

Final Project Report - Achieving Hydrogen Storage Goals through High-Strength Fiber Glass

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Executive Summary

Led by PPG and partnered with Hexagon Lincoln and Pacific Northwest National Laboratory (PNNL), the team recently carried out a project “Achieving Hydrogen Storage Goals through High-Strength Fiber Glass”. The project was funded by DOE’s Fuel Cell Technologies office within the Office of Energy Efficiency and Renewable Energy, starting on September 1, 2014 as a two-year project to assess technical and commercial feasibilities of manufacturing low-cost, high-strength glass fibers to replace T700 carbon fibers with a goal of reducing the composite total cost by 50% of the existing, commercial 700 bar hydrogen storage tanks used in personal vehicles.

In Budget Period 1, low-temperature, high-strength fibers were developed with pristine tensile strength of 5,200 – 5,500 MPa. However, the corresponding glass fiber strands (with two sizing chemistries) produced from a small-scale pilot platform missed the target 5,000 MPa in terms of fiber strand tensile breaking stress. Significantly lower fiber strand performance is attributed to translation losses, primarily insufficient melt refining in cullet re-melting, temperature conditioning during fiber drawing, and assembling process of multiple smaller packages. The high-strength fiber reinforced tanks were built according to Composite Overwrapped Pressure Vessels (COPV) per the STEB02-250 design at Hexagon Lincoln. The tanks passed burst test and pressure cycle test without an exception, whereas all tanks reinforced using E-Glass fibers failed. The tests were performed, following the procedures of “Hydrostatic Burst Test for Project 4548 REVB 150423” and “Ambient Cycle Test for Project 4548 REVB 150423” protocol (Hexagon Lincoln), respectively. All of the tanks, however, failed on stress rupture test at 80% burst pressure within a very short time.

PNNL conducted stress rupture tests using fiber strand samples impregnated in epoxy, the same type as used for the tanks, under the conditions of $23\pm 1^{\circ}\text{C}$ and $55\pm 10\%\text{RH}$, at various loading levels; similar results were generated. When compared with a commercial E-glass strand’s stress rupture curve, the high-strength fiber strands exhibit higher breaking stress values for the same failure time or longer failure time under the same absolute tensile loading level. However, the slope of the stress rupture curve did not change significantly, with each slope more or less parallel to each other. These results do not disconfirm the use of the existing design safety factor of 3.5 for glass fibers.

Considering all of the above findings, the primary factor impacting the performance of the tanks tested in the present study is believed to be flaws in the high-strength fibers produced by using the non-standard, small-scale fiber production platform. A secondary factor, yet to be confirmed, may be the significant elongation mismatch between the glass fibers and the epoxy resin; the former is much greater than the latter. This large mismatch can induce cracks at the fiber/matrix interface from the resin side, resulting in stress redistribution in fibers, and may lead to the final tank failure under 80% high static loading. For T700 carbon fiber reinforced tanks, on the other hand, the opposite is true; stiffer carbon fibers can prevent resin from being over-stretched at the fiber/matrix interface under the same static load level.

Ultimately high-quality, high-strength glass fibers are required, plus better composite system management to reduce glass fiber and epoxy elongation mismatch in order to produce whole glass fiber reinforced Type IV COPV 700 bar tanks for the hydrogen storage application. The high-strength glass fiber technology is currently not ready to replace T700 carbon fibers and significant effort is required to commercially demonstrate ultimate performance of the high-strength glass fibers developed in this project. The project funded by DOE was given a No-Go decision before entering into Budget Period 2. PPG believes the only path to continuing the evaluation of newly developed high-strength glass fiber, i.e., INNOFIBER HP2 glass chemistry, is to use a proper production platform in order to achieve high-quality low-flaw fibers. PPG, however, has no near term plans to continue such evaluations.

Overall Objectives

The project objective was to demonstrate a Type IV composite overwrapped pressure vessel (COPV) reinforced exclusively with glass fiber achieved through the following steps:

- Develop high-strength glass fiber strands with tensile strength of 5,000 MPa, exceeding Toray T-700 carbon fiber at less than half its cost.
- Demonstrate a pilot, novel glass fiber manufacturing process.
- Conduct composite validation laboratory tests to determine the safety factor for tanks made by using new high-strength glass fiber.
- Build cost models to demonstrate the new tank will reduce the composite contribution to system cost by nearly 50% with minimal impact on tank weight and capacity compared to tanks made with T-700 carbon fiber.

Accomplishments

The project completed the Budget Period I, during which the team fulfilled the following deliverables to DOE:

- PPG completed the development of two high-strength glass fiber chemistries, which exhibit pristine single fiber tensile strength values greater than 5,000 MPa (5,357 MPa, 5,583 MPa).
- PNNL completed tensile strength measurements of the high-strength fiber strands; both types of fibers in combination of binder chemistry did not meet the design target of 5,000 MPa due to translation losses that resulted from using a non-standard, pilot production process.
- PPG produced more than 2,400 lbs. fiber roving packages, from which 1,200 lbs. roving packages (spools of produced fiber glass – see figure 1) were assembled to build Type IV COPV tanks. The new glass chemistry and binder chemistry were both used during the small scale, pilot production.
- PPG successfully demonstrated a 4X (40 lbs. /hr) high-temperature induction melting unit run, producing high-strength fiber glass cullet directly from batch materials at PPG. Producing cullet is an intermediate step that replaces the traditional process of making fiber glass directly from glass ingredient batch. The cullet has a lower melting temperature than the batch, enabling the use of a lower temperature melting platform.
- PPG provided initial total high-strength fiber glass production costs at different production capacities projected by using the limited small scale production data. The estimated costs at a commercial, large scale show that high-strength fiber products in direct draw package form can potentially sell for well below 50% of the published T-700 carbon fiber costs (as listed in DE-FOA-0000827).
- Hexagon Lincoln (HL) successfully produced 38 Type IV COPV tanks for burst, pressure, and stress rupture tests at the HL facility.
- Hexagon Lincoln completed mechanical tests on Type IV COPV tanks comparing E-Glass fibers with the two types of high-strength glass fibers - testing burst

pressure, pressure cycle, and stress rupture at 80% burst pressure. The high-strength fiber reinforced tanks passed both burst and pressure cycle tests, while E-Glass reinforced tanks failed both tests. All fiber glass reinforced tanks showed very short failure time at 80% burst pressure, although high-strength fiber tanks were longer than the E-Glass tanks. Carbon fiber tanks at 80% effectively do not fail.

- PNNL built a special temperature and humidity tensile test array, and a special sample grip for handling high-strength fibers, used to conduct stress rupture tests of strand samples.
- PNNL completed stress rupture tests characterizing the differences between E-Glass and two types of high-strength fiber glass. The results showed that the stress rupture behavior, defined as the slope of log (time-to-failure) vs. relative tensile stress level to ultimate failure stress, was nearly the same. There was little difference in stress rupture behavior due to glass chemistry and conditions of the tests, such as humidity in the controlled air chamber or if the samples were immersed in water. Based on the results, the current safety factor of 3.5 should be used unless better quality high-strength glass fiber can be produced and re-evaluated.
- Hexagon Lincoln test results showed an initial performance and translation assessment of 81% for high-strength fiber COPV, compared against 91% for Toray T-700 COPV.
- PNNL completed initial cost modeling for a high-strength glass fiber COPV based on the current high-strength fiber performance in comparison with a Toray T-700 carbon fiber COPV. In terms of composite cost contribution (\$/kWh) and storage system tank cost (\$/kWh net), the current high-strength glass fiber COPVs are too high by 5.2X and 2.8X, respectively. However, this result is solely based on the lower than expected fiber strength, which results in higher mass and cost of the fiber required in the tank design.

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:

(B) System Cost

Technical Targets

The project goal is to demonstrate the technical and commercial feasibility of using high-strength glass fibers to match the tensile strength of Toray T-700 carbon fibers, at about 50% of the cost. At the completion of the project in Budget Period I, experimental results and modeling output will enable the team to benchmark with the key parameters shown in Table 1 and Table 2. The actual targets for the project will be detailed in the Introduction section of this report.

Table 1: Technical System Targets: Onboard Hydrogen Storage for Light-Duty Fuel Cell Vehicles [1]

Storage Target	Units	2020	Ultimate	Project towards targets (2015)
System Gravimetric Capacity	kWh/kg	1.8	2.5	0.31 Well below target
System Volumetric Capacity	kWh/L	1.3	2.3	0.43 Well below target
Storage System Tank Cost	\$/kWh net	10	8	34.1 Well above target
	\$/kg H ₂ stored	333	266	1136 Well above target

Table 2: Projected Performance of Hydrogen Storage Systems [1] ^a

Hydrogen Storage System (including balance of tank cost)	Gravimetric (kWh/kg sys)	Volumetric (kWh/L sys)	Cost (\$/kWh; projected to 500,000 units/yr)	Project towards targets (2016)
700-bar compressed Type IV ^b (Estimated Project Performance)	1.4 (0.31)	0.81 (0.43)	14.8 (34.1+3.64= 37.74)	Gravimetric and Volumetric below targets. Cost well above target.

^a Assumes a storage capacity of 5.6 kg of usable H₂.

^b DOE Hydrogen and Fuel Cells Program Record # 15013, “Onboard Type IV Compressed Hydrogen Storage System–Cost and Performance Status 2015.” September 30, 2015. This includes a balance of tank cost of \$3.64/kWh.

Detail Project Report

1. Introduction

This project addresses the Fuel Cell Technologies Office’s intermediate 2017 goals for onboard hydrogen storage for light-duty fuel cell vehicles. Specifically, the team targets a fiber cost less than \$6/lb., a composite contribution to system cost of less than \$6/kWh, a volumetric capacity of 0.86 kWh/L (26 g/L), and a gravimetric capacity of 1.3 kWh/kg (4 wt.%), while minimizing increased tank mass compared to T-700 carbon fiber vessels. The project tasks are organized to continually decrease project risk, moving from a technology readiness level of 4 to 6.

2. Approach

In Budget Period 1 (BP1), the team develops fibers at the laboratory bench and characterizes stress rupture at the fiber level. The team then develops a pilot version of the new glass manufacturing process to produce the high-strength fibers. BP1 ends with test data from prototype tanks built from up to four new fiber samples, i.e., fiber chemistry and sizing chemistry in combination.

In Budget Period 2 (BP2), the team optimizes the best performing fiber and the production process, characterizes stress rupture at the composite level, and investigates alternate tank designs. The project ends with a prototype tank built according to a design tailored to the properties of the new glass that can be tested against a wide range of

industry testing standards. The project did not progress into BP2 because the goals of BP1 could not be met with the resources available.

3. Results

3.1 *Task 1 Novel Fiber Development and Pilot Production (PPG)*

In BP1, under Task 1, Subtask 1.1, two candidate high-strength fiber chemistries were selected from the chemical composition – property tests (see Appendix A). The two glasses were named as Composition A and B for simplicity, (Sample ID, HP2-I and HP2-4/5b, respectively).

Table 3 summarizes processing and mechanical properties of the two high-strength glasses used for the project demonstration. Under the Subtask 1.3, PPG produced a total of approximately 3,000 lbs. of glass cullet from batch materials for Composition A and B combined. Subsequently, using two different candidate sizing selected, Type I and II, more than 2,400 lbs. of roving packages were produced using PPG small scale, pilot production unit, from which 1,200 lbs. of final roving packages were made and shipped to Hexagon Lincoln to build Type IV COPV tanks under Task 2, Subtask 2.1.

Table 3: Glass and Glass Fiber Properties of Composition A and B

ID	Composition A	Composition B
$T_L(^{\circ}\text{C})$	1219	1235
$T_F(^{\circ}\text{C})$	1289	1320
$\Delta T_{F-L}(^{\circ}\text{C})$	70	85
$T_M(^{\circ}\text{C})$	1491	1519
$\rho(\text{g}/\text{cm}^3)$	2.64	2.63
$E(\text{GPa})$	91.8	92.6
$\sigma_f(\text{MPa})$	5243 ± 144	5583 ± 58
$\epsilon_f(\%)$	5.7	6.0

Note 1: T_L – liquidus temperature; T_F – fiber reference drawing temperature at 1000 Poise (or 100 Pa·s) melt viscosity; ΔT_{F-L} – difference between fiber drawing temperature and liquidus temperature (should be no less than 55°C); T_M – reference glass melting and fining temperature at melt viscosity of 100 Poise (or 10 Pa·s); ρ – average fiber density; E – average pristine fiber Young’s modulus by sonic method per ASTM E1875; σ_f – average pristine fiber strength; ϵ_f – average pristine fiber failure strain.

Glass cullet, Composition A or B, was separately re-melted in an electrically heated pre-melter and the melt was directly fed to a bushing well situated below the pre-melter for fiber drawing using a 200-tip bushing. Fibers were drawn at temperatures slightly above their perspective forming temperatures (cf. Table 3) and small packages were collected, 3-5 lbs. /each. Fiber yardage (TEX¹) was checked during the production to select qualified packages for making the final roving packages. Prior to roving package assembly, the small packages were dried using a commercial oven according to the specifications for the two sizing chemistries.

¹ The metric unit, TEX, measures fiber linear density; 1 TEX = 1 g/km, and yield is the inverse, yd./ lb.

The small fiber production unit has a drawback in managing molten glass above the bushing well to maintain a stable temperature, which is critical for a stable fiber drawing process for two primary reasons. First, in the pre-melter, high temperature about 1500°C is required for the new glasses to have sufficiently low viscosity to remove air bubbles that are trapped during cullet re-melting. Second, for fiber drawing, much lower temperature (approximately 1300°C) is required to draw fibers in a stable fashion, which is close to viscosity of 1000 Poise. With a very short channel to flow very hot melt from the top to the bushing well, melt cooling was not fast enough to achieve the target melt viscosity or glass temperature for drawing. Adjusting fiber winder speed had a limited success to control fiber strand TEX. To compensate the temperature needs for processing the glass, a lower melting temperature was considered, but somewhat higher seed counts in fibers resulted. Because of the limited capacity of the pre-melter, temperature of the molten glass was also more sensitive to the rate of cullet feeding. In turn, the melt temperature at the bushing varied due to the short channel passage, which ultimately affected fiber TEX range. In addition, the gasket insulating refractory material (aluminum oxide and alumina cement) at the joint between the bottom of the pre-melter and the top of bushing well corroded faster than in the commercial production furnace. This was because the melt temperature was much higher than the commercial production. These deficiencies are believed to account for much of the overall high translation loss.

Mechanical properties and density of the high-strength fiber strands are summarized in Table 4. The properties of the reference E-Glass strands and T-700 carbon fiber strands are also provided for comparison. Due to various limitations previously mentioned, the final strands of assembled high-strength glass fiber roving showed about 40% translation losses against the pristine fiber strength values reported (cf. Table 3). Fiber products from typical commercial production furnaces generally exhibit about 15% translation losses as compared with their counterpart, i.e., single filament pristine strength. The observed differences point out that the current small scale fiber production platform is inadequate in making high quality fiber strands.

Table 4: Mechanical Properties and Density of Glass Fiber Strands Compared with T-700 Carbon Fibers

Composition Type	A	A	B	B	E (Reference)	T-700
Sizing Type	I	II	I	II	I	N/A
Tensile Strength (MPa)	3192 ± 79	3289 ± 96	3372 ± 45		2848 ± 138	4900
Tensile Modulus (GPa)	88.1 ± 1.1	89.8 ± 0.7	87.7 ± 0.7		82.8 ± 1.1	230
Elongation at Break (%)	5.5	5.6	5.8		5.5	2.1
Density (g/cm ³)	2.58	2.58	2.58	2.58	2.64	1.8

Under Task 1, Subtask 1.3, PPG produced a total of 1,200 lbs. of final multi-end roving packages (with nominal 450 yield or yd. /lb.) of high-strength fibers of A-I, A-II, and B-I types. A Type IV composite overwrapped pressure vessel design based upon reference E-glass fiber was completed under Task 2, Subtask 2.1 by Hexagon Lincoln. Based on the

design, 38 all glass fiber COPVs, using E-Glass, A-I, A-II, and B-I packages, were built for mechanical testing under Task 2, Subtask 2.2. The two selected fiber sizings were shown to be compatible with the commercial epoxy resin used in Hexagon Lincoln processing line making Toray T-700 carbon COPV; no processing issues were noticed during fabrication of the all glass fiber COPVs. The all glass fiber design is designated as STEB02-250, which is a 250 bar tank designed to a 3.5 factor of safety (875 bar). In comparison, STEB01-250 is an all carbon fiber (T-700) 250 bar design to 2.25 factor safety (563 bar).

Figure 1 provides a simplified processing illustration from fiber drawing to vessel winding. The induction melting unit for demonstration of batch melting with increased glass throughput for high-strength glass was evaluated under Task 1, Subtask 1.2. The batch-melting was done by using a newly designed hot-wall induction melter. For the demonstration, a conventional furnace approach was not economically feasible.



Figure 1 Process flow of high-strength glass fiber production, multi-end roving package assembling, and tank winding processes

Figure 2 shows a high-temperature, hot-wall induction melting unit developed at PPG, which was utilized to demonstrate batch-to-glass melting process, making high-strength glass cullet at 4X (40 lbs. /h) discharge rate compared to a previously built melter. The smaller unit was used with glass cullet to test the key process controls and reduce risk when using the larger unit to directly melt batch material and control the discharge tube for regulating glass pouring rate.

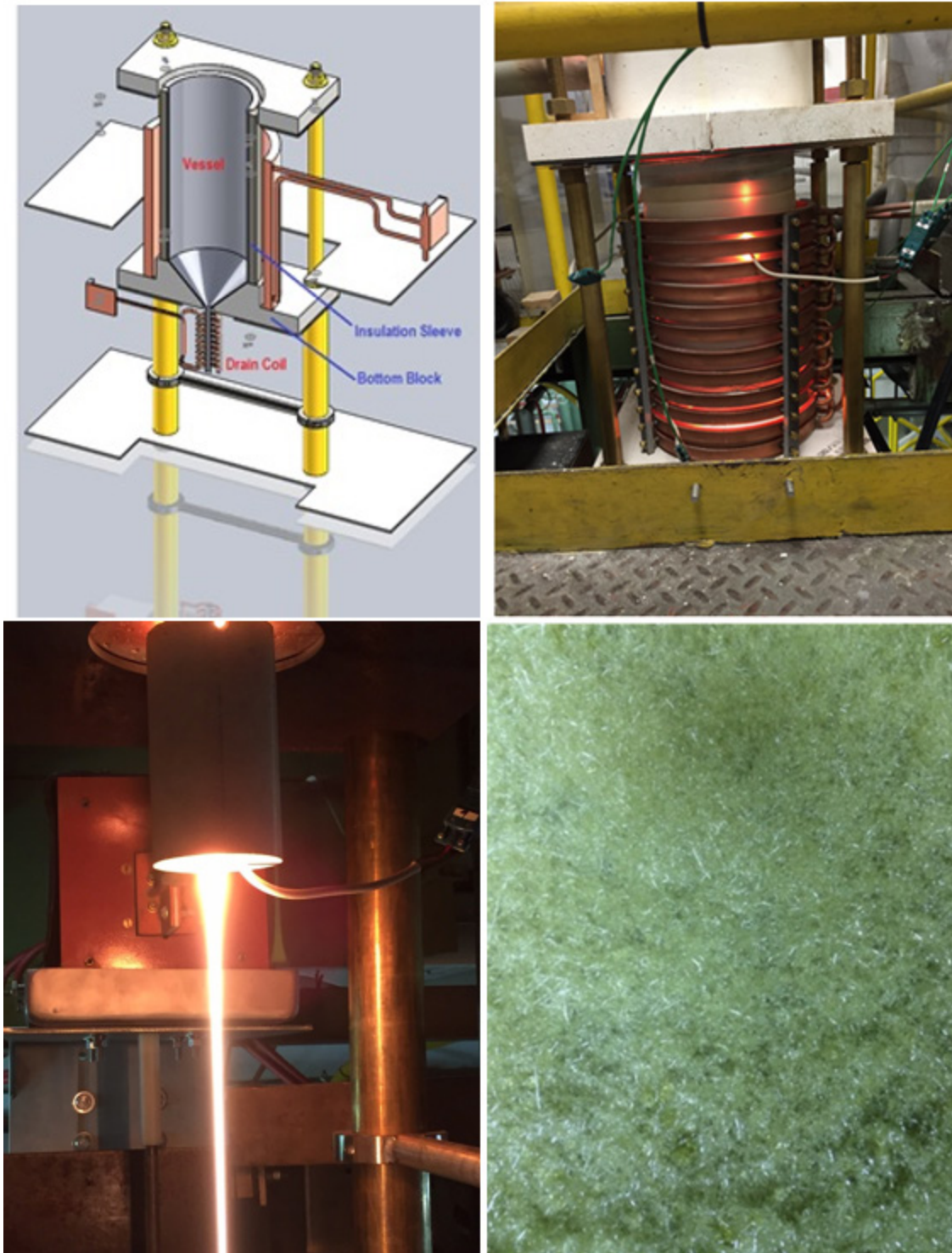


Figure 2 PPG demonstration of high-throughput induction melting technology (top left- schematic induction melting furnace with glass discharge at the bottom, top right – side view of actual melting compartment in operation, bottom left – melt discharge, and bottom right – final cullet made), illustrating the batch-to-melt process for high-strength fiber glass batch of the composition A.

For the large induction melting unit (cf. Fig. 2), a main induction coil was used to control batch melting and glass fining around 1600°C at about 28 kW power. After a typical 6h batch melting, molten glass was discharged from the bottom of the melting vessel. The opening or the melt flow rate of the discharge tube was controlled by a second, independently controlled induction coil, with the discharge temperature around 1470°C at about 2 kW power. During the melt discharge, to maintain vessel temperature, while new batch material was fed, the melting vessel was temporarily powered to approximately 30 kW. The melting vessel and discharge tube were made of platinum/rhodium alloys.

From the batch-to-glass melting evaluation at different discharge rates, PPG determined the total cost of making high-strength glass cullet, including costs of batch, labor, utility (primarily electricity), and fabrication cost of the precious melting vessel and refractory materials, excluding onetime equipment (power control and structures) cost. The subsequent fiber production processes, including drawing, roving package drying and assembling allow the project team to determine the total cost of making fibers at a fixed production rate or bushing throughput - including labor of fiber drawing, drying and assembling, product yield, fiber sizing material, utility (electricity, water), and fabrication cost of the pre-melter and 200-tip bushing.

For commercial production of both Composition A and B high-strength glass fibers, conventional furnace technology with modest improvement in firing and electrical boosting can be considered based on their melting and forming characteristics against the current PPG current operating parameters.

Figure 3 illustrates the total relative cost of making high-strength fibers using the current small platform setup with a 200-tip bushing. The project team calculated the cost against T700 carbon fiber cost of \$28.67/kg currently published by DOE. Using the present manufacturing platform, the cost of making high-strength glass fibers is higher than the project target value, i.e., no more than 50% of T700 carbon fiber cost. If we could make modest improvements to the existing setup, it will be possible to lower the production cost towards the target (as indicated by the predictions - green circles). However, the current process faced a number of challenges in operating the existing unit to make high-temperature fibers with a high yield on a consistent basis.

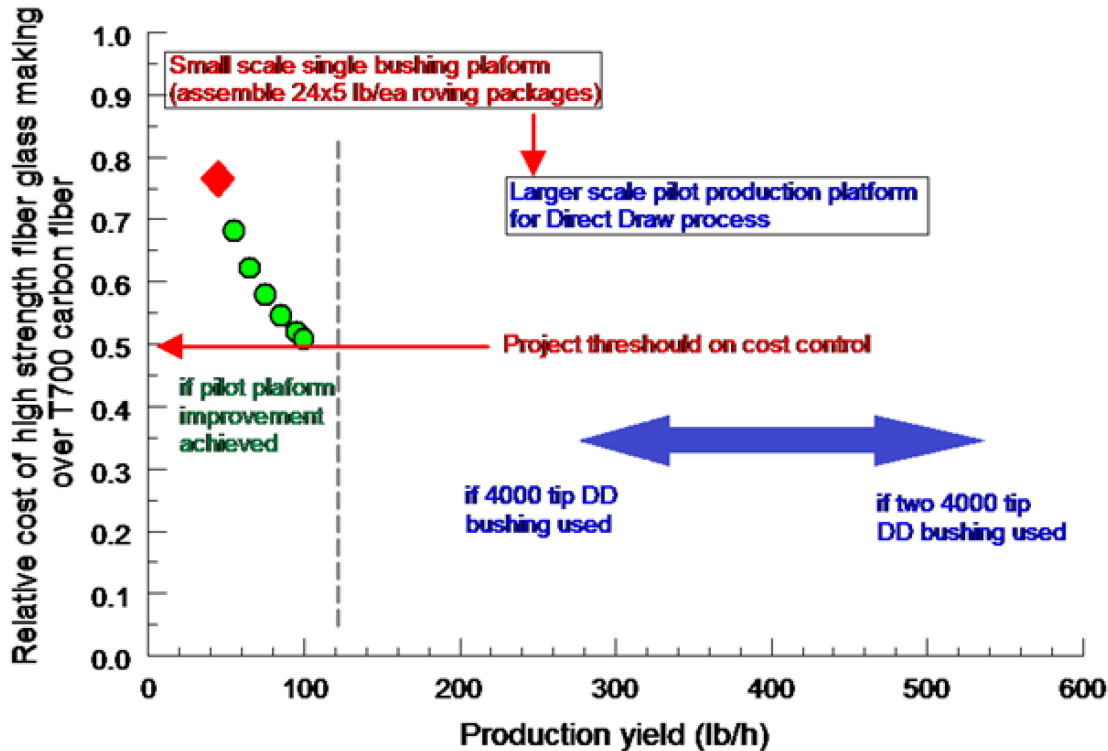


Figure 3 Relative cost analysis of producing high-strength glass fibers as a function of production yield (red diamond – current production cost, green circle – potential improvements using the current production platform, blue arrow – larger scale, commercial pilot production platform estimates)

3.2 Task 2 Tank Modeling and Validation (Hexagon Lincoln)

Under Task 2, Subtask 2.2, Hexagon Lincoln built 38 all fiber COPV vessels for mechanical evaluation. Each vessel can be generally characterized as follows: overall length of approximately 28 inches (711.2 cm), outside diameter of approximately 9.4 inches (238.8 cm), wall thickness of approximately 0.125 inch (3.2 mm), and nominal internal volume of approximately 24.2 liters. Within about 5% uncertainty, the average fiber volume fraction of each vessel was estimated to be approximately 62.5%. Table 5 summarizes the all glass fiber COPVs made by Hexagon Lincoln and the related mass and individual test results.

Table 5: Type IV STEB02-250 Bar (10" x 28") All Glass Fiber COPVs

Glass Type	Sizing Type	Vessel Serial Number	Test Request	Vessel Mass, lb.	Test	Result	Date of Test
INNOFIBER CR 2026	Baseline	T014-002	TR3847	40.016	Burst, psi	12,889	10-Jun-2015
		T014-003	TR3848	40.190		12,424	10-Jun-2015
		T014-004	TR3849	40.248		11,331	10-Jun-2015
		T014-005	TR3926	39.868	Pressure Cycling, cycles	3,460	6-Aug-2015
		T014-006	TR3927	39.596		6,358	8-Aug-2015
		T014-007	TR3928	39.728		922	5-Aug-2015
		T014-008	TR3929	39.536	Stress Rupture, Time to fail, minutes	232	10-Aug-2015
		T014-009	TR3930	39.720		3	17-Aug-2015
		T014-010	TR3931	39.702		49	17-Aug-2015
A	I	T035-001	TR4137	40.014	Burst, psi	13,422	9-Oct-2015
		T035-002	TR4138	40.710		12,870	9-Oct-2015
		T035-003	TR4139	40.542		12,894	9-Oct-2015
		T035-004	TR4140	40.558	Pressure Cycling, cycles	45,000	7-Dec-2015
		T035-005	TR4141	40.484		45,000	7-Dec-2015
		T035-006	TR4142	40.194		45,000	7-Dec-2015
		T035-007	TR4143	40.036	Stress Rupture, Time to fail, minutes	633	23-Oct-2015
		T035-008	TR4144	40.224		314	11-Dec-2015
		T035-009	TR4145	40.174		1,035	25-Nov-2015
	II	T043-001	TR4366	44.514	Burst, psi	14,011	4-Feb-2016
		T043-004	TR4367	44.928		14,290	4-Feb-2016
		T043-007	TR4368	45.160		13,769	4-Feb-2016
		T043-002	TR4369	44.842	Pressure Cycling, cycles	45,000	6-Mar-2016
		T043-005	TR4370	44.246		45,000	6-Mar-2016
		T043-008	TR4371	43.196		45,000	6-Mar-2016
		T043-003	TR4372	42.728	Stress Rupture, Time to fail, minutes	175	5-Feb-2016
		T043-006	TR4373	42.794		49	12-Feb-2016
		T043-009	TR4374	42.884		198	19-Feb-2016
B	I	T051-001	TR4527	36.238	Burst, psi	12,486	13-Apr-2016
		T051-004	TR4528	36.132		12,393	13-Apr-2016
		T051-007	TR4529	37.252		12,098	13-Apr-2016
		T051-010	TR4584	37.742		12,769	6-May-2016
		T051-002	TR4524	36.186	Pressure Cycling, cycles	25,891	5-May-2016
		T051-005	TR4525	36.056		29,435	6-May-2016
		T051-008	TR4526	37.158		26,659	5-May-2016
		T051-003	TR4530	36.162	Stress Rupture, Time to fail, minutes	57	25-Apr-2016
		T051-006	TR4531	35.496		95	26-Apr-2016
		T051-009	TR4532	37.178		1,870	29-Apr-2016
		T051-011	TR4585	37.880	SR, min	957	6-May-2016
	II				Burst, psi		
					Pressure Cycling, cycles		
					Stress Rupture, Time to fail, minutes		

Note – COPV reinforced by B-II high-strength fibers were not produced because we had already proven A-I had the best performance.

Three vessels were grouped together for mechanical testing to determine their burst pressure (according to internal procedure, NGV2-2012, Hydrostatic Burst Test for Project 4548 REVB 150423), pressure cycle (NGV2-2012 Ambient Cycle Test for Project 4548 REVB 150423), and stress rupture (Hexagon Lincoln Stress Rupture Test for Project 4548 REVB 150423).

Figure 4 summarizes all mechanical evaluations for E-Glass, A-I, A-II, and B-I reinforced COPVs. Relative to the E-glass reference fibers, tanks made from all of the high-strength fiber and sizing combinations exhibited improved performance. The A-I fiber tanks performed the best overall, passing both the burst and pressure cycle tests. They also had the longest time to stress rupture when held at 80% of the average burst pressure. However, significant variations were found in the stress rupture tests. Figure 5 shows optical micrographs illustrating failures seen for some of A-I and E-Glass reinforced vessels.

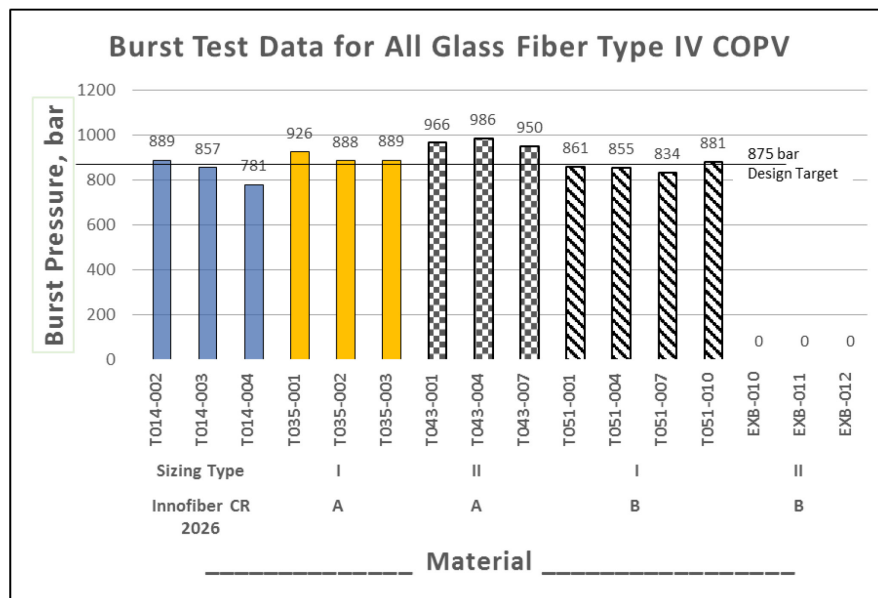


Figure 4a Mechanical evaluations of COPV E-Glass, A-I, A-II, and B-I: burst pressure

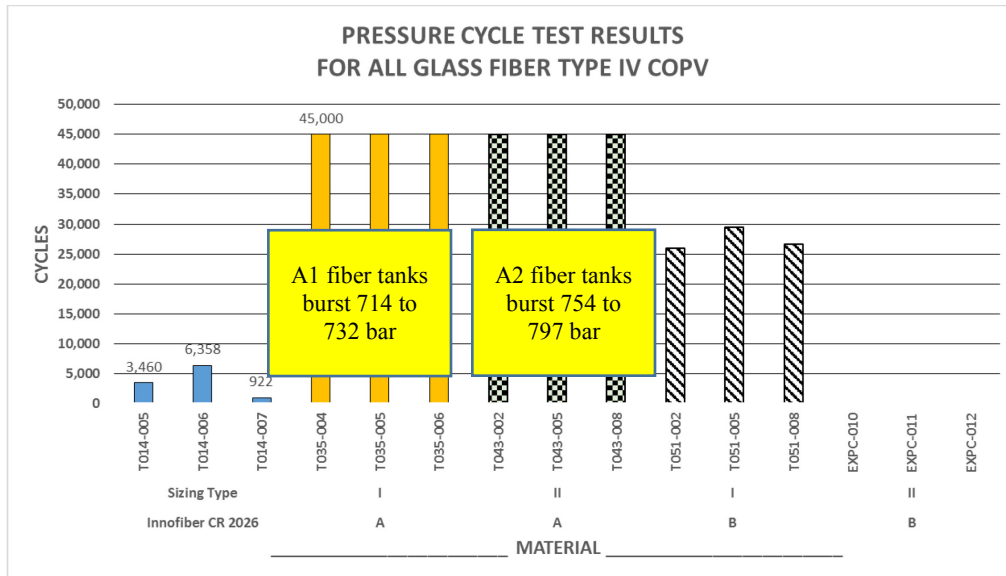


Figure 5b Mechanical evaluations of COPV E-Glass, A-I, A-II, and B-I: pressure cycle

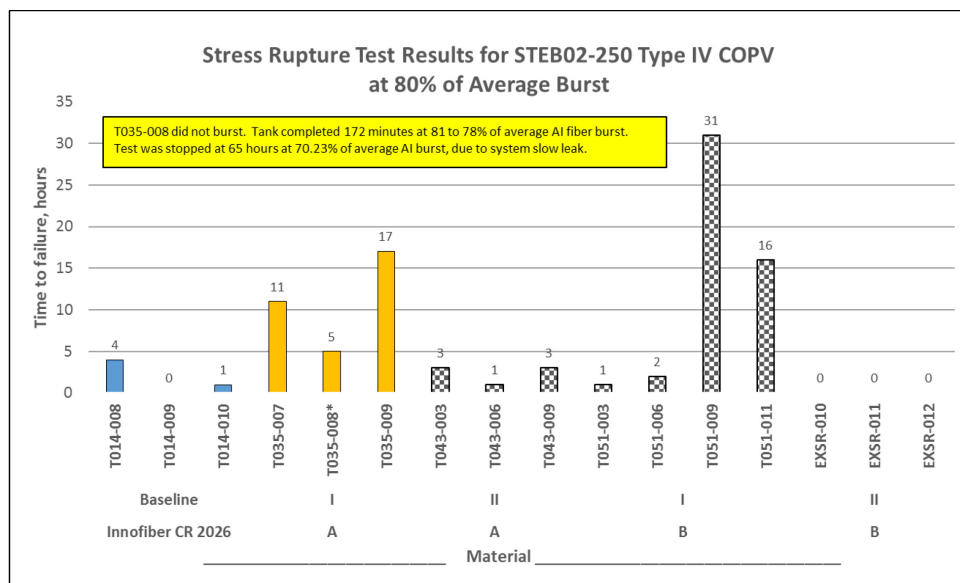
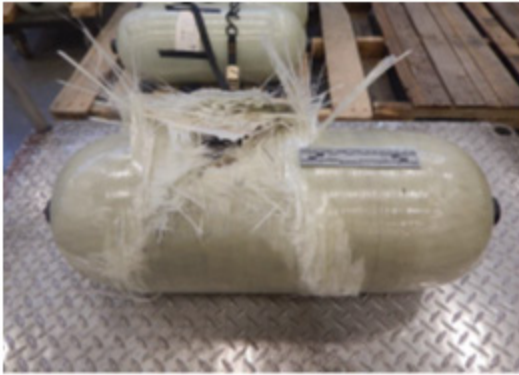


Figure 6c Mechanical evaluations of COPV E-Glass, A-I, A-II, and B-I: stress rupture



(a) COPV A-I STEB 250 bar (b) COPV A-I: Post 45,000 Cycles & Post Cycle Burst (10.6 KSI)



(c) COPV A-I: 80% load for 17.2 hours (d) COPV A-I: -80% load for 10.5 hours



(e) COVP E-Glass: 79% load for 3 min (f) COVP E-Glass: 922 cycles

Figure 7 Optical micrographs: (a) COPV A-I made from high-strength glass fibers, (b) COPV A-I post cycle burst after 45,000 cycles, (c & d) COPV A-I: stress rupture test to determine time of failure at 80% load using COPVs, (e) COPV E-Glass: 79% load for 3 min, and (f) COPV E-Glass: 922 cycles

Based on the best overall results from the mechanical evaluations under Subtask 2.1, Hexagon Lincoln completed vessel tests of tanks made from A-II fibers. Table 6 compares geometry and performance of vessels made from high-strength glass fiber (A-I) and T700 carbon fibers. Deficiency of high-strength glass fibers (cf. Table 4) translates to poor performance of the vessels against the commercial vessels made from T700 carbon fibers. High-strength fiber reinforced vessels had average translation of 81% as compared with 91% of T700 carbon fiber reinforced vessels.

Table 6: Vessel Parameters and Vessel Test Results and Comparison between High-Strength Glass Fiber and T700 Carbon Fiber Reinforcement

Parameter and Property	STEB01-250 Bar T700 Carbon	STEB02-250 Bar A-I Glass Fiber	Difference relative to T700 (%)
Tank Length (in)	27.8	27.8	0.0%
Tank OD (in)	9.95	10.65	7.0%
Nominal Internal Volume (liter)	24.2	24.2	0.0%
Tank Weight (lbs)	17.0	40.3	137.1%
Liner Weight (lbs)	6.3	6.3	0.0%
Fiber Weight (lbs)	7.1	26.3	270.4%
Resin Weight (lbs)	3.6	7.7	113.9%
Safety Factor	2.25	3.50	55.6%
Burst Pressure (avg) (PSI)	10323	13062	26.5%
Actual Burst Relative to Service Pressure	2.85	3.60	26.5%
Avg. Translation	91%	81%	-11.0%
Stress Rupture at 80% Peak Load (min)	indefinite	661	-
Total Wind Time (min)	35	75	114.3%

3.3 Task 3 Stress Rupture Characterization and DOE Target Modeling (PNNL)

Under Task 3, Subtask 3.1, PNNL built an array of temperature and humidity controlled test units for test conditions of $23 \pm 1^\circ\text{C}$ and $50 \pm 10\%\text{RH}$. Grips were based on a PPG design after comparing with other sample tabbing methods shown in Figure 6. As shown in Figure 7, PNNL used the set up to perform stress rupture tests using fiber strands or rods of the reference E-glass and high-strength glass A-I, and A-II, which were impregnated with the epoxy resin used for T-700 carbon reinforced Type IV COPV.



Figure 8 Early evaluation of other tapping methods for stress rupture test setup

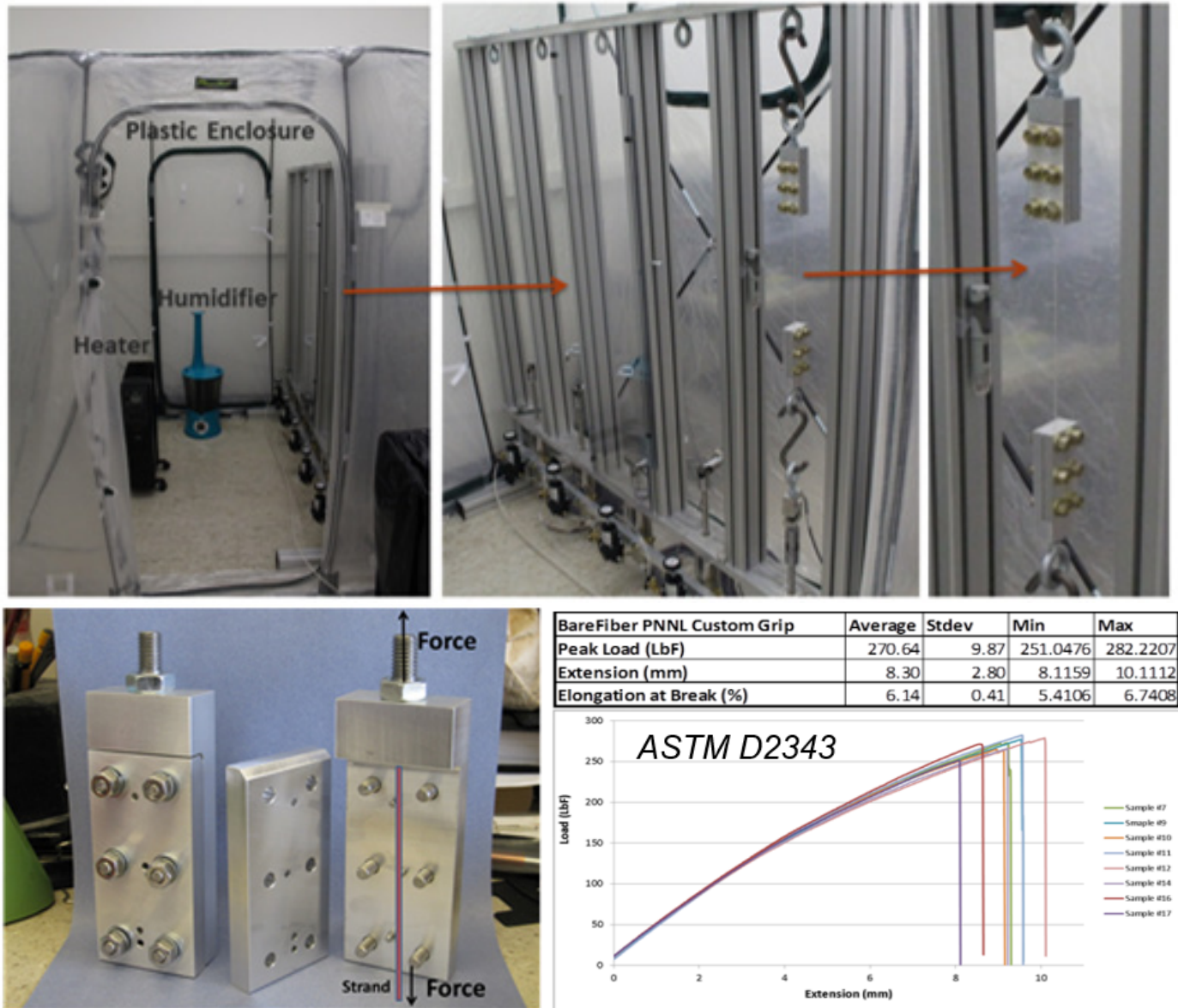


Figure 9 Stress rupture test setup at PNNL (top two - test frame in the environmental chamber, bottom left – sample grip designed for high-strength glass fiber tensile test, bottom right – examples of test evaluation under a continuous tensile loading)

Figure 8 summarizes the stress rupture test data, the S-glass strand data from the literature (used to establish the current 3.5 value) [2], and the reference E-glass stress rupture data from PPG's previous tests [3]. The slopes from the A-I, and the A-II high-strength strand tests are similar to the S-glass strands and the reference E-glass (2026-CR) fibers. The similar slopes suggest that a similar safety factor of 3.5 is required for the high-strength glass fibers (Composition A and B) used.

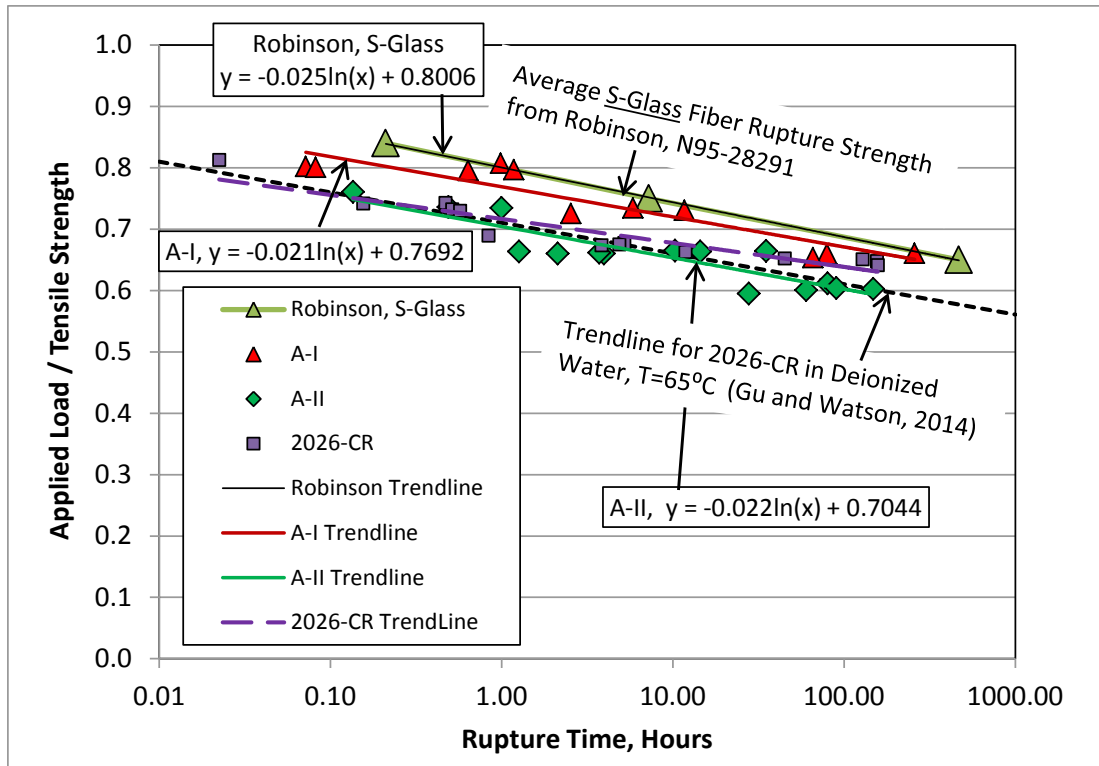


Figure 10 Stress rupture test data comparing reference E-glass (2026-CR), A-I, and A-II. The literature data for 2026-CR tested in water plus the S-glass stress rupture data reported in literature [2] are included for comparison. Each glass type has similar stress rupture characteristics in terms of the slope of the normalized load vs time at rupture.

The stress rupture curve of the reference E-Glass strands tested by complete immersion in 65°C water showed a nearly parallel line of relative failure stress vs rupture time as that of the E-Glass fiber strands tested at 23°C under 50%RH and the high-strength fiber strands (A-I, A-II). All fiber strands, independent of composition, were all encapsulated in the epoxy used for COPV. The results suggest that humidity environments used in the stress rupture tests has little effect on fiber stress rupture characteristics. This implies that the composite rupture under static tensile loadings is mostly influenced by the strain mismatch between the glass fibers and epoxy matrix. The glass is larger than the matrix, which is opposite of a carbon fiber/epoxy composite. Under a high tensile strain at the interface between glass fiber and epoxy, a local interfacial failure originated from the matrix can significantly shift load distributions in the fibers, destroying the composite integrity. This will result in its early failure after a short time.

Under Task 3, Subtask 3.2, a model developed by PNNL was used to assess the cost, volumetric, and gravimetric performance of a DOE standard-sized compressed hydrogen tank (5.8 kg hydrogen, 700 bar, 147.3 L, inside length/diameter = 3.3 in, T-700 carbon fiber) using the A-I glass fiber strengths. As a benchmark, the PNNL model gives tank composite masses that are within 5% of the 2013 and 2015 DOE tank estimates (DOE Records 13010 and 15013). The model was also used to estimate the mass of the standard test evaluation bottles (STEBs) wound by Hexagon Lincoln using the glass fibers. Using the liner dimensions of the Hexagon Lincoln and the A-I average strand strength (3,192 MPa), Table 7 shows that the model predicts composite mass and outside tank dimensions that are very similar to the A-I fiber, 250 bar STEB.

Table 7: Comparison of As-Wound Tank Mass and Dimensions with PNNL Model Predictions for the A-I Glass Fiber, 250 bar STEB Tank.

Parameter and Property	STEB02-250 Bar A-I Glass Fiber	PNNL Model A-I Glass STEB
Tank Length (in)	27.8 With End Bosses	25.8 Without End Bosses
Tank OD (in)	10.65	10.70
Nom. Internal Volume (L)	24.2	24.3
Tank Weight (lb.)	40.3	42.4
Liner Weight (lb.)	6.3 With End Bosses	4.1 Without End Bosses
Fiber Weight (lb.)	26.3	29.2
Resin Weight (lb.)	7.7	9.1
Safety Factor	3.5	3.5
Design Burst Pressure (psi)	12690	12690
Avg. Translation	81%	79%

OD – Outside diameter

Table 8 presents model results for the DOE standard size compressed hydrogen tank (5.8 kg stored/5.6 kg usable hydrogen, 700 bar, 147.3 L, inside length/diameter = 3.3 in). Seven different design cases are presented along with the 2020 DOE performance targets.

Table 8: The estimated performance of glass fiber tanks compared with the BP1 and BP2 goals. Estimated performance of the carbon fiber reference tank is also listed. All calculations are for the DOE standard size pressurized hydrogen tank (5.8 kg stored/5.6 kg usable hydrogen, 700 bar, 147.3 L, inside length/diameter = 3.3 in).

Case #	1	2	3	4	5	6	7
			BP1 Goal	BP2 Goal	BP1 Actual	BP1 Actual	Conceptual
Summary Metrics	T-700 Carbon Fiber	E-Glass	High-Strength Glass Design-1	High-Strength Glass Design-2	2026-CR E-Glass	Glass A-I	Increased Strength Glass A-I
Fiber Cost (\$/lb.)	13	1.3	5.2	5.2	1.3	5.2	5.2
Average Fiber Strand Strength, S, MPa	4900	3000	6111	6111	2848	3192	5500
Coefficient of Variation, Cv	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Design Strand Strength, S*(1-Cv)	4410	2700	5500	5500	2563	2873	4950
Resin Density (g/cm ³)	1.25	1.20	1.20	1.00	1.20	1.20	1.20
Safety Factor	2.25	3.50	3.50	3.00	3.50	3.50	3.50
Storage System Tank Cost (\$/kWh net)	14.2	13.0	9.7	7.8	15.6	28.1	11.3
Composite Cost Contribution (\$/kWh)	12.2	12.8	9.4	7.5	15.4	27.9	11.0
Gravimetric Capacity (kWh/kg)	1.44	0.34	1.02	1.24	0.28	0.38	0.88
Volumetric Capacity (kWh/L)	0.85	0.45	0.79	0.85	0.40	0.48	0.76
Tank Mass without H ₂ (kg)	123	543	178	145	653	487	205
Tank Composite Mass (kg)	103	523	157	124	632	466	184

NOTE: The cases in the following paragraphs reference the cases shown in Table 8.

Cases 1 through 4 are the reference cases presented in the original proposal. Cases 1 and 2 are tanks with T-700 carbon fiber and E-glass properties. Cases 3 and 4 were the projected BP1 and BP2 performance targets. These numbers are slightly different from the original proposal, due to small adjustments in the fiber stress equations of the model. Case 5 estimates the mass and cost performance of a tank with the properties of 2026-CR E-glass measured during BP1. Cases 2 and 5 with common E-glass strengths estimate very large composite masses. With tank pressure of 700 bar and strand strengths around 3,000 MPa, the tank wall is so thick that the through-thickness composite compression makes it difficult to limit the inner layer stresses by adding more thickness. This is illustrated in Case 5 for the 2026-CR E-glass (2,848 MPa average strand strength) with

estimated composite mass of 653 kg, compared to the Case 2 E-glass (3,000 MPa average strand strength) with estimated composite mass of 543 kg.

Case 6 estimates the tank performance for the A-I glass fibers (3,192 MPa average strand strength) produced in BP1. The volumetric capacity is predicted to be 0.48 kWh/L compared to the BP1 goal of 0.81 kWh/L, gravimetric capacity of 0.38 kWh/kg compared to the BP1 goal of 1.1 kWh/kg, and the composite contribution to system cost is predicted to be \$27.9/kWh compared to the BP1 goal of \$8/kWh. A projected fiber production cost of \$5.2/lb. (4X standard E-glass at \$1.3/lb.) is used in the cost estimate. These trends result entirely from the large composite thickness required to support the pressure load with the lower-than-expected fiber strand strengths produced in BP1. An approach to increase the fiber strand strengths to meet the project goals has been developed and was discussed with the DOE.

Case 7 estimates the tank performance if an improved A-I glass can be produced with a higher average strand strength of 5,500 MPa. The 10% coefficient of variation results in a design strand strength of 4,950 MPa, 0.76 kWh/L volumetric capacity, 0.88 kWh/kg gravimetric capacity, and a composite contribution to system cost of \$11.0/kWh.

Additional cases were simulated with average strand strengths ranging from 3,000 MPa to 7,000 MPa to show the sensitivity of the tank performance trends to strand strength. Figure 9 shows the trends in composite cost, volumetric capacity, and gravimetric capacity. It is estimated that an average strand strength of 6,111 MPa (design strand strength of 5,500 MPa) is required to meet the BP1 goal of 0.81 kWh/L with a gravimetric capacity of 1.0 kWh/kg, and composite cost of \$9.6/kWh (based on \$5.2/lb. fiber cost). At average strand strength of 6,500 MPa (5,850 MPa design strand strength), the estimated volumetric capacity is 0.82 kWh/L with a gravimetric capacity of 1.07 kWh/kg, and a composite cost of \$8.8/kWh. At 7,000 MPa (6,300 MPa design strand strength), the estimated volumetric capacity is 0.84 kWh/L with a gravimetric capacity of 1.16 kWh/kg, and a composite cost of \$8.1/kWh. It is important to note that these are only model trends (not actual glass fiber performance), which are useful to project glass composite performance at higher strand strengths.

The trends in Figure 9 suggest that high-strength glass fibers must exceed T-700 tensile strength to reach the project goals. Gravimetric capacity is particularly challenging since glass fiber has a higher density than carbon fiber. It is estimated that the best expected performance of the team's current A or B fibers would be 5,500 MPa. In practice, the best achievable strand tensile strength would then be about 4,600 MPa (based on 15% loss). Therefore, at 4,600 MPa strand strength, Figure 9 would estimate tank performance to be about 0.68 kWh/L volumetric capacity, 0.71 kWh/kg gravimetric capacity, and about 14.2 \$/kWh composite contribution in a 700 bar pressure vessel capable of storing 5.6 L of usable hydrogen at room temperature.

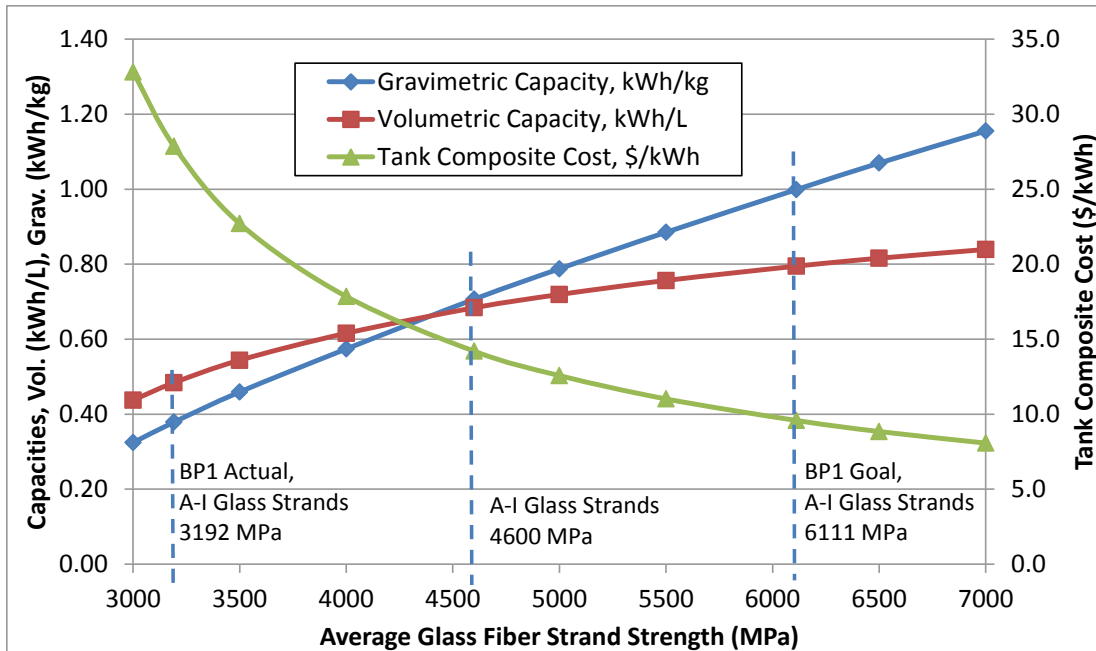


Figure 11 Sensitivity of cost, volumetric, and gravimetric performance to glass fiber strand strength

The assessment discussed above was performed using a safety factor of 3.5. The original planning of the project, Budget Phase 2 (BP2) would rely on new high-strength fibers exhibiting improved stress rupture characteristics, i.e., the rupture time would need to be less sensitive to the level of applied tensile stress than what was determined for the A-I fibers or S-fibers reported in literature [2]. If achieved, this improved performance could be used to justify the use of a lower safety factor for tank design, making it possible to close the gap reaching the target strand tensile of 5,500 MPa instead of 6,500 MPa by the projection discussed earlier (cf. Fig. 9).

4. Conclusions and Future Directions

BP1 goals to demonstrate high-strength fiber strand with 5,500 MPa tensile strength was not achieved because of the high translation losses (around 40%) by using a non-standard fiber forming process. The losses were caused primarily by processing issues rather than glass intrinsic chemistry; pristine single fiber strength of both glass chemistry passed 5,500 MPa. These deficiencies can be resolved in future commercial operation using standard batch melting and fiber forming processes.

At the composite tank, it is important to confirm actual impact of the fiber/resin elongation mismatch on the composite stress rupture characteristics through mechanical modeling and testing composite materials with close matched elongation characteristics. This can be done by using alternative resins with higher elastic elongation. For this project, we chose to limit our investigations to the resin system used by HL. When high quality, high-strength glass fibers are produced with the target strand tensile property and a suitable high-elongation resin is identified, PPG recommends a new study to evaluate high-strength reinforced COPVs. Alternatively, PPG also recommends a hybrid approach to resolve the glass fiber/resin elongation mismatch (COPV reinforced by T700 carbon fibers and high quality, high-strength glass fibers). Using the hybrid solution, it could be possible to reduce cost of fibers by 25 – 30% compared to the original goal of 50% cost reduction. The opportunity arising from making COPVs by using the hybrid fiber composite approach is recommended for further investigation.

5. Special Recognitions & Awards/Patents Issued

None

6. Publications/Presentations

1. H. Li, “Achieving Hydrogen Storage Goals through High-Strength Fiber Glass,” at 2016 U.S. DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting, Washington D.C., June 16, 2016.
2. H. Li, “Achieving Hydrogen Storage Goals through High-Strength Fiber Glass,” at U.S. DRIVE Technical Meetings in Detroit, MI, on May 19, 2016.
3. H. Li, “Achieving Hydrogen Storage Goals through High-Strength Fiber Glass,” at 2015 U.S. DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting, Washington D.C., June 9, 2015.

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1. <http://energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>
2. Robinson, E.Y. 1991. “Design Prediction of Long-Term Stress Rupture Service of Composite Pressure Vessels.” The Aerospace Corporation. El Segundo, CA.
3. Gu, P., Watson J., “Corrosion Resistance of E-Glass Fiber Reinforced Composites: Boron and Interface Factors,” CAMX 2014 Conference Proceedings, Orlando, FL, USA, October 13–16, 2014. CAMX–The Composites and Advanced Materials Expo.

Appendix A

Properties of High-Strength Fiber Glass Compositions under Task 1, Subtask 1.3

ID: DOE HT-#	1	2	3	4	5	6	7	8	4/5a	4/6a	4/5b	4/6b
T_L (°C)	1235	1234	1227	1230	1259	1258	1260	1252	1243	1242	1235	1236
T_F (°C)	1343	1329	1320	1337	1280	1285	1286	1297	1305	1309	1320	1316
ΔT_{F-L} (°C)	108	95	93	107	21	27	26	45	62	67	85	80
T_M (°C)	1549	1534	1520	1547	1467	1479	1475	1488	1502	1504	1519	1518
ρ (g/cm ³)	2.59	2.60	2.62	2.61					2.64	2.64	2.63	2.63
E (GPa)	90.4	91.3	91.9	91.0					92.6	92.6	92.6	92.0
σ_f (MPa)	5376	5322	5479	5424	5377				5357	5393	5583	5385
Stdev $\Delta\sigma_f$ (MPa)	226	180	117	75	132				71	91	58	95
Weibull α	5477	5393	5542	5461	5433				5390	5435	5612	5432
Weibull β	23.1	37.8	58.8	78.8	45.3				89.4	66.6	90.2	55.2
ε (%)	6.0	5.8	6.0	6.0					5.8	5.8	6.0	5.9

ID: HP2-#	a	b	c	d	e	f	g	h	i	j	k	l
T_L (°C)	1188	1188	1200	1185	1208	1154	1153	1167	1219	1253	1226	1201
T_F (°C)	1319	1307	1297	1320	1338	1294	1336	1291	1289	1247	1307	1299
ΔT_{F-L} (°C)	131	119	97	135	130	140	183	124	70	-6	81	98
T_M (°C)	1522	1508	1494	1521	1549	1493	1547	1447	1491	1434	1501	1493
ρ (g/cm ³)	2.61	2.62	2.63	2.62	2.61		2.62		2.64			
E (GPa)	92.3	92.0	92.8	91.9	90.0		91.1		91.8			
σ_f (MPa)	5490	5492	5340	5467			5321		5243			
Stdev $\Delta\sigma_f$ (MPa)	135	167	101	113			116		144			
Weibull α	5546	5552	5391	5500			5346		5318			
Weibull β	46.3	35.1	50.5	79.6			36.9		43.5			
ε (%)	6.0	6.0	5.8	6.0			5.8		5.7			

Note: T_L – liquidus temperature, T_F – fiber reference drawing temperature at 1000 Poise (or 100 Pa·s) melt viscosity, ΔT_{F-L} – difference between fiber drawing temperature and liquidus temperature (should be no less than 55°C), T_M – reference glass melting and fining temperature at melt viscosity of 100 Poise (or 10 Pa·s), ρ – average fiber density, E – average pristine fiber Young's modulus by sonic method, σ_f – average pristine fiber strength, ε – average pristine fiber failure strain, Stdev. ($\Delta\sigma_f$) – one standard deviation of fiber pristine strength (sample size greater than 25), α and β – fitting parameters of Weibull analysis of pristine fiber tensile strength.