IV.D.3 Conformable Hydrogen Storage Pressure Vessel Project

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Subcontractors:
- High Energy Coil Reservoirs, LLC, (HECR) Fort Wayne, IN
- University of Texas at Austin, Center for Electromechanics, Austin, TX

Project Start Date: September 1, 2015
Project End Date: August 31, 2016

Overall Objectives

- To develop and demonstrate a conformable, lightweight, 700 bar gaseous hydrogen storage system with nominal capacity of approximately 1 kg.

Fiscal Year (FY) 2016 Objectives

- Order tooling to support a 700 bar capable pressure vessel.
- Demonstrate 2,170 bar burst pressure capability.
- Build test and data collection rig to safely test prototype hydrogen pressure vessels.
- Build pressure vessels using new tooling and test hydrogen permeability.

Technical Barriers

- Resin selection that offers low permeability, flexibility, durability, impact resistance and thermoplastic (extrusion) performance
- Over braiding design to reach 2,170 bar
- Safe testing of prototype hydrogen pressure vessels

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

Technical Targets

- The key material requirements to meet for resin selection:
  - Low hydrogen leakage (<0.05 g/hr/kg H_2 stored at 700 bar)
  - Operational temperature limit (-40°C ≤ T ≤ 85°C)
  - Corrugation process compatibility (i.e., needs to be process compatible, range of viscosity, melt temperature, and durometer)
- Burst pressure exceeding 2,170 bar

This project seeks to address the high cost of conventional gaseous 700 bar hydrogen storage, as well as the overall weight of the hydrogen storage system. Although this project will not improve the volumetric efficiency of gaseous storage, the pressure vessel design should allow a more flexible on-vehicle packaging than a conventional rigid cylinder. Possible tank layouts could optimize the use of areas in the same way that current gasoline tanks are molded to best use available space. Using HECR's pressure vessel technology for hydrogen storage promises to provide breakthroughs in commercially available pressure vessel costs, conformability, and weight.

At the time of this progress report, the project has not produced the prototype vessels, and the targets are the predictions based on the project proposal.

Table 1 shows how the proposed HPM Vessel technology compares to existing Type IV vessels and DOE's 2017 and ultimate targets for passenger vehicle hydrogen storage systems.

FY 2016 Accomplishments

- The tooling required to produce the resin liner was specified, ordered and delivered during FY 2016. This tooling fits into a commercial plastic corrugation and extrusion machine, and will produce the liners that will prevent the hydrogen permeating out of the vessel (Figure 1).
- Resin candidates selected include Hytrel 5556, Acetal, EVAL M100, and EVAL F101. Acetal and EVAL resins have an acceptable predicted thickness (<0.060 in) based on predicted hydrogen permeability and compatibility with the liner extrusion and corrugation process.
- Completed thermodynamic model of vessel filling.

TABLE 1. Performance Target Summary

	DOE Projections for Type IV 700 bar Storage at 500,000 units/yr	DOE 2017 Target	DOE Ultimate Target	Proposed HPM Vessel
Gravimetric **Capacity**	1.5 kWh/kg (4.5 wt% H_2)	1.8 kWh/kg (5.5 wt% H_2)	2.5 kWh/kg (7.5 wt% H_2)	3.7 kWh/kg (10.0 wt% H_2)
Volumetric Capacity	0.8 kWh/L (24 g H_2/L)	1.3 kWh/L (40 g H_2/L)	2.3 kWh/L (70 g H_2/L)	0.7 kWh/L (20 g H_2/L)
Cost	$17/kWh ($570/kg H_2 stored)	$12/kWh ($400/kg H_2 stored)	$8/kWh ($267/kg H_2 stored)	$8.40/kWh ($280/kg H_2 stored)

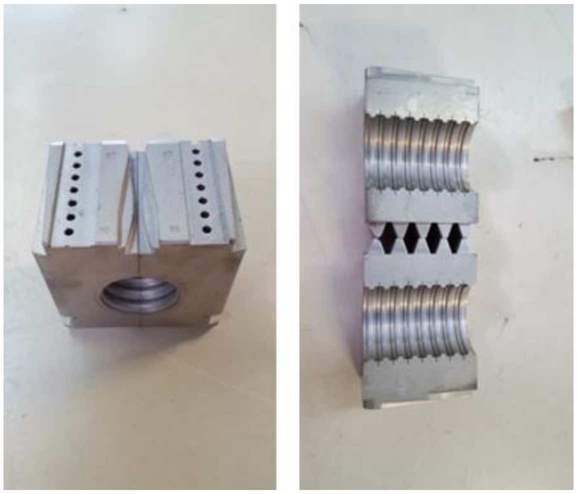

FIGURE 1. Example tooling to create resin liner

  - Filling rate to meet J2601 fueling standard (11.5 MPa/min) does not seem restricted by smaller vessel connecting end sections.
  - Temperature rise in end vessels is above 85°C in initial models.
- Completed fabrication of test safety containment vessel: designed to withstand 5,000 psi
- Completed initial testing with baseline compressed natural gas vessels to prove test system workability and data collection system, and measure baseline permeability performance for Hytrel resin. The measured permeability value is about half of the expected value. More detail is shown in Table 2.

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INTRODUCTION

This project consists of three organizations, (1) Center for Transportation and the Environment, project prime recipient responsible for project management; (2) HECR, responsible for design and prototype development of the storage vessel; and (3) The University of Texas Center for Electromechanics, responsible for permeability testing and resin technical information.

The overall goal of this research and development project is to develop an approach for compressed hydrogen gas storage that will provide a cost-effective and conformable storage solution for hydrogen. The team will develop and demonstrate a conformable, lightweight 700 bar gaseous hydrogen storage system with a nominal capacity of approximately 1 kg. The nature of the HECR's technology allows for a higher capacity pressure vessel to be constructed simply by creating a longer vessel through the same process.

APPROACH

The hydrogen storage system development will occur over two budget periods beginning with an initial design, including candidate resin down selection and over-braid final development. The design includes overwrapping an extruded thermoplastic elastomeric resin liner with high performance Kevlar™. The team will then build test vessels and perform key testing to validate the suitability for hydrogen containment. This testing will include hydrostatic burst testing, hydrostatic pressure cyclic testing, and hydrogen permeability testing conducted on a number of resin liners.

RESULTS

Following an extensive decision matrix search, three resin candidates were identified which have appropriate characteristics to serve as low permeability liners for a conformable hydrogen storage vessel. Available data for CO_2, N_2, and He and H_2 permeability showed Acetal and EVAL resin to have superior permeability resistance. While the team did not find clearly linear and general relationships between permeability for any one gas and hydrogen, generally those resins with greater permeability resistance were better with hydrogen. As process compatibility is critical, candidates were selected to be similar to Hytrel 4275, the current resin used in pressure vessels for other applications.

Three candidate resins have a predicted permeability below the limit calculated to meet the proposed hydrogen leakage rate, with a liner thinner than 0.60 in. This is the upper end of the expected resin liner thickness than can be

TABLE 2. Selected Resin Characteristics

Resin / Polymer	Permeability (cm³ (cm)/ atm sec cm²)				Required thickness to meet 0.05 g/hr-kg H2 stored @ 700 bar		
	H_2	CO_2	He	N_2	*(cm)*	*(in)*	
Hytrel 5556	na	1.80E-07	9.90E-08	1.40E-08	na	na	
Acetal	1.50E-10	2.30E-09	na	na	0.0192	0.049	★
EVALM100	1.62E-11	na	na	na	0.0021	0.005	★
EVAL F101	1.30E-11	1.90E-12	3.70E-10	3.94E-14	0.0017	0.004	★

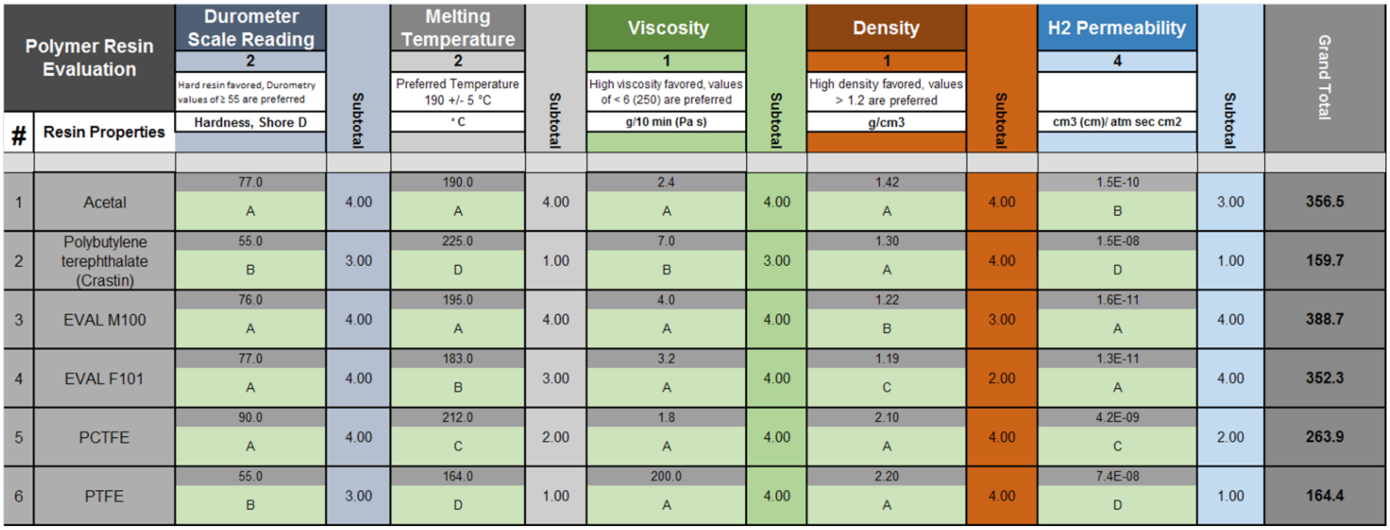
reliably produced. The calculated liner thickness is shown on the right column of Table 2.

Resin candidates were narrowed down using a decision matrix. The decision matrix was based on density (>1.2 g/cm^3), melting temperature (190 +/-5°C), durometery (>55), and melt flow rate (<6 g/10 min), and viscosity (<250 Pa*s) characteristics. In the final selection round, hydrogen permeability was also added to the characteristics considered. Three candidate resins which have predicted hydrogen permeability to allow the vessel to be less than 0.060 in and otherwise meet the decision matrix criteria are Acetal, EVAL M100, and EVAL F100 (Table 3).

A conceptual design and fabrication of the hydrogen leak test cell was completed, and initial testing was conducted using HECR's existing 2-in diameter pressure vessels. The first testing was completed with nitrogen to validate the test rig. Results are shown in Table 4. The measured nitrogen permeability was about 50% lower than available data, and in the expected order of magnitude.

Leakage testing was then done using hydrogen at 1,000 psig and 1,800 psig to study the effects of pressure on leak rate (Table 5). An interesting observation from the leak tests was that the leak rate scaled with approximately

TABLE 3. Final Filtered Decision Matrix



Polymer Resin Evaluation		Durometer Scale Reading	Subtotal	Melting Temperature	Subtotal	Viscosity	Subtotal	Density	Subtotal	H2 Permeability	Subtotal	Grand Total
		2		2		1		1		4		
		Hard resin favored, Durometry values of ≥ 55 are preferred		Preferred Temperature 190 +/- 5 °C		High viscosity favored, values of < 6 (250) are preferred		High density favored, values > 1.2 are preferred				
#	Resin Properties	Hardness, Shore D		°C		g/10 min (Pa s)		g/cm3		cm3 (cm)/ atm sec cm2		
1	Acetal	77.0 A	4.00	190.0 A	4.00	2.4 A	4.00	1.42 A	4.00	1.5E-10 B	3.00	**356.5**
2	Polybutylene terephthalate (Crastin)	55.0 B	3.00	225.0 D	1.00	7.0 B	3.00	1.30 A	4.00	1.5E-08 D	1.00	**159.7**
3	EVAL M100	76.0 A	4.00	195.0 A	4.00	4.0 A	4.00	1.22 B	3.00	1.6E-11 A	4.00	**388.7**
4	EVAL F101	77.0 A	4.00	183.0 B	3.00	3.2 A	4.00	1.19 C	2.00	1.3E-11 A	4.00	**352.3**
5	PCTFE	90.0 A	4.00	212.0 C	2.00	1.8 A	4.00	2.10 A	4.00	4.2E-09 C	2.00	**263.9**
6	PTFE	55.0 B	3.00	164.0 D	1.00	200.0 A	4.00	2.20 A	4.00	7.4E-08 D	1.00	**164.4**

PCTFE - Polychlorotrifluoroethylene; PTFE - Poly-tetrafluoroethylene

TABLE 4. Permeability Data from Initial Nitrogen Testing with Hytrel

Measured PV N_2 dP	Measured TC N_2 dP	Mass N_2 leaked from PV	Resulting TC N_2 dP	Leak Rate N_2	Duration	Measured Permeability	Permeability in Literature	Permeability Difference	Permeability Difference
(psi)	(psi)	(g)	(psi)	(g/hr-kg N_2)	(hr)	(cm^3-cm/ atm-s-cm^2)	(cm^3-cm/ atm-s-cm^2)	(cm^3-cm/ atm-s-cm^2)	(%)
6	0.9	1.29	0.881	0.25542	24	5.51E-09	1.41E-08	-8.57E-09	-61%
13.4	2.2	2.87	1.968	0.28522	48	6.16E-09	1.41E-08	-7.92E-09	-56%
10	1.3	2.14	1.469	0.2838	36	6.13E-09	1.41E-08	-7.95E-09	-56%
13.212	1.09843	2.83	1.94	0.37496	25	7.07E-09	1.41E-08	-7.01E-09	-50%

TABLE 5. Permeability Data from Initial Hydrogen Testing

Measured PV H_2 dP	Measured TC N_2+H_2 dP	Mass H_2 leaked from PV	Resulting TC N_2+H_2 dP	Leak Rate H_2	Duration	Measured Permeability
(psi)	(psi)	(g)	(psi)	(g/hr-kg H_2)	(hr)	(cm^3-cm/ atm-s-cm^2)
Nominal Test Pressure 1,000 psig						
23.1	3.52	0.33	3.142	0.306	10.3	4.83×10^{-8}
122.7	19.43	1.76	16.755	0.264	63.3	4.18×10^{-8}
145.8	22.95	2.09	19.896	0.270	73.6	4.27×10^{-8}
Nominal Test Pressure 1,800 psig						
52	6.88	0.70	6.670	0.543	12.3	8.58×10^{-8}
31.7	4.78	0.43	4.092	0.458	8.9	7.24×10^{-8}
39.4	6.6	0.53	5.037	0.449	11.2	7.09×10^{-8}
123.1	17.66	1.66	15.799	0.487	32.4	7.70×10^{-8}

linearly with pressure as expected. The average permeability at 1,000 psi was 4.43, and at 1,800 psi was 7.65, in the above units. Linearly scaling the permeability rate for 1,000 psi up by 1.8X predicts a permeability of 7.97, which is approximately 5% off the expected value for a linear permeability variation with pressure.

Figure 2 shows the pressure and temperature variation between the high pressure vessel, and low pressure safety containment vessel over approximately 40 hr of testing. The temperature variation shows the building temperature changing over the course of the two-day test. The red line shows the fairly linear pressure loss of the high pressure vessel through permeation. The steep drop shown in the red curve at the beginning of the test is thought to be due to the initial relaxation of the pressure vessel following filling. The black line shows the increase of pressure in the containment vessel corresponding to the hydrogen permeated through the pressure vessel.

Modeling of a 10- and 20-vessel hydrogen storage system was done to observe the effects of a single chain of vessels in series versus a manifold system of vessels in parallel. There was a significant temperature variance in the vessels, which could also be the potential limiting issue for the conformable hydrogen storage concept and its fill rate. The results shown in Figure 3 include heat transfer between the internal hydrogen and, through the pressure vessel wall, to

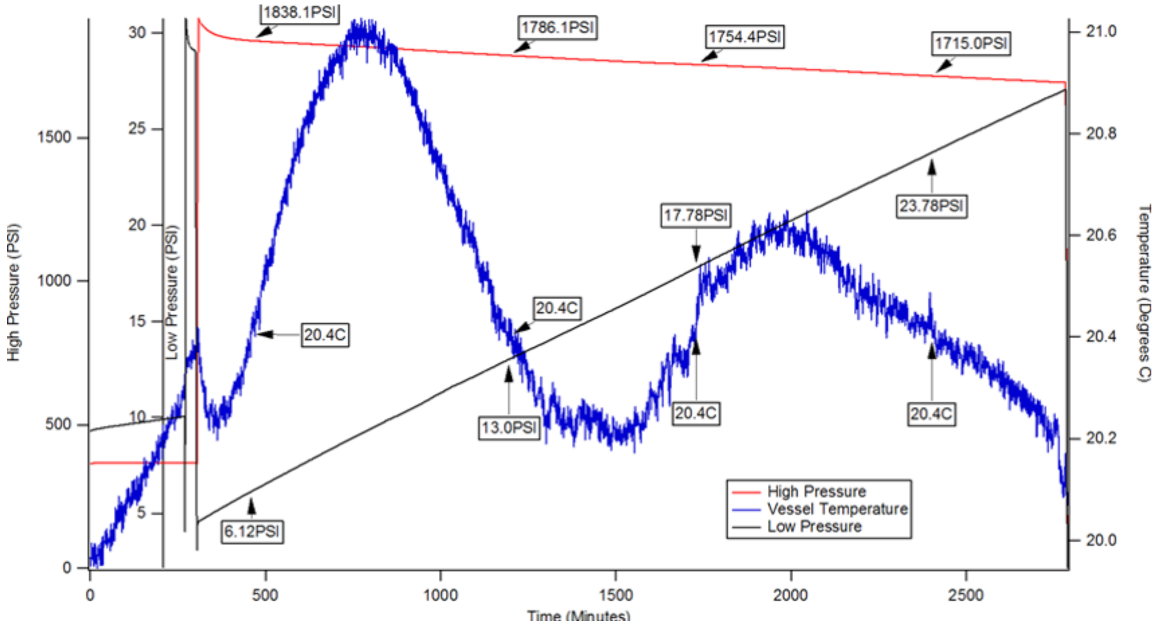
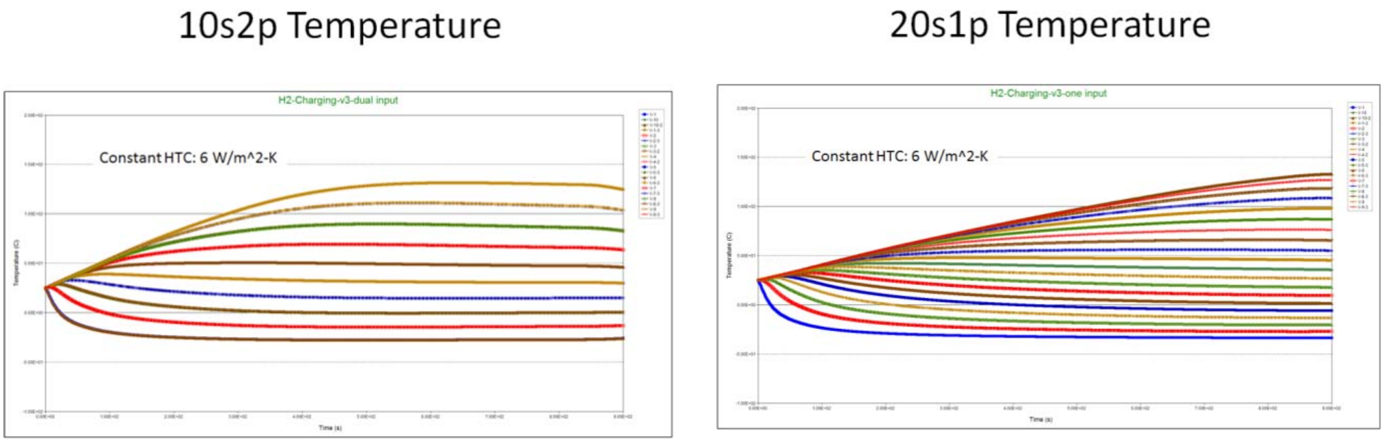


FIGURE 2. Captured pressure data from initial hydrogen testing



HTC – Heat transfer coefficient

FIGURE 3. Temperature results of hydrogen filling simulations

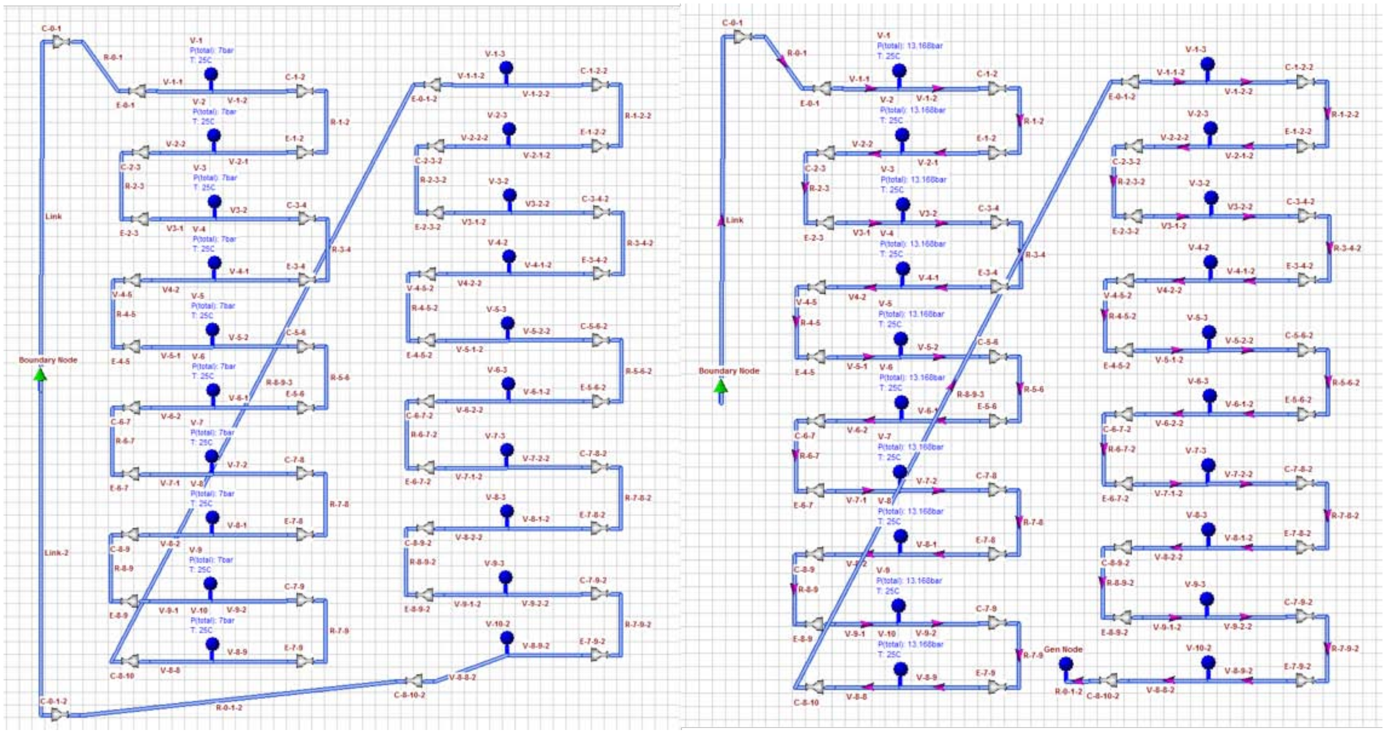


FIGURE 4. Macroflow network models of a 20-vessel conformable storage system. Left: 10 series, 2 parallel configuration. Right: 20 series configuration.

ambient air at 40°C with an effective heat transfer coefficient of 6 W/m^2-K. The vessels at the end of the chain experience a significant rise in temperature approaching 150°C. The first pressure vessels quickly approach the hydrogen filling temperature, which is modeled at -40°C. While this simulation is preliminary, it does suggest that close attention needs to be paid to thermal performance during filling, and system survivability from exposure to high temperature.

The series and parallel configurations are shown in Figure 4.

CONCLUSIONS AND FUTURE DIRECTIONS

Some conclusions that can be drawn at this point in the project are:

- Hydrogen filling in a long, conformable vessel at J2719 will likely see temperatures in excess of 85°C.
- Selecting a resin with all needed processing characteristics will still likely be difficult in advance of prototype production testing.

- The Center for Electromechanics test apparatus is capable of measuring pressure loss due to permeability through the pressure vessel and correlating this with a pressure rise in the containment vessel.

Future work for this project includes:

- Start prototype production of resin cores.
- Achieve 2,170 bar burst pressure.
- Measure permeability with baseline resin and new prototype resins.

FY 2016 PUBLICATIONS/PRESENTATIONS

1. 2016 DOE Hydrogen and Fuel Cells Program Annual Merit Review Presentation.