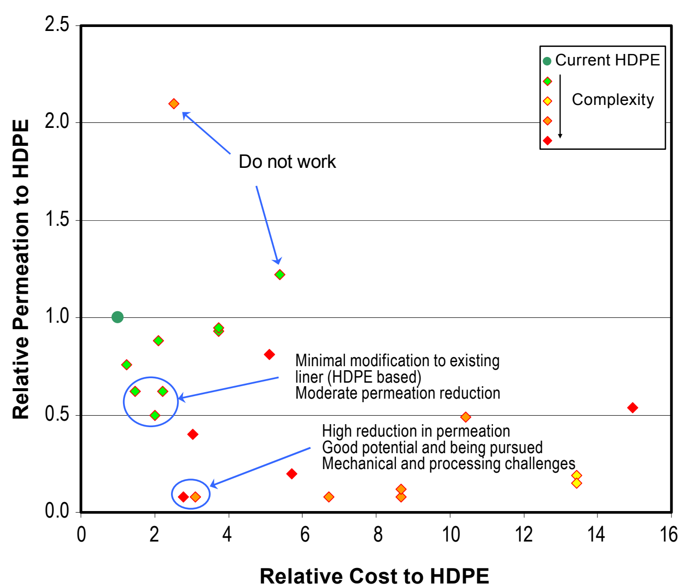

FIGURE 1. Permeation Rate versus Cost Relative to HDPE Liner Material

protection, if necessary. This task is on hold pending location of additional partners and funding.

Conclusions and Future Directions

The studies above have provided progress to meeting DOE goals for hydrogen storage. The full effectiveness of these improvements must be evaluated as part of a full system. However, improvements for the composite vessel itself are as follows:

- Reduced cost and weight from improved boss material.
- Reduced fiber cost by developing alternate fibers of equal strength.
- Reduced cost, potential reduced weight and increase volume, by reducing carbon fiber factor of safety.
- Reduced weight, increased volume, by reducing liner thickness.

For the cylinder itself, these improvements indicate the potential for:

- 11% lower weight
- 4% larger internal volume
- 10% lower cost

Future work for this project will be to continue progress on evaluating potential improvements, particularly as noted above for projects not yet completed. After completion of Phase 1, Lincoln Composites will down-select the most promising engineering concepts and evaluate against DOE 2010 and 2015 Hydrogen Storage Go/No-Go criteria.

Plans are being solidified for the evaluation of liner materials that can withstand high and low temperatures. Current materials in use have an operating temperature range of -40° to +85°C. We plan to look into materials at -200°C on the low end and up to 375°C on the high end. Testing has begun to cycle tanks cold to ambient and hot to ambient followed by a burst test to evaluate our current materials. This was not part of the original scope of the project, but is being requested by team members of the HSECoE. Initial results show cold temperature exposure, to liquid nitrogen and soaking, does not affect the strength. Additional testing will be conducted.

Phase 2 is continuation of container development in support of system requirements. Specific attention will be directed to input from partners in support of concepts selected to go forward with Phase 3 and the fabrication of subscale vessels to support assembly of prototype systems for evaluation.

FY 2011 Publications/Presentations

1. Co-authored paper/presentation, **"Potential Diffusion-Based Failure Modes of Hydrogen Storage Vessels for ON-board Vehicular Use",** Yehia Khalil (UTRC), Norman Newhouse (LC), Kevin Simmons (PNNL), Daniel Dedrick (SNL), at AICHhE 2010 Annual Meeting, Salt Lake City, November 2010.

2. 2011 DOE Hydrogen Program Annual Merit Review, May 11, 2011.