Precursor Processing Development for Low-Cost, High-Strength Carbon Fiber for Composite Overwrapped Pressure Vessel Applications

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Project End Date: Project continuation and direction determined annually by DOE

Overall Objectives

- Demonstrate ≥100-filament, air gap spinning of the small diameter TechPAN precursor polymer, followed by oxidization, carbonization, and characterization of the resultant carbon fiber.
- Demonstrate single filament carbon fiber properties approaching 4.9 GPa strength and 230 GPa modulus (similar to T700S).
- Achieve <1 wt % residual solvent in fiber with minimal residence time for the water minimization strategy.
- Demonstrate ≥10-filament, air gap, hollow fiber spinning of TechPAN precursor polymer with outer diameter (OD) <100 µm and inner diameter (ID) <50 µm with specific strength and modulus approaching 635 MPa/g/cc and 8.5 GPa/g/cc.
- Demonstrate lower energy solvent recovery through sorption in activated carbon modules with capability to capture >50% of the solvent effluent, and their thermal regeneration with <15% loss in specific surface area.
- Demonstrate hollow carbon fiber tensile properties approaching 4.9 GPa strength and 230 GPa modulus (similar to T700S), with an analysis of specific strength pertaining to part weight consideration.
- Deliver a cost analysis of the precursor and carbon fibers with a targeted cost potential of $12.60/kg.

Fiscal Year (FY) 2019 Objectives

- Demonstrate ≥10-filament, air gap, hollow fiber spinning of TechPAN precursor polymer with OD <100 µm and ID <50 µm with specific strength and modulus approaching 635 MPa/g/cc and 8.5 GPa/g/cc.
- Demonstrate lower energy solvent recovery through sorption in activated carbon modules with capability to capture >50% of the solvent effluent, and their thermal regeneration with <15% loss in specific surface area.
- Deliver a cost analysis showing a reduction of ≥19%, from $29.40/kg to $23.82/kg, is possible by means of low-cost polymer, water minimization, and low energy solvent recovery.

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[1]:

- System Weight and Volume
- System Cost
- Materials of Construction.

Technical Targets

This project is focused on developing a new precursor fiber for low-cost, high-strength carbon

[1] https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22

fiber (CF). Insights gained from these studies will be applied to composite overwrapped pressure vessels (COPVs). The carbon fibers developed here seek to fulfill the following DOE hydrogen storage targets:

- CF cost: $12.60/kg CF
- Tensile strength: 4.9 GPa (711 ksi)
- Tensile modulus: 230 GPa (33.4 Msi)

The DOE technical targets and our current project status are listed in Table 1 for comparison.

FY 2019 Accomplishments

- Demonstrated ≥10 filament, air gap, hollow fiber spinning of TechPAN precursor polymer with OD <100 μm and ID <50 μm with specific strength and modulus approaching 635 MPa/g/cc and 8.5 GPa/g/cc.
    - TechPAN is a low-cost, non-exclusive special acrylic fiber-grade terpolymer that can be supplied to the fiber industry at the 10s of kilotonne scale at an anticipated cost of $3/kg (typical exclusive, aerospace grade polyacrylonitrile [PAN] polymer costs $7.05/kg [2].)
    - Currently we are spinning 25-filament hollow fiber tow, with dimensions averaging 56 μm OD and 32 μm ID. Specific strength is approaching 635 MPa/g/cc (currently averaging 414 MPa/g/cc) and specific modulus has exceeded 8.5 GPa/g/cc (currently averaging 11.2 GPa/g/cc). All tensile measurements are based on force per area defined by the fiber's OD.
- Demonstrated lower energy solvent recovery through sorption in activated carbon modules with capability to capture >50% of the solvent effluent, and their thermal regeneration with <15% loss in specific surface area.
    - Currently, the use of activated carbon modules allows for the capture of 58% of the solvent effluent. Regeneration of the sorbed activated carbon results in a loss of 2.4% specific surface area.
    - With improved activated carbon regenerability, the overall concept is capable of reducing the overall CF cost by up to 8%.
- Delivered a cost analysis showing a reduction of ≥19%, from $29.40/kg to $22.99/kg, is possible by means of low-cost polymer, water minimization, and low energy solvent recovery.

Table 1. Progress toward Meeting Technical Targets for Hydrogen Storage for Light-Duty Fuel Cell Vehicles

Characteristic	Units	DOE 2020 Hydrogen Storage Targets	Project Status (initial carbon fiber cost of $29.40/kg)
Storage system cost	$/kg CF	12.60[a] (57.1 % reduction)	22.99 (21.8% reduction)
Carbon fiber (CF) cost [1]			

[a] Per DE-FOA-0001647

INTRODUCTION

CF is central to produce lightweight, high-pressure COPVs, which are used for on-board storage of hydrogen for fuel cell vehicles. In 2015, (raw) CF cost accounted for 62% of the cost of a hydrogen storage system for representative COPVs manufactured with T700S CF at $29.40/kg CF [3]. The high cost of on-board hydrogen storage systems, stemming primarily from CF cost, is a barrier for the adoption of hydrogen fuel cell vehicles. Therefore, we are developing new precursor fiber processing to demonstrate CF tensile properties similar to T700S with a production cost potential of $12.60/kg: less than half the T700S cost.

We are investigating solutions to **critical issues stemming from precursor** that significantly contribute to the cost of CF, namely high polymer cost, inefficient water use and solvent recovery, energy intensive conversion with low fiber throughput, and high coefficient of variation between fibers. We are developing hollow precursor fibers to significantly increase the throughput rate of thermal processing while maintaining high specific tensile properties of their resultant hollow carbon fibers.

APPROACH

To achieve the dramatic cost reduction and CF performance required, we proposed a three-front approach, leveraging our unique precursor fiber processing capabilities and skillsets.

1. Utilize and prove-out a *new, low-cost, high-volume, high quality* PAN-based precursor terpolymer, exclusively under investigation at the University of Kentucky Center for Applied Energy Research, known as TechPAN.
2. Develop *air-gap* solution spinning of small diameter and *hollow* precursor filaments in multifilament continuous tows.
3. Drastically increase water and energy-use *efficiency* incurred in wash-water/solvent separations utilizing a specially designed wash bath and activated carbon recovery system.

RESULTS

To achieve dramatic cost reduction, we proposed to produce hollow precursor fiber, largely on the bases that (1) hollow precursor fiber would allow for significantly faster thermal processing (particularly during oxidation), and (2) the majority of the stress in the fiber is concentrated in the outer surface region—due to the relatively disordered core region of solid fiber [4]. For FY 2019, significant focus went to process development for solution spinning hollow TechPAN precursor fiber in a scalable, multifilament tow form. Leveraging our unique expertise and fiber processing equipment, we were successful in spinning and drawing hollow filaments to an average OD of 56 um and average ID of 32 um, shown in Figure 1. These are the smallest diameter multifilament solution-spun hollow PAN filaments ever produced by this method [5].

Mechanical properties of the hollow PAN precursor fibers were analyzed, and the resulting tensile strengths and moduli are shown in Figure 1. As the OD of the filaments decreased, both break strength and elastic modulus increased. Currently, the 56 µm OD fibers (11% diameter COV for N = 17) have a specific break strength of 414 MPa/g/cc, which will increase with further diameter reduction. We expect to achieve 635 MPa/g/cc in the next quarter. The target specific modulus of 8.5 GPa/g/cc was exceeded at 11.2 GPa/g/cc. Although no direct causality can be prescribed between precursor fiber and CF tensile properties, CF tensile improvement is generally consistent with decreasing precursor fiber dimensions.

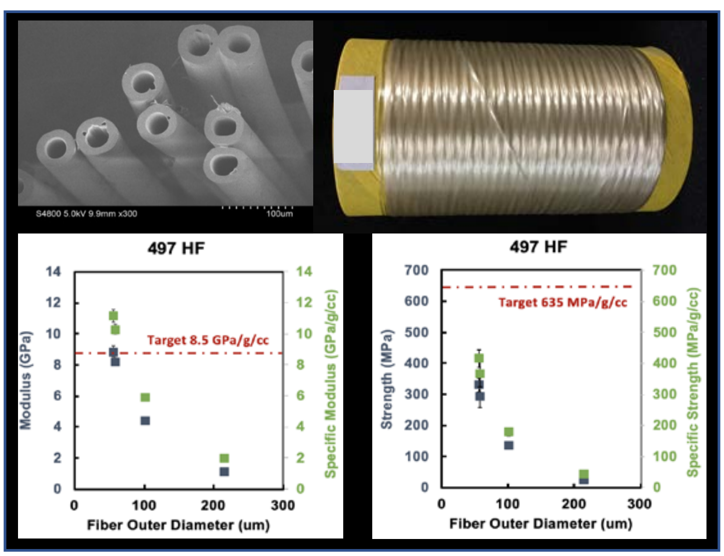

Figure 1. Scanning electron microscopy image of TechPAN precursor hollow filament cross sections and tensile results for hollow precursor fibers spun with varying ODs. (N = 25 for each point, 25.4 mm gauge length, all tensile measurements based on force per area defined by the hollow fiber OD, density based on mass per volume defined by the hollow fiber OD)

Ahead of schedule, we began running initial batch thermal conversion experiments to gauge the response of hollow fiber during oxidation and carbonization. Observations to date support oxidation occurring from both the interior lumen of the fiber as well as the exterior. At scale, this could significantly increase fiber throughput. Figure 2 shows an energy-dispersive X-ray spectroscopy (EDS) image of an oxidized fiber cross section showing oxygen content in blue. Additionally, despite high tensions applied during thermal conversion, the resulting hollow carbon fibers (HCF) remained hollow and did not collapse, as shown in Figure 2. This is very encouraging for our Year 3 work. Continuous tow hollow fiber (HF) precursor has been sent to Oak Ridge National Laboratory (LightMat Consortium collaboration) to further investigate the performance of the fiber during a continuous conversion process.

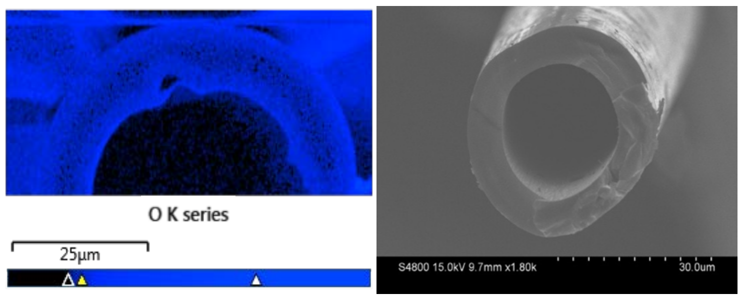

Figure 2. (Left) EDS image of an oxidized hollow PAN fiber showing oxygen content (blue), demonstrating oxidation is occurring from both the interior lumen of the fiber as well as the exterior. (Right) Cross section of a hollow carbon fiber produced at University of Kentucky Center for Applied Energy Research.

The efficient solvent recovery and water utilization task was largely completed this year. To maintain acceptable washing, a dimethylsulfoxide (DMSO) concentration less than 3.1 wt % in the wash bath was found to be necessary. In Year 2 Q1, we successfully demonstrated the ability of a special activated carbon (AC) sorption system, with counter-current recirculation, to prevent the DMSO concentration from exceeding 3.1 wt % over a 100 min spinning run (Figure 3). Without AC, the DMSO concentration would have peaked at 7.3 wt %. This accounts for a 58% capture of solvent effluent by the AC sorption system, which surpassed the 50% target and milestone (Go/No-Go 2). Moreover, concerning total effluent, only 2.8 L of wash water (up to 3.1 wt % DMSO) was recirculated at 300 mL/min with the AC sorption system over the 100 min spin run. By comparison, a similar flow of fresh wash water (as used in plants currently) generated 30 L of wash water at a concentration of 0.58 wt % DMSO. Both effluent streams would require treatment by distillation to recover the solvent and treat the water. This represented a 90% reduction in total effluent to distillation.

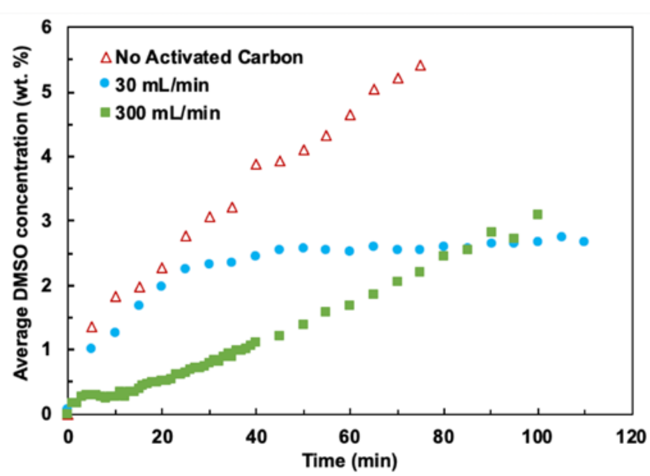

Figure 3. Comparison of the average DMSO concentration in the bath vs. spinning time for three solvent recovery conditions: no activated carbon, 30 mL/min through AC, and 300 mL/min through AC. Standard air gap spinning of 100-filament TechPAN tow. (2.8 L water-solvent total, 480 g of AC—up to 0.18 g DMSO per 1 g AC, 0.05 kg precursor spun)

Additionally, in Year 2 Q3, regeneration of the DMSO-sorbed activated carbon in our labs showed a 2.4% loss in specific surface area per regeneration cycle. The target was <15 %. Therefore, with regard to Go/No-Go 2, the water minimization and low energy solvent recovery milestone was achieved.

At manufacturing scale, approximately 10 gal of wash effluent is generated per 1 kg precursor produced. Utilization of the AC system offered up to a 90% reduction in total water-solvent effluent to distillation. However, we also found that the AC lost 2.4% specific surface area (or adsorption capability) per regeneration cycle. We considered the potential cost savings by extrapolating our findings and normalizing them per 1 kg precursor. The cost calculation is shown in Table 2. It accounts for the costs of water, distillation energy, and activated carbon replacement.

Without the use of AC, solvent recovery and water treatment cost $1.31/kg of precursor fiber. With AC and accounting for 2.4% AC loss, the cost increased to $8.98/kg of precursor due to replacement of spent AC. To realize cost savings, vastly improved regenerability of the AC is essential. The AC supplier claims typical regeneration sorption capacity loss of only 0.02% per cycle, which would offer cost savings of 82%, lowering the cost to $0.23/kg, shown in Table 2. Given 2.2 kg of precursor is required to produce 1 kg of CF, this would reduce CF cost by **$2.36 or 8%**. The goal set forth for Year 2 was to reduce CF cost from $29.40/kg to $23.82/kg or less. In Year 1, cost was reduced from $29.40/kg to $25.35/kg by demonstrating the low-cost TechPAN polymer. Our AC concept findings here suggest that this could be further reduced to **$22.99/kg**. However, dramatically increased regenerability of the AC must be achieved. Reviewer feedback from the 2019 Annual Merit Review and Peer Evaluation Meeting indicated a desire for the University of Kentucky team to move forward from Task 3.0 Energy Efficient Solvent Recovery and Water Use and to focus on the hollow fiber work.

Table 2. Cost Evaluation for Low Energy Solvent Recovery to Produce 1 kg of Precursor fiber

	Without AC	With AC (2.4% loss)	With AC (0.02% loss)
Upfront AC cost[a] (480 g at $10/lb)	-	$367.50	367.50
Amount of water used (gal)	10	1	1
Water use cost ($0.8775/1,000 gal)	$0.0088	$0.0009	$0.0009
Distillation energy cost	$1.30	$0.13	$0.13
Activated carbon regeneration cost	-	$0.0277	$0.0277
Percent non-regenerable AC	-	2.4	0.02
Non-regenerable activated carbon cost	-	$8.82	$0.07
TOTAL COST	$1.3088	$8.9786	$0.2324
% benefit from use of AC		-586%	82%

[a]Along with capex, initial AC cost was not used in the water use and solvent recovery costs per kg of precursor. Assuming a latent heat of water vaporization of 2.37 kWh/gal, a latent heat of DMSO vaporization of 0.0001676 kWh/g, and an electricity cost of 0.055 $/kWh.

CONCLUSIONS AND UPCOMING ACTIVITIES

The work completed in Year 2 (Budget Period 2) has successfully shown hollow TechPAN fiber spinning to the smallest diameters reported, utilizing a shaped-spinneret, multifilament spinning approach—drop-in scalable at existing plants. To date, the HF precursors are the smallest diameter produced by this method and have desirable tensile properties. Initial thermal conversion experiments indicate the HF precursors oxidize from both the interior and exterior, which could dramatically increase throughput, lowering cost. And they retain their hollow form following thermal conversion to CF. Finally, results of the AC concept for efficient solvent recovery and water use suggest that CF cost could be reduced by up to 8%—if supplier metrics for AC regeneration can be achieved. Overall, the current project supports CF cost reductions from $29.40 to $22.99, or 21.8%. In Year 3, dramatic CF cost reduction potential (a further 30%–45% reduction) will be systematically investigated. We hypothesized these cost reductions to be enabled by the HF precursor, namely high-speed oxidation and conservation of specific tensile properties with HCF. Now that we have achieved HF spinning, Year 3 will focus on achieving them.

Future work and accomplishments by University of Kentucky Center for Applied Energy Research include:

- Demonstrating hollow carbon fiber tensile properties approaching 4.9 GPa strength and 230 GPa modulus (similar to T700S), with an analysis of specific strength pertaining to part weight consideration.
- Delivering a cost analysis of the precursor and carbon fibers with a cost potential of $12.60/kg.

FY 2019 PUBLICATIONS/PRESENTATIONS

1. E. Ashley Morris, Nik Hochstrasser, Jordan Burgess, Ruben Sarabia-Riquelme, Anne Oberlink, and Matthew C. Weisenberger, "The Importance of Precursor Fiber in the Production of High-Quality Carbon Fibers and Composites," Carbon Fibers and Composites Workshop, Oak Ridge, TN, July 2019.
2. E. Ashley Morris, Nik Hochstrasser, Jordan Burgess, Ruben Sarabia-Riquelme, Anne Oberlink, and Matthew C. Weisenberger, "Progress on the Development of Small Diameter Hollow PAN Precursor and Resultant Carbon Fibers," Carbon 2019, Lexington, KY, July 2019.
3. Ruben Sarabia-Riquelme, Emil Hochstrasser, E. Ashley Morris, David Eaton, and Matthew C. Weisenberger, "Drastically Reduced Waste-Water Generation During Solution Spinning of PAN Fibers Using an Activated Carbon Solvent Sorption System," Carbon 2019, Lexington, KY, July 2019.

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