# IV.D.4 Next Generation Hydrogen Storage Vessels Enabled by Carbon Fiber Infusion with a Low Viscosity, High Toughness System

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Subcontractors:
- Montana State University, Bozeman, MT
- Spencer Composites Corporation, Sacramento, CA

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Project End Date: August 30, 2017

## Overall Objectives

The project is focused on supporting the key DOE metrics for a 700-bar, Type IV tank by meeting the following objectives:

- Reduce the carbon fiber (CF) composite volume by 35%.
- Demonstrate cost of composite materials of $6.5/kW-hr. This component cost is an important element of the DOE 2020 system cost target of $10/kW-hr.
- Demonstrate industry-standard performance (burst strength of 1,575 bar and 90,000 cycle life).

## Fiscal Year (FY) 2016 Objectives

- Optimize infusion on full-scale tanks with aid of infusion models.
- Manufacture full-size tanks with CF reduction and test.
- Conduct key tests to confirm performance current standards.

## 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

(D) Durability/Operability

(G) Materials of Construction

## Technical Targets

The project is focused on the technical targets highlighted in Table 1 related to the gravimetric and cost metrics of onboard automotive hydrogen storage systems. Since a significant portion of the cost is directly from the carbon-fiber composite overwrap, the project aims to reduce the amount of composite necessary to meet the tank specifications. During FY 2016, the project has met some key milestones to provide updated estimates on the progress towards the technical targets in Table 1.

**TABLE 1.** Progress towards Technical Targets for Onboard Automotive Hydrogen Storage System

| Characteristic | Units | 2020 Target | FY 2016 Status |
|---|---|---|---|
| Gravimetric | kW-hr/kg sys | 1.8 | 1.6 to 1.8 Estimated* |
| System Cost | $/kW-hr at 500,000 units/yr | 10 | 9 to 10.5 Estimated* |

*Estimates based on assumptions of 30% and 15% CF reduction

## FY 2016 Accomplishments

- Demonstrated improved vacuum processing with reduced fabrication time from 2.0 hours to 0.5 hours for high-quality 7.5-liter prototype vessels.
- Leveraged infusion modelling in order to optimize vacuum infusion processing by refining the infusion/vacuum port placement.
- Achieved equivalent burst strength in static testing of small prototype vessels (Type III, 7.5 L) for vacuum-infused version versus wet-wound epoxy (26,586 psi).
- Pursued process scale-up to full-size pressure vessel from 7.5 liters to 133 liters.

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## INTRODUCTION

DOE Office of Energy Efficiency and Renewable Energy has established aggressive performance targets for Type IV hydrogen storage vessels for Year 2020. Current designs and materials of construction for composite-overwrapped pressure vessels (COPVs) within the industry do not reach the performance targets, as shown by the base-case published by Ahluwalia et al. from Argonne National Laboratory. The specialty chemical producer, Materia, has developed a novel composite resin system, Proxima®, with ultra-low viscosity (5 cP to 10 cP) that enables vacuum infusion processing for thick CF composite components. The use of this process with Proxima circumvents some challenges inherent with traditional wet filament winding, such as the presence of voids and dry spots. The use of vacuum infusion processing, also known as VARTM (Vacuum-Assisted Resin Transfer Molding), for fiberglass composite parts is commonplace in several large-scale industries (marine, wind blades), but the feasibility of VARTM for compressed gas vessels is not clear. While the concept of infusing dry-filament wound structures has been mentioned in the open literature, the small inter-fiber gaps associated with high-performance CF composites potentially presents significant processing difficulties. Therefore, the commercial application of this approach appears to be limited—which may be related to traditional resin possessing viscosities >200 cP.

In addition to reducing void content, Proxima-based composites also have significantly improved fracture toughness (>3X higher interlaminar fracture toughness) and fatigue performance over currently employed composites for hydrogen storage tanks. The project seeks to leverage this combination of tough resin and new processing to produce CF composite overwrap with better performance, especially in fatigue and damage-tolerance testing. These high-performing composites will enable the reduction of the quantity of CF composite overwrap, which alone can account for over 75% of the storage tank system cost. The processing-related costs for this new approach are expected to be similar to current processing costs with wet-winding. By reducing the CF composite content in COPVs by 35%, the project aims to reduce the cost and weight of COPVs and contribute to meeting the DOE 2020 cost target of $10/kW-hr.

## APPROACH

Since the project requires expertise in a variety of fields, the project team includes Spencer Composites Corporation to lead the specialized filament-winding effort. Montana State University-Bozeman will experimentally characterize composite materials and also use finite element analysis (FEA) models to anticipate problem areas in tanks designs. Materia is leveraging its experience in infusion process optimization with low-viscosity resin (<10 cP) to demonstrate a series of prototype parts, including tanks and model flat plates of filament wound composites. In order to manage the risks associated with a new resin and a new process for COPVs, the project activities have been divided into stages and the objectives (1) process optimization, (2) COPV design, (3) design optimization, and (4) scale-up of process for vessel testing.

## RESULTS

During FY 2016, important progress was made to support the transition from smaller prototype vessels (Type III, 7.5 L) to full-scale pressure vessels (Type IV, 133 L). The smaller vessels were useful for optimization of the vacuum infusion process to confirm low void content and good burst strength compared to epoxy controls. For example, the team found a preferred port placement for resin infusion (shown in Figure 1) resulting in shorter infusion time (0.5 hr vs. 2.0 hr). In this new set-up, resin is first introduced at each dome to ensure complete infusion past the tangent region. Then a third resin inlet located at the bottom of the cylinder is opened to help complete the infusion more quickly.

In addition to process optimization, the team made progress in vessel performance by preparing and testing a small vessel based on a new winding pattern to eliminate a stress concentration in the shoulder region of the 7.5-liter vessel. The desired failure mode was obtained with the new winding pattern (hoop failure vs. dome failure). Accordingly, excellent values of burst pressure and demonstrated fiber strength were observed. In Table 2, the most recent results in the last row are compared to results obtained in the previous report period, FY 2015.

Moving forward from the small vessels, full-size prototypes were prepared for vacuum infusion studies at Spencer Composites. In Figure 2, the full-scale, dry-wound tank is shown just before resin infusion begins. Several infusion trials have been conducted with increasing degrees of success; however, a vessel ready for testing has not yet been achieved due to some vacuum leaks before curing. Necessary changes in the process have been identified to obtain a high-quality vessel and reduce the chance of a process upset, such as vacuum leaks. Lastly, the efforts have been sufficient to provide preliminary cost estimates for the full-scale COPV along with sensitivity analysis, as shown in Figure 3. As expected, the cost benefits of CF reductions can

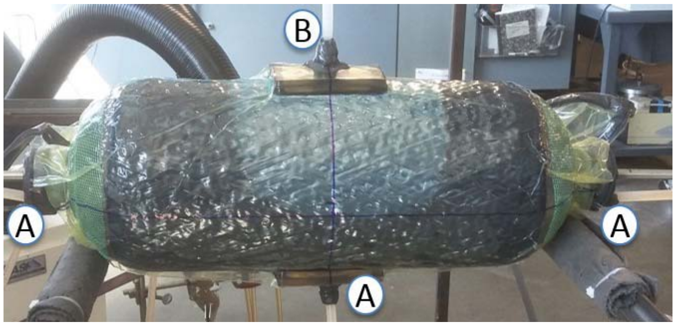

**FIGURE 1.** A 7.5-liter vessel during the optimized vacuum infusion process with "A" ports allowing introduction of resin and the "B" port providing the vacuum outlet

**TABLE 2.** Improvements in Small Prototype COPV (Type III, 7.5 L)

| Fabrication Type | Resin | Winding | Burst Strength | Demon. Fiber Strength | % Deliv. Fiber Strength |
|---|---|---|---|---|---|
| Wet Wound | Anhydride-Cured Epoxy | Winding Pattern #1 | 1,834 bar (26,595 psi) | 693 ksi | 92 |
| Dry Wound/ Resin Infused | Proxima ACR | Winding Pattern #1 | 1,001 bar (14,524 psi) | 356 ksi | 47 |
| Dry Wound/ Resin Infused | Proxima ACR | Winding Pattern #1 | 1,694 bar (25,569 psi) | 634 ksi | 84 |
| **Dry Wound/ Resin Infused** | **Proxima ACR** | **Winding Pattern #2 to minimize gaps** | **1,833 bar (26,586 psi)** | 732 ksi | 97 |

ACR – Area coverage ratio

**FIGURE 2.** Full-scale tank (133 L) prepared for vacuum infusion

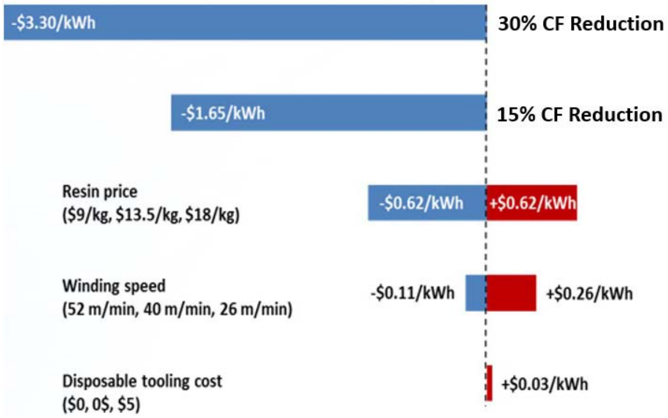

**FIGURE 3.** Sensitivy analysis of COPV cost based on preliminary processing and design estimates. The dotted line denotes a baseline cost of $12.03/kWh before any CF reductions. (Analysis performed by Strategic Analysis, Inc.)

counter-balance the extra processing time for the additional processing steps for vacuum infusion.

In order to compare the damage tolerance of composite laminates using different resins, epoxy-based and Proxima-based laminates were prepared using triaxial glass-fiber fabrics. While we are in the process of conducting similar studies with carbon fiber laminates, the initial study employed a readily obtainable triaxial glass fabric as a preliminary step. After cycling (tension-tension stress ratio, R = 0.1, for 90,000 cycles) at strain levels expected for the maximum operating pressure, as shown in Table 3, Proxima composite laminates showed excellent retention of static tensile strength (>95%). In a comparative test, a low-void laminate based on anhydride-cured epoxy was tested to have only 70% strength retention after 90,000 cycles. Initial strengths were equivalent for the two types of laminates. Panels with higher void content (3–5 vol%) were pursued but proved to be difficult to prepare in a reproducible manner.

**TABLE 3.** Comparison of Residual Strength of Composite Laminates after Cycling

| Resin Type | Anhydride- Epoxy | | Proxima ACR | |
|---|---|---|---|---|
| Void % | 1.1 | | 1.6 | |
| Specimen Conditioning | Initial | 90,000 Cycles | Initial | 90,000 Cycles |
| Tensile Strength (MPa) | 680 | 477 | 667 | 631 |
| Strength Retention after Cycling | | 70% | | 95% |

Epoxy = Dow DER 354 Epoxy/Lindride 36 V Anhydride Cure System, cured at 90°C

## CONCLUSIONS AND FUTURE DIRECTIONS

From the current results of the project, the team has derived the following conclusions:

- Optimization of dry-fiber placement yielded measurable improvements in burst strength.
- Preparation of small COPV (Type III, 7.5 L) can achieve complete resin infusion within 30 min.
- Residual strength of composite plates after fatigue cycling is improved with tougher Proxima matrix resin.

The following activities will be the area of focus in the future:

- Optimize the process to produce full-scale vessels in a reliable and manufacturing-friendly manner.
- Update current cost model of tanks based on design and processes.
- Generate key performance data including drop-testing and pressure cycling for full-scale vessels with lower CF content.