Next Generation Hydrogen Storage Vessels Enabled by Carbon Fiber Infusion with a Low Viscosity, High Toughness Resin System

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DOE AMR 2017

Project ID: ST114

Overview

Timeline

Project Start Date: 08/05/2014
Project End Date: 08/30/2016 (Original)
Proposed End Date: 08/30/2017
(No-Cost Extension)

Barriers

A. System Weight and volume
B. System Cost

Budget

Total Project Budget: $2.96 M

- Total Federal Share: $2.0 M
- Total Recipient Share: $0.96 M
- Actual Spent: $1.8 M / $0.87 M

Key Partners

- Montana State Univ. Composite Technologies Research Group(Doug Cairns)
- Spencer Composites Corp.
- Hypercomp Engineering

Relevance

Overall Objective for 2-Year Project:

Demonstration of a 700-bar, Type IV Composite Overwrap Pressure Vessel (COPV) with:

(1) Reduction in Carbon-Fiber (CF) composite volume/mass by 35%

(2) Cost of composite materials of $6.5 - 7.5/kW-hr. This component cost is an important element of the system cost project target of $12/kW-hr

(3) Performance maintained (burst strength of 1575 bar and 45° drop test)

Objectives, FY 2016/2017	**Completion Date**
Evaluate static properties and void content on test plates	**Done**
Prepare and burst small tanks via infusion process	**Done**
Scale up process to full scale COPVs	5/30/2017
Demonstrate path to savings on CF and cost	6/30/2017

Impact on FCTO Technical Barriers: A. System weight and volume
B. System Cost

Approach: Technical Premise

Enabling CF reduction through alternative processes and resins

- Reduction in void defects in the composite wall by using vacuum infusion processing of dry-wound forms enabled by a very low viscosity resin
- Use of high fracture-toughness resin (Proxima® ACR) with better fatigue performance and crack resistance for resin-sensitive tangent region
- More aggressive COPV design which leverages toughness / low void

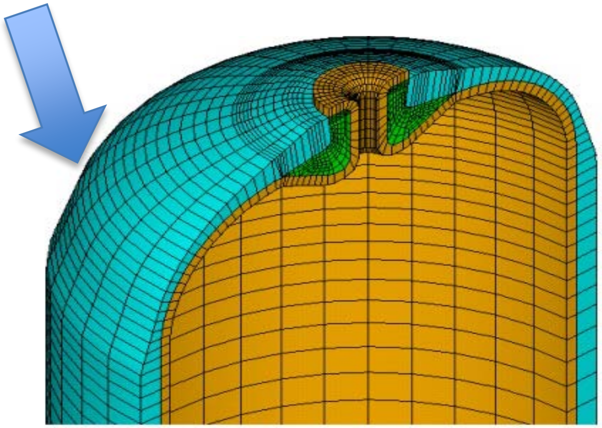
Project Challenge

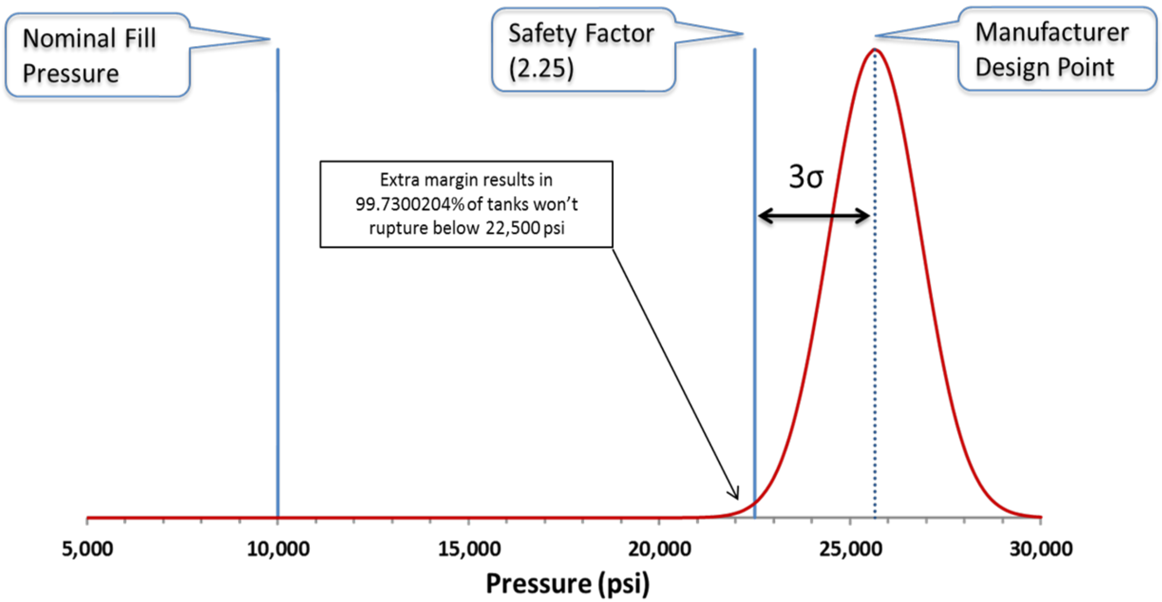
- Optimizing process for low void CF composite in thick walled sections using vacuum infusion processing at economical cycle times
- Optimizing COPV design and dry-winding for optimal performance-cost ratio
- Developing sufficient data on residual strength after drop tests

Approach: Maximizing Damage Tolerance

- COPVs perform efficiently during static burst tests (fiber dominated), But..

  Damage during 45° drop test can force otherwise "efficient designs" to become larger in volume (foam pads)
- Designs are usually targeted to allow 3 STD above the 2.25 safety factor





[1] Binetruy, C., Hilaire, B. and Pabiot, J., *Journal of Composite Materials*, Vol. 32 (1998) 223-245.

Approach: Project Phases and Key Milestones

FY2015

- ☑ Project start-up
- ☑ Infused Thickness, > 30 mm
- ☑ Show low void content (<1 %)

Demonstrate infusion process feasibility (Thin and thick plates)

FY2015 / 16

- ☑ Predict effect of toughness, voids, fiber on tank (M6.1, 6.2, 6.3)
- ☑ Design tank with lower CF content (M9.2)

Design tank using models and materials data (static and fatigue)

FY2016/17

- ☑ New process proof of concept
- ☑ Scale equipment for larger COPV

Extend process to small tank prototypes

FY2016/2017

- ☐ Produce a series of tanks during optimization
- ☐ Test tanks for performance

Demonstrate and refine process / performance in full-scale design

Approach: Project Team

- Materia's low viscosity resins (< 20 cP) enable vacuum infusion of thick carbon fiber laminates with low void content (<1%).
- Project partners bring expertise in composite testing, characterization and modeling (Montana State Univ) and non-traditional filament winding (SCC)

Composite Materials (Materia)

- Resin qualification / selection
- Subscale/ Full-scale part manufacture
- Resin infusion optimization

Filament Winding (SCC)

- Dry winding (small-scale)
- Fiber path optimization
- Prototype testing
- Liner Molding
- Full-scale tanks

Testing and Modeling (MSU / Cairns)

- FEA & design studies
- Static / Fatigue testing
- Void analysis
- Infusion process modelling

Accomplishment and Progress: **Summary**

Task	Status
Optimize processing / Formulation for infusion of plates	**Completed**
Develop data set of key mechanical properties (static)	**Completed**
Conduct dynamic testing on composite plates	**Completed**
Prepare small tanks (Type 3) as "Proof of Principle" for process	**Completed**
Design COPV winding pattern for full-size Type 4 tanks	**Completed**
Optimize infusion approaches for small and larger tanks	June 2017
Manufacture large tanks for drop test residual strength	July 2017
Complete costing estimates based on realized CF reduction	July 2017

Time	Key Milestones & Deliverables
Year 1	Demonstrate 35% reduction in composite cost of 6.5 $/kW-hr in subscale parts **(Completed)**
Year 2	Produce prototype tanks with reduced CF that reach DOE 2020 Gravimetric target (1.8 kW-hr / kg)

Accomplishments: Design Summary from Year 1

Model Parameters for 700 bar, Type IV tank (147 Liter)

Parameter	DOE 2013 Model	Project Model	Comment
CF Tow	711 psi (Toray T700)	800 psi (MRC 37-800)	Higher potential strength
Allowable Fiber Stress	512 ksi	650 ksi	
Stress Ratio	0.60	0.75	Assumed lower dome failure risk with tough, low void resin
Thickness, cylinder	31.9 mm (ABAQUS)	21 mm (Netting) 25 mm (ABAQUS)	22% to 34% CF reduction anticipated from models

Team member SCC has burst testing history with Stress Ratio = 0.75 showing cylinder hoop failures when dome shape and fiber placement are optimized.

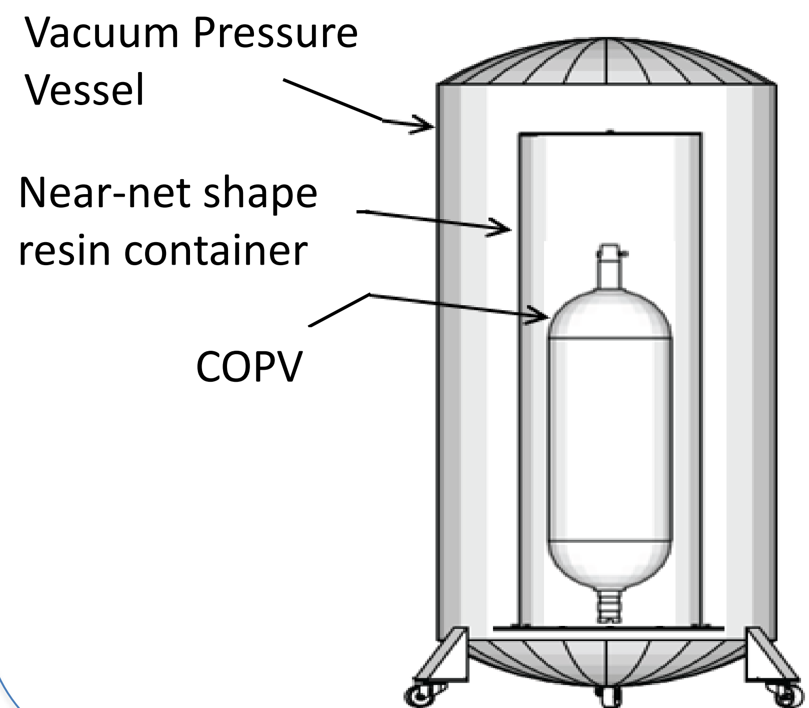
The cylinder-dome transition region where shear stresses are observed is especially sensitive to defects.

Take Home: Models suggest CF savings obtainable assuming tough, low-void matrix can support hoop failures for SR > 0.6

Accomplishment: Scale-up of Approaches

- Traditional vacuum infusion of large COPVs with bagging film showed challenges and was viewed to have poor scalability.

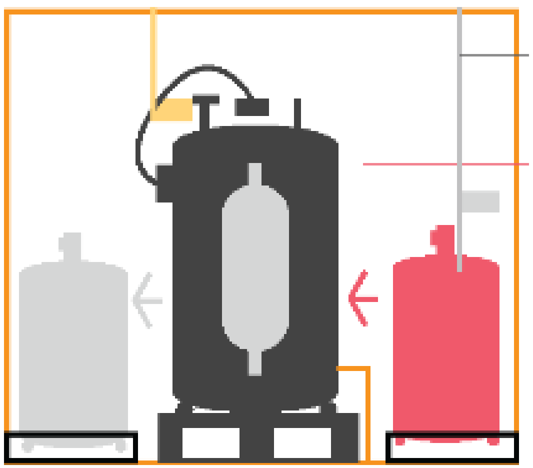
Assembly for Vacuum Bagging **vs.** **Nested Assembly for New Process**



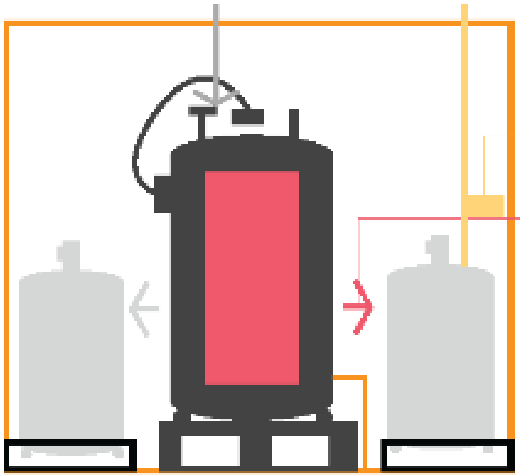
Take Home: Cumbersome bagging replaced by near-net shape tooling

Accomplishment: New Vacuum Process

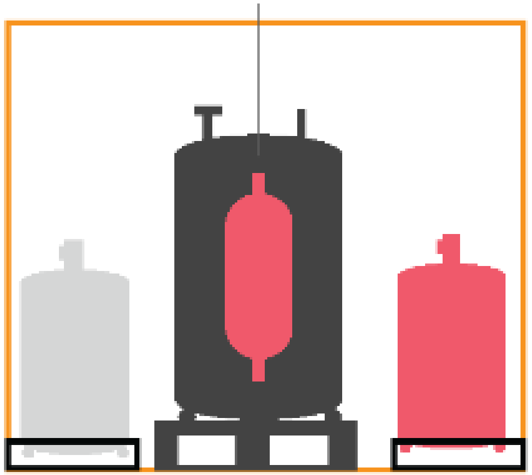
Prep resin/curative Mixture (red)



Vacuum Transfer Resin to dry-wound COPV



Remove Excess Resin; Cure infused COPV



Take Home: New process reduces infusion time from 30 min. to 15 min. for 7.5 Liter tanks with shorter set-up times.

Accomplishments: Small COPVs Burst Tests

- Through optimization of infusion process and winding (elimination of inter-tow gaps), equivalent burst strength was shown at equivalent CF weight
- Very high translational efficiency for Proxima suggests more efficient utilization of CF

Fabrication Type	Winding Pattern	Resin	Burst Strength	CF Translational Efficiency
Traditional Filament Winding	Pattern #1, Wet wind	Anhydride-Cure Epoxy	1834 bar (26,595 psi)	92%
Vacuum Infusion (bagging film)	Pattern #1, dry-wind	Proxima ACR	1694 bar (24,564psi)	83%
New Vacuum Process (hard tooling)	Pattern #1, dry-wind	Proxima ACR	1683 bar (24,404 psi)	83%
Vacuum Infusion (bagging film)	**Pattern #2, dry-wind**	Proxima ACR	1833 bar (26,586 psi)	97%

All tanks were prepared with same amount of CF tow (Toray T700, 24K)
COPV Type: 7.5 Liter, Type III

Take Home: New vacuum process shows consistent burst strength

Accomplishments: Comparison of CF Type

Substitution with different CF tow products did not show similar high translational efficiency

Fabrication Type	Winding	CF Tow	Resin	Burst Strength
Traditional Filament Winding	Pattern #1	Toray T700, 24K	Anhydride-Cure Epoxy	1834 bar (26,595 psi)
Vacuum Infusion (bagging film)	Pattern #1	Toray T700, 24K	Proxima ACR	1694 bar (25,569 psi)
Vacuum Infusion (bagging film)	Pattern #2	Toray T700, 24K	Proxima ACR	1833 bar (26,586 psi)
Vacuum Infusion (bagging film)	Pattern #2	Grafil 37-800, 30K	Proxima ACR	1417 bar (20,558 psi)

All tanks were 7.5 L tanks, Type III

Take Home: Substitution of CF may be complex and outside project scope

Accomplishment: Residual Strength (sub-scale)

- Cyclic loading at moderate deformation strains did not induce significant differences in residual strength in model plate laminates.
- Feedback from COPV manufacturers suggest that voids has been less of a concern compared to residual strength after drop testing

Fabrication Type	Tensile Strength (MPa)	Tensile Strength (MPa)
	Initial	Residual after fatigue
Infusion Epoxy Momentive RIM R 135/ H137	1266	1257.3
Anhydride Cured Epoxy System Dow DER 354 Epoxy/ Lindride 36V	1322	1365.3
Proxima	1271	1245.3

Lay-up: 4 plies of Unidirectional fabric based on Toray T7000 : 90 / 0 / 0 / 90
Cyclic loading: 0.7% strain for 45,000 cycles at 5 Hz

Take Home: Effect of fatigue appears small – focus remains on drop tests

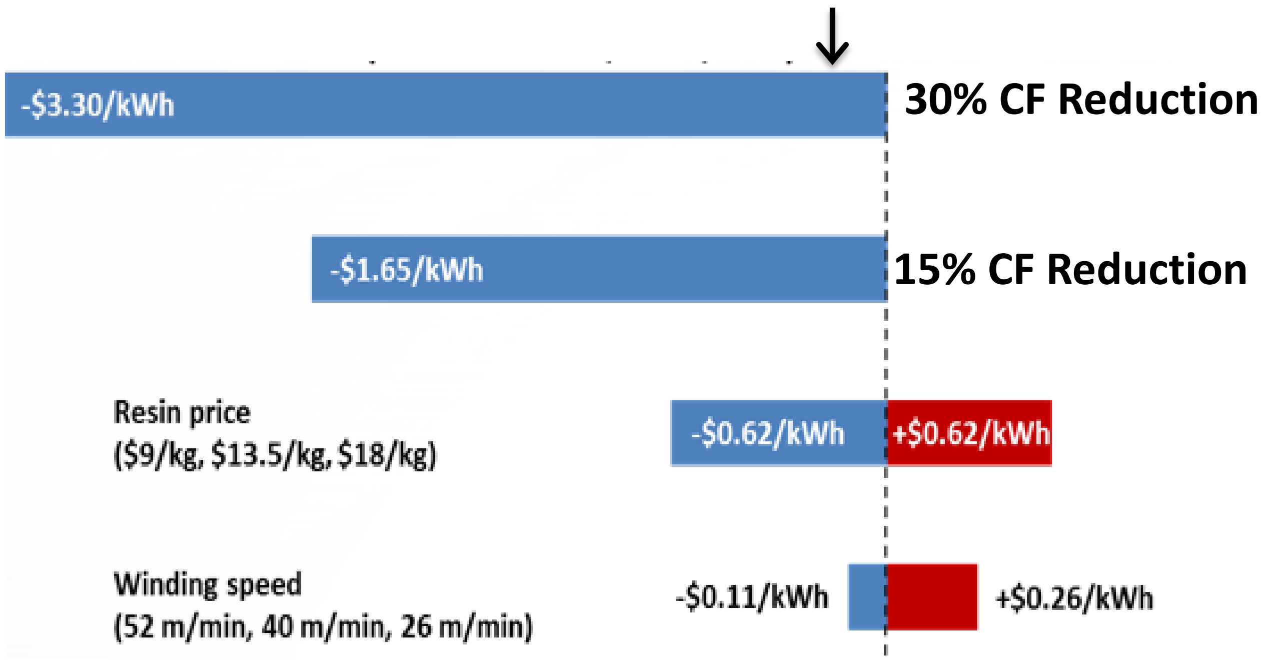
Accomplishment: Cost Estimation

Sensitivity Analysis of Costs

Baseline cost without CF reduction = $11.19 / kWh

Manufac. Cost = $0.79 / kWh ; Composite Cost = $ 10.4 / kWh

2013 Cost = $11.04 / kWh



Take Home: CF weight has a strong cost-reduction potential even with a longer process

Response to Previous Year Reviewers' Comments

"Adding feedback with a series production tank supplier would help in formulating a commercial path and ensure other important parameters are not overlooked in the manufacturing development."

The team has held face to face discussions with 4 large companies involved in series production of tanks. The reception was generally supportive if the drop tests show promising results, in spite of the unusual processing approach.

"Difficulties may be encountered in changing between Mitsubishi and Toray fibers. No two fibers handle alike and achieving the necessary degree of fiber property translation could be tricky."

After preliminary comparison of CF tow, the need for further time investment was confirmed to be outside of project scope. Efforts will remain on Toray T700.

"The project team should continue on their objective for vacuum infusing of the their full-scale prototype tank."

The team has maintained a focus on vacuum infusion with the more robust approach.

Collaborations

Organization	Category	Role
Materia Inc	Industry (Chemicals)	Resin selection and infusion process optimization
Spencer Composites Corp. (SCC)	Industry (Fila. Winding)	Filament winding, fiber winding, modelling, burst testing
Montana State University – Bozeman (MSU)	University (Composites Lab)	FEA modelling, mechanical testing
Hypercomp Engineering	Industry (Fila. Winding)	Filament winding, burst testing, some modeling

Remaining Challenges and Barriers

Effect of Drop test on residual burst strength still unknown

- Mitigation: Immediately prepare at least 3 COPVs (Type IV) of larger geometry (>10” diameter)

Although technical progress has been achieved, large COPV infusion not yet demonstrated.

- Mitigation: New process has been scaled-up and is ready for COPV prep BUT timeline is short

Acceptance of new processes (e.g. infusion) within COPV industry is not straightforward.

- Mitigation: Team will engage COPV manufacturers on new approach

Proposed Future Work

(1) Produce tanks for residual strength from drop testing (FY 2017)

(2) Develop relationship between residual strength after drop and resin type to determine the extent of potential CF saving.

(3) Create final cost saving estimate

Any proposed future work is subject to change based on funding levels

Technology Transfer Activities

- Materia has engaged various COPV producers and understands the importance of COPV burst data and drop test data
- Further discussions will continue as key data becomes available
- No IP has been identified at this time

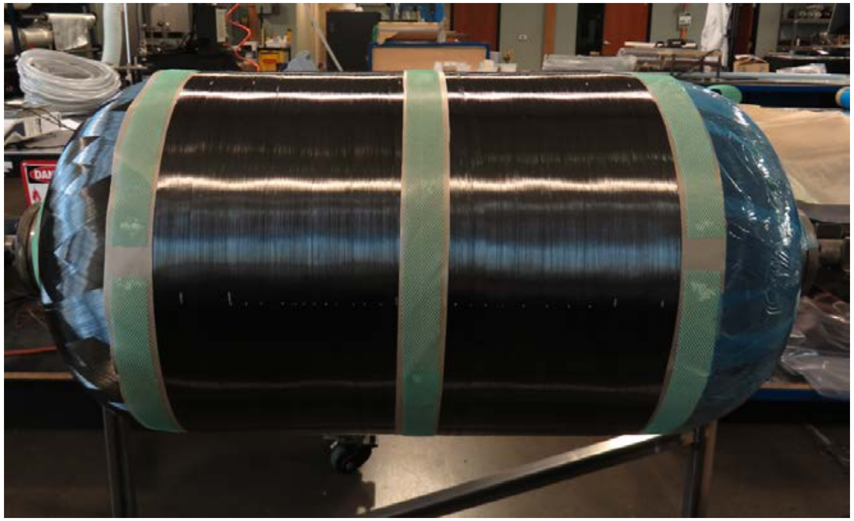
Summary Table

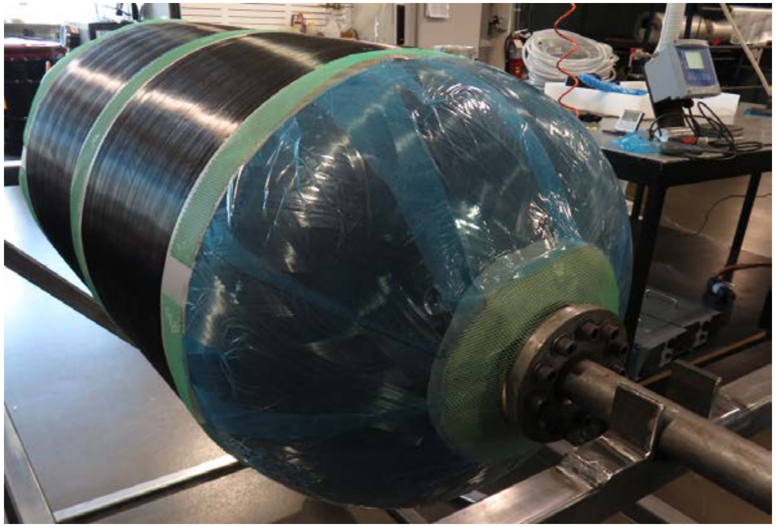
Objective	Project Target	FY17 Status
Prepare full size COPVs and simplify process	Low void tanks	Process simplification demonstrated but large COPVs are still to come
Demonstrate good performance in 45°drop test	March 2017	May 2017
Demonstrate CF reduction in 45°drop test	May 2017	June 2017

- As a result of equipment delivery delays for new process, timing is tight to complete tanks
- Team has offered to infuse other dry-wound tanks if supplied from series producers

Back-Up Technical Slides

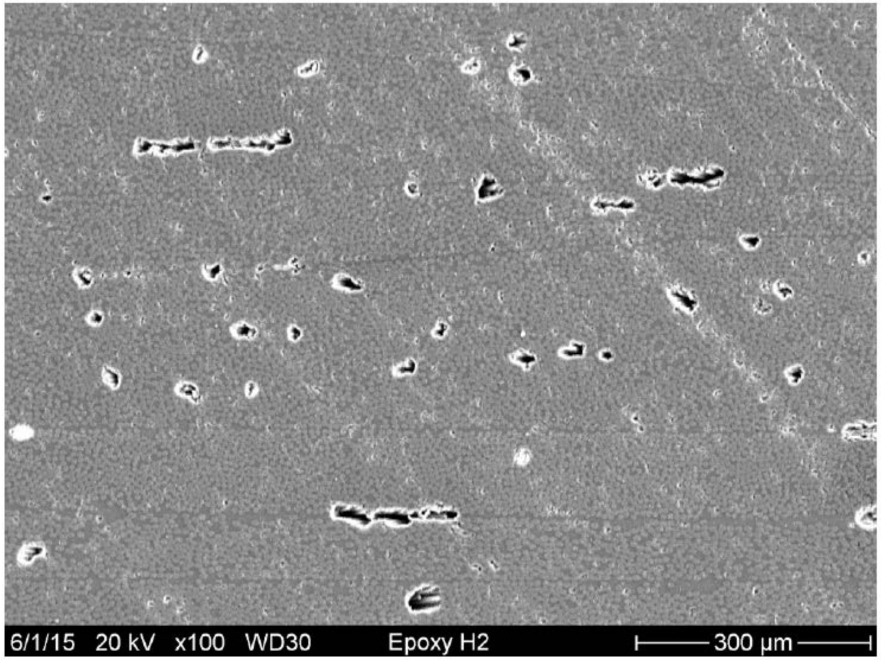
Lay-up Steps





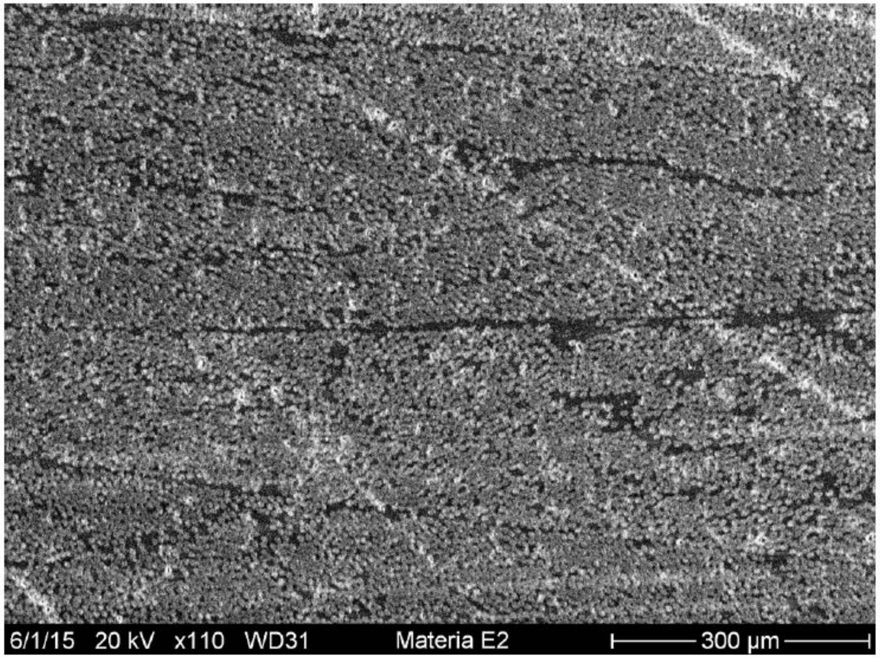
Accomplishment: Lower Void Content Confirmed

Void characterization conducted on small tanks



Epoxy coupon H at 100X magnification.

Wet-wound epoxy tank with voids (3 to 9% voids across 7 regions)



Proxima coupon E at 110X magnification.

Infused tank with no voids across 7 regions. Some evidence of resin-rich areas may suggest wrinkles in early tanks

<u>Take Home:</u> COPV with low void content (<0.5 vol.%) is achievable with infusion

Progress toward DOE Targets

Project goals were created to respond to DOE targets

Comparative Summary of Key DOE Metrics for Hydrogen Storage Systems

Hydrogen Storage Systems	System Wt. (kg)	System Vol (L)	System Cost ($ / unit)	Key DOE Metrics for Hydrogen Storage Projects			
				Gravimetric (kW-h/kg sys)	Volumetric (kW-h/L sys)	System Cost ($/kW-h, at 500k units/yr)	Comment
Year 2017 DOE Target	104	224	2238	**1.8**	**1.3**	**12**	**Ref. 1**
Yr 2013 700-bar Type IV, Base Case	128	224	3171	1.5	0.8	17	**Ref. 1**
Proposed 700-bar Type IV	106	215	2313	1.8	0.9	12	Proposed

		Year 2013	Proposed
Composite Material cost	$/kWh	$10.4	$6.5
Composite Processing Costs	$/kWh	$1.0	$0.5
Other System costs (Non-composite)	$/kWh	$5.4	$5.4
Total System Cost	$/kWh	17	12

Ref. 1: McWhorter, S., Ordaz, G., "Onboard Type IV Compressed Hydrogen Storage Systems – Current Performance and Cost," *DOE Fuel Cell Technologies Office Record Number 13010*, June 11, 2013.