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

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Center for Applied Energy Research

May 1, 2019

Project ID # st146

Overview

Center for Applied Energy Research

DE-FOA-0001647 Topic 4

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

Timeline

Project Start Date: 1 September 2017
Project End Date: 31 August 2020*
Percent Complete: 55%

Barriers

A: System Weight and Volume
B: System Cost
G: Materials of Construction

Budget

Total Project Budget:	$1,122,042
Total Cost Share:	$137,217 (12%)
Total Federal Share:	$984,826
Actual FY18 Received:	$321,916
Total Planned FY19:	$307,406
Total DOE Funds Spent as of 3/1/19:	$475,151

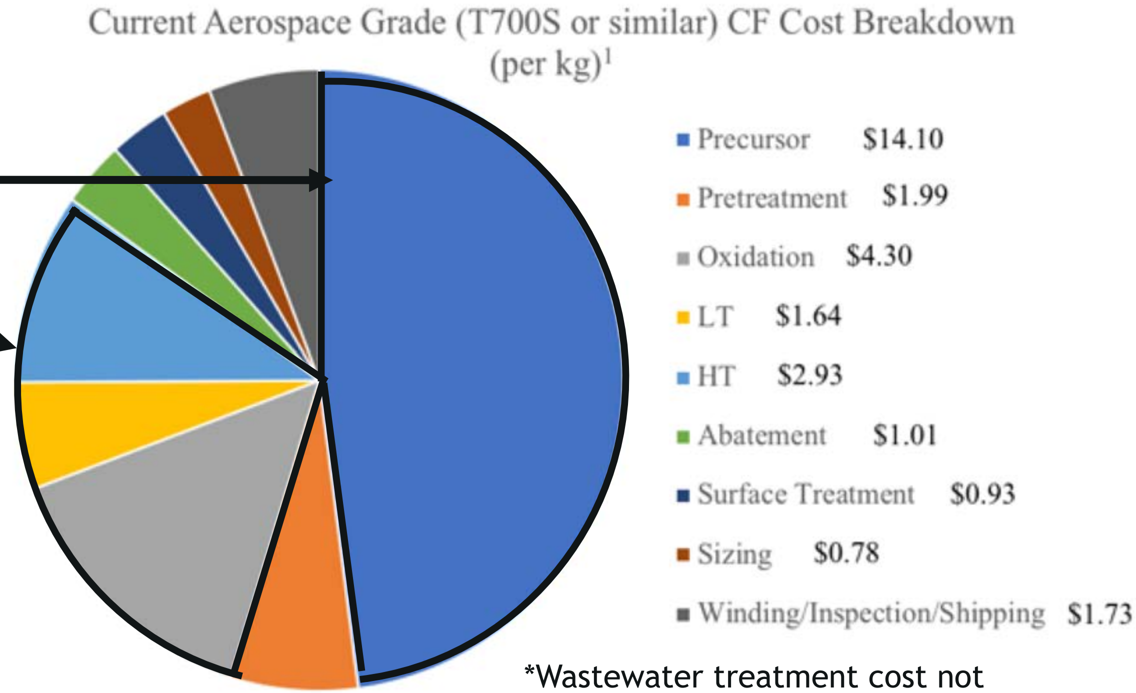
Partners

Project lead: UK CAER
Collaborator: ORNL (LightMAT funded)

*project continuation and direction determined annually by DOE

Relevance – Hydrogen Storage Materials

Important costs in CF production
- ✓ Precursor manufacture
- ✓ Wastewater treatment*
- ✓ Fiber oxidation and carbonization



*Wastewater treatment cost not accounted for in this ORNL model

T700S CF properties

4.9 GPa tensile strength

230 GPa tensile modulus

2.1% strain

1.80 g/cm^3 density

7 µm filament diameter

Current T700S CF cost: **$29.40/kg** → DOE Target CF cost: **$12.60/kg**

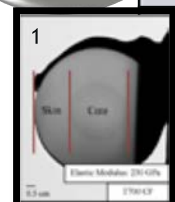
[1]Warren, C. D. Development of low cost, high strength commercial textile precursor (PAN-MA); ORNL: 2014

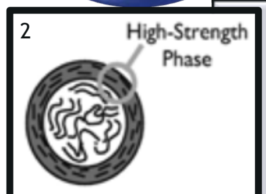
[2]Ordaz, G., C. Houchins, and T. Hua. 2015. "Onboard Type IV Compressed Hydrogen Storage System - Cost and Performance Status 2015," DOE Hydrogen and Fuel Cells Program Record, https://www.hydrogen.energy.gov/pdfs/15013_onboard_storage_performance_cost.pdf

Relevance – Proposed Work & Cost Impact

Objective (Life of Project)
Develop fiber processing to demonstrate carbon fiber tensile properties similar to T700S with cost potential of \$12.60/kg or less

Current State of the Art (T700S)	Our Work
Proprietary PAN polymer	Non-exclusive, low cost, high quality PAN polymer **"TechPAN"** CF Cost impact: -13.8%
Skin-core carbon fiber structure	Hollow carbon fibers forego core structure, improve specific properties CF Cost impact: -15.4%
Slow oxidation	Hollow fibers oxidize up to 35x faster CF Cost impact: -29.3%
Millions of gallons of solvent wastewater per day	Water minimization and solvent recovery using activated carbon CF Cost impact: -5.2%
HIGH COST **\$29.40/kg**	LOW COST **\$10.68/kg**

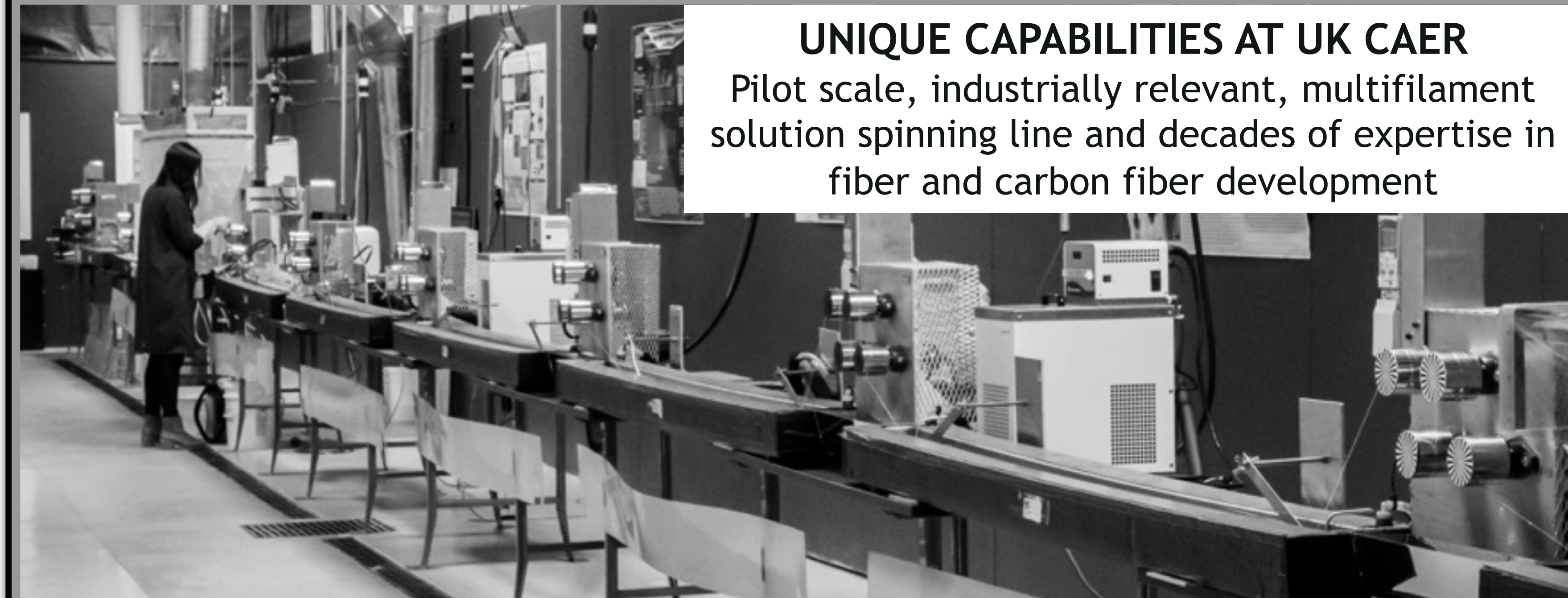




FOA Target CF cost ≤ \$12.60/kg

[1]Morris, E. A., et.al., *Carbon* **2016,** 101, 245-252
[2]Steiner III, S. A., et al., *ACS Appl. Mater. Interfaces* **2013,** 5, (11), 4892-4903

Overall Technical Approach



UNIQUE CAPABILITIES AT UK CAER

Pilot scale, industrially relevant, multifilament solution spinning line and decades of expertise in fiber and carbon fiber development

UK CAER multi-faceted method for producing low cost CF

- Multifilament hollow TechPAN precursor spinning
- Fast oxidation and carbonization
- Low cost TechPAN precursor spinning
- Energy efficient solvent recovery and water use

Low cost carbon fiber for H_2 storage

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Approach – Technical Barriers Progress

Barrier A:
System Weight and Volume

- Successfully spun multifilament, spooled hollow fiber

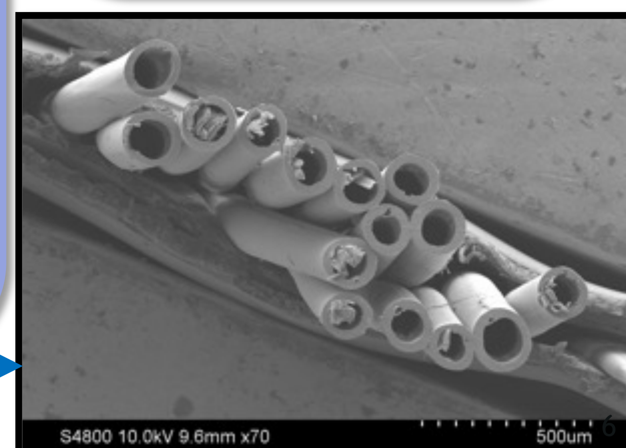
Barrier B:
System Cost

Current cost reduction achievement:

1) Use of low cost TechPAN
   - $29.40 → $25.35
   - 13.8%
2) Use of activated carbon for solvent capture
   (In progress)
   - $25.35 → $23.82
   - 5.2%

Barrier G:
Materials of Construction

All efforts are toward reducing the production costs of carbon fiber used in strength-driven COPV applications



Approach – Integration within the Hydrogen and Fuel Cells Program

- UK CAER has shared materials and/or expertise with the other two awardees of this FOA (ORNL – S. Dai and Penn State - M. Chung) in order to support their fiber development efforts
- UK CAER continues to work with ONRL – B. Norris, with LightMAT funding, to further improve continuous thermal conversion of the TechPAN precursor to T700S CF properties

Approach – Planned Milestones FY19 & FY20

FY19

Milestones

2.1.2: Demonstrate coagulated fiber with hollow core, coalesced shell, and circular cross section (100%)

2.1.4: Demonstrate spooled HF with <100 um OD, <50 um ID (90%)

3.3.3: Demonstrate the activated carbon regeneration proof of concept by thermal desorption with <15% loss in specific surface area utilizing thermal gravimetric analysis (TGA) and Brunauer-Emmett-Teller (BET) methods (80%)

Go/No-Go Review Points

G2: Demonstrate ≥10 filament, air gap, hollow fiber spinning of TechPAN precursor polymer with OD <100 um and ID <50 um 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. (50%)

FY20

Milestones

2.1.6: Demonstrate spooled HF with <50 um OD, <25 um ID (20%)

3.3.4: Summarize and deliver a cost analysis on the impact of water minimization and low energy solvent recovery from hollow TechPAN precursor fiber (40%)

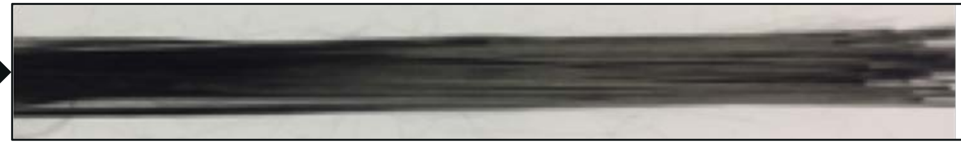
2.2.1: Demonstrate that ≥10x faster oxidation rate is possible for HF compared to solid fiber (0%)

Go/No-Go Review Points

G3: (End of Project Goal) Demonstrate hollow CF 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, and deliver a cost analysis of the precursor and carbon fibers with a cost potential of $12.60/kg. (10%)

Technical Accomplishments and Progress
Air gap spun TechPAN and resulting carbon fibers

Continuous multifilament TechPAN fiber
(900 m, fiber diameter ~10 um)



TechPAN-Derived Carbon Fiber Tensile Strength (10 mm Gauge Length)						
RUN	Average Tensile Strength (MPa)	Stdev (MPa)	Filaments with Strengths >4 GPa	Filaments with Strengths >4.85 GPa	Modulus (GPa)	Stdev (GPa)
29 (N=17)	3810	1188	35%	18%	319	45
36 (N=16)	3371	1362	32%	11%	308	24
T700S DATA SHEET						
Toray T700S	4850				230	

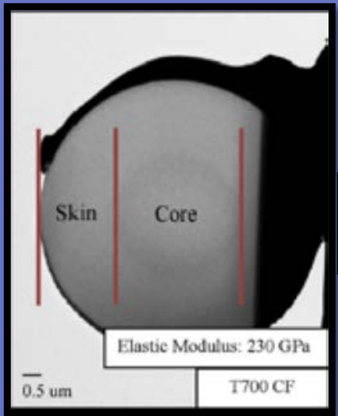
Relevant Completed Milestones

GNG 1 Demonstrate multifilament, air gap spinning of TechPAN precursor polymer. Oxidize, carbonize, and characterize the resultant carbon fiber. Demonstrate properties similar to T700S (Prove the TechPAN polymer's potential for a carbon fiber precursor). Demonstrate functionality of the water minimization strategy, and low energy solvent recovery processes

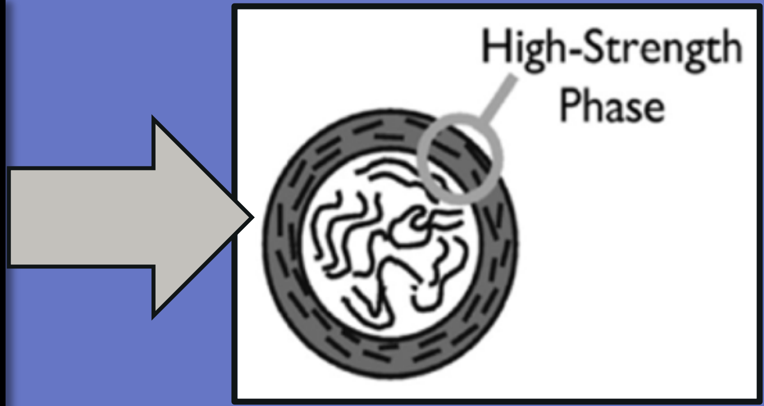
Technical Accomplishments and Progress
TechPAN *hollow* fiber spinning

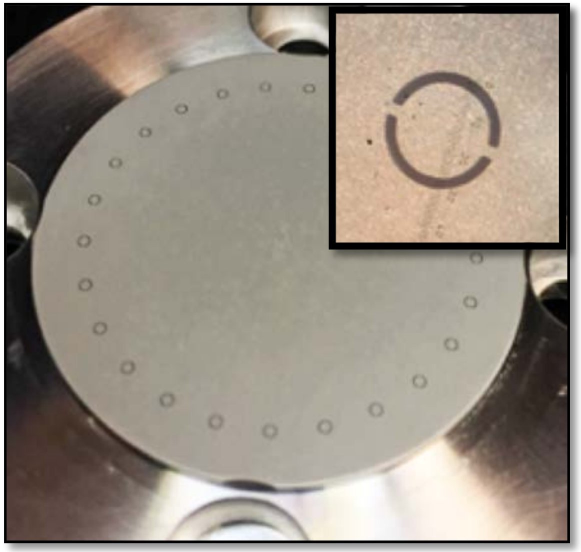
Background

Skin-core structure T700 CF[1]



Skin-core model of PAN CF[2]





UK CAER Approach:

- ✓ Eliminate fiber core
- ✓ Utilize segmented-arc slip shaped spinneret for multifilament, small diameter hollow fiber spinning
- ✓ Hollow fiber proposed to oxidize up to **35x faster** than conventional solid fiber due to reduced oxygen diffusion length ($l_H << l_S$)

[1] Morris, E. A., et.al., *Carbon* **2016,** 101, 245-252
[2] Steiner III, S. A., et al., *ACS Appl. Mater. Interfaces* **2013,** 5, (11), 4892-4903

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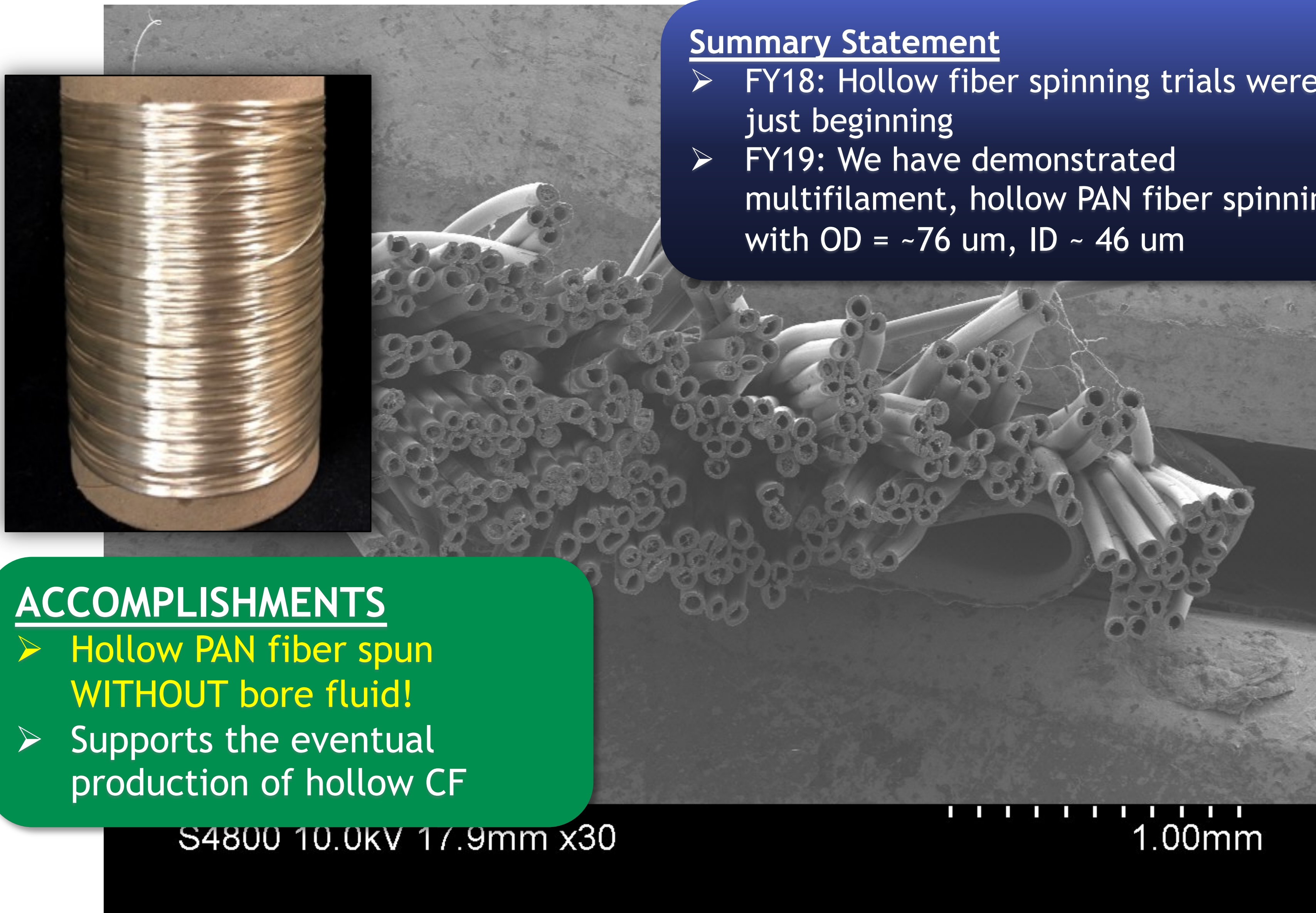
Technical Accomplishments and Progress TechPAN *hollow* fiber spinning



Summary Statement

- FY18: Hollow fiber spinning trials were just beginning
- FY19: We have demonstrated multifilament, hollow PAN fiber spinning with OD = ~76 um, ID ~ 46 um

ACCOMPLISHMENTS

- Hollow PAN fiber spun WITHOUT bore fluid!
- Supports the eventual production of hollow CF

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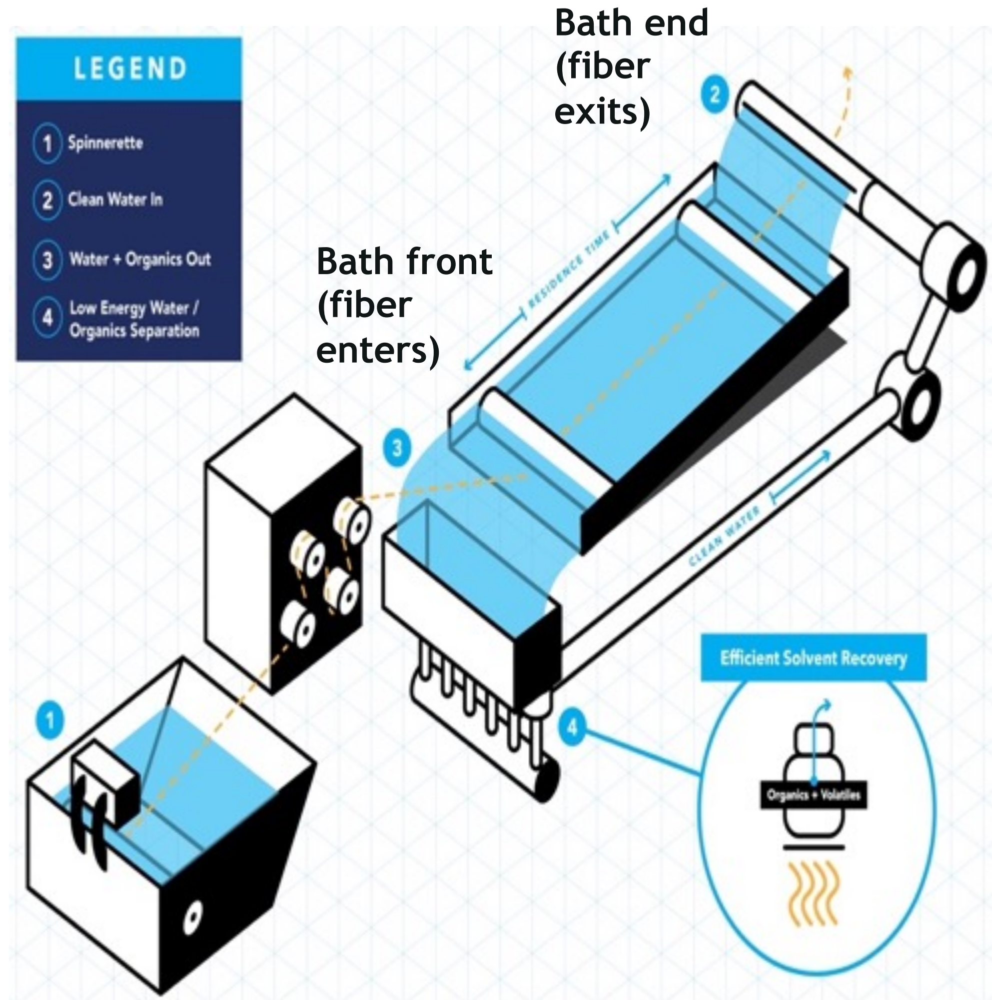
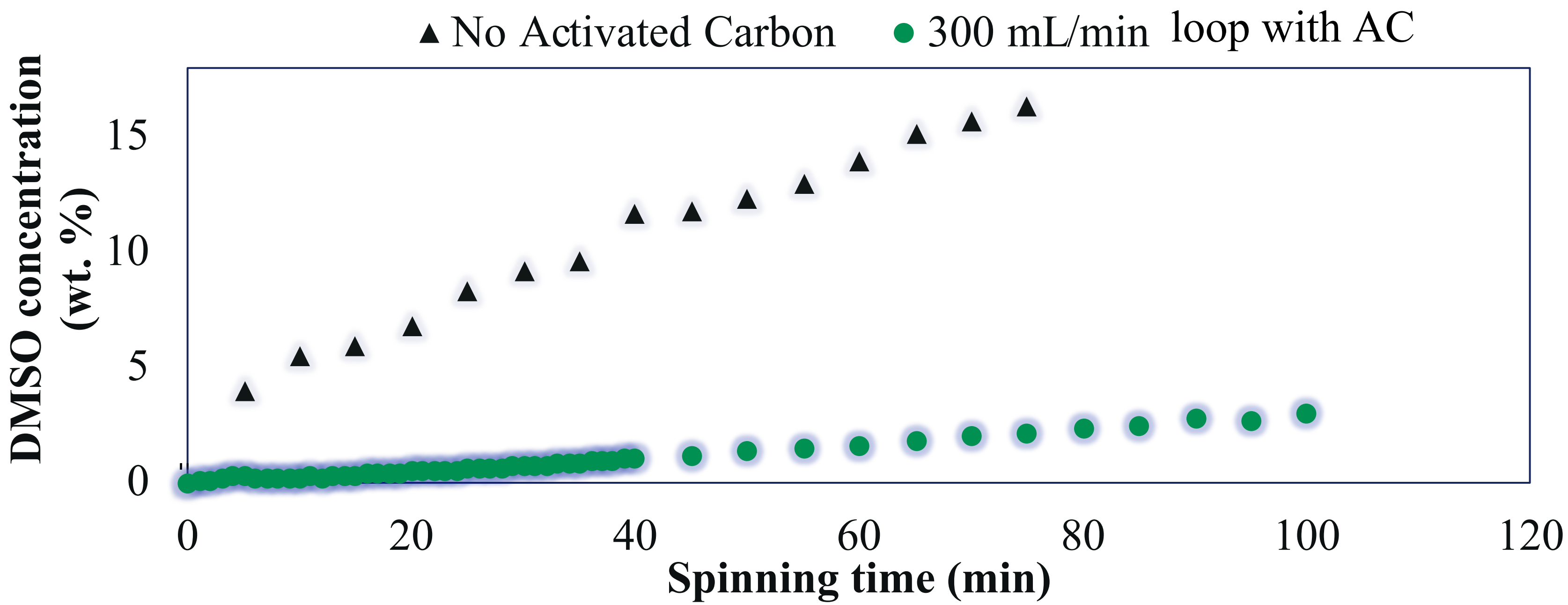
Technical Accomplishments and Progress
Energy efficient solvent recovery and water use

50% reduction in wastewater generated = 5% carbon fiber cost reduction



Technical Accomplishments and Progress
Energy efficient solvent recovery and water use



ACCOMPLISHMENTS

- When using activated carbon during a 100 min spinning run, there is a 10X reduction in the amount of wash water generated
  - >50% target set forth in proposal for 5% carbon fiber cost reduction)
- 5 g of AC is capable of adsorbing 1 g of DMSO
- Currently, use of AC enables a 90% reduction* in solvent recovery costs

* Please note that this is a simple cost evaluation, and does not yet include the upfront cost of the AC (~$10/lb), the change in AC surface area as a function of number of regenerations, and has not been normalized to the mass of precursor produced, all of which are currently under investigation.

Responses to Previous Year Reviewers' Comments

This project was not reviewed last year

Collaboration

<u>Oak Ridge National Lab (ORNL)</u>

✓Funded via LightMAT, the Lightweight Materials Consortium (outside of DOE Hydrogen and Fuels Cells Program)

Importance to project objectives

- ➢Provides industrially relevant continuous stabilization and carbonization capabilities to convert the UK CAER TechPAN precursor fiber to carbon fiber.
- ➢Allows comparisons between carbon fiber made with the UK CAER batch carbonization system
- ➢Gives insight into defect formation which limits tensile strength

Remaining Challenges and Barriers

~14 um OD hollow precursor fibers

Fast oxidation of hollow fibers

Hollow carbon fiber with T700S strength

Activated carbon regeneration

Reduce water use by 50%

Produce hollow CF with cost potential ≤$12.60/kg

Proposed Future Work

Remainder FY2019

Develop

Small diameter, multifilament, hollow filaments

- Focus on further reduction of OD/ID of hollow filaments (MS 2.1.4)

Activated carbon regeneration processing

- Focus on regeneration of DMSO sorbed on the activated carbon for reuse during the spinning process (MS 3.3.3)

Risk Mitigation

- Novel design of multifilament bore fluid hollow fiber spinneret being considered should arc-slip spinneret fail to produce hollow fiber
- UK CAER is open to collaboration with the other two FOA awardees (ORNL and Penn State), particularly in fiber spinning, in order to develop carbon fibers from their novel polymers/precursors

FY2020

Develop

Multifilament, hollow filaments to carbon fiber

- Achieve dimensional and concentricity control and downstream spinning optimization (MS 2.1.6)
- Develop fast oxidation and decreased temperature carbonization for the production of high strength, hollow, carbon fibers (MS 2.2.1)

Activated carbon regeneration processing

- Utilize AC sorption for the production of hollow precursor PAN filaments

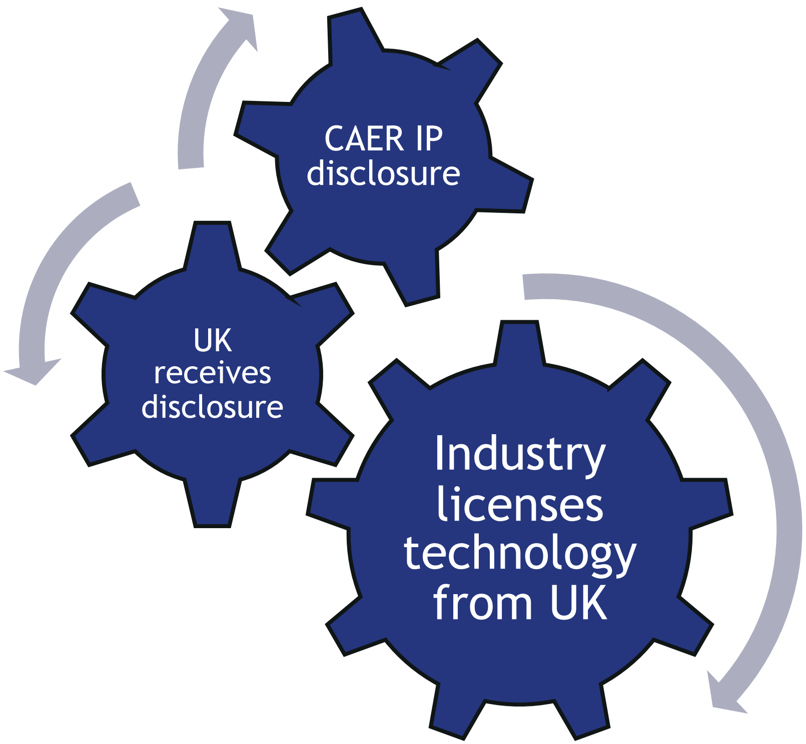
Deliver

Cost evaluation (MS 3.3.4)

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

Technology Transfer Activities

Tech-to-Market Plan



Potential Future Funding

- **DOE**
  - IACMI
  - VTO
  - Wind Energy
- **DOD**
  - DARPA
  - AFOSR
  - Army RDECs
- **Industry**
  - Fiber OEMs
  - Aerospace Industry
  - Industrial / Automotive

Patents/Licensing

To date, none to report

Summary

Objective:	Develop fiber processing to demonstrate carbon fiber (CF) tensile properties similar to T700S with cost potential of $12.60/kg or less.
Relevance:	Compressed overwrapped pressure vessels which store hydrogen for FCEVs are limited in widespread commercialization due to the high cost of T700S CF ($29.40/kg). The CF cost accounts for 62% of the COPV system cost. Highest costs in the manufacture of CF include precursor manufacture (polymer and spinning process), fiber oxidation/carbonization, and wastewater treatment
Approach:	UK CAER is focused on a multi-faceted approach to decreasing CF costs including: low cost TechPAN precursor spinning, multifilament hollow TechPAN precursor spinning, fast oxidation and carbonization, and energy efficient solvent recovery and water use.
Accomplishments:	Multifilament, concentric hollow PAN fiber has been successfully spun (~150 um OD) using an arc slip shaped multifilament spinneret. The use of activated carbon has been shown to reduce the amount of wastewater generated during spinning by 90% (much greater than our projected estimation of 50%) and the activated carbon is successful in adsorbing 1 g of DMSO for every 5 g of activated carbon.
Collaborations:	UK CAER is assisted by ORNL (funded by LightMAT) in the continuous thermal conversion of UK CAER TechPAN precursor to carbon fiber.

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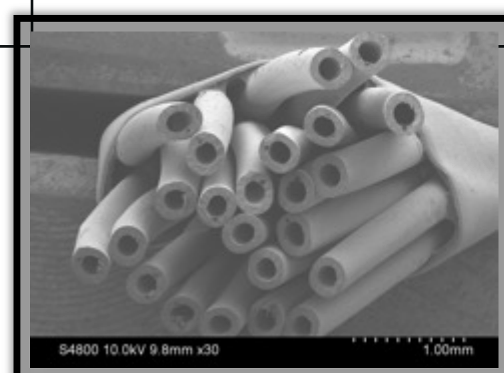
Summary Table
FY18 Results vs Current FY19 Results

FY18 Results	Current FY19 Results
○ High quality TechPAN precursor fibers successfully spun ○ TechPAN produced CF similar to T700S ○ GNG 1 was successfully completed ○ Variables influencing the formation of hollow TechPAN fibers were being evaluated ○ Fundamental adsorption studies with activated carbon were completed ○ AC columns were fabricated	○ A small effort in CF defect analysis continues ○ Consistently producing multifilament, continuous, drawn TechPAN hollow filaments ○ The use of activated carbon during spinning runs has demonstrated a 90% reduction in the amount of wastewater generated ○ 5 g of AC is capable of sorbing 1 g of DMSO ○ AC regeneration experiments are underway



Summary Table - Remaining Targets

Remaining Technical Targets for FY19

Go/No-Go 2:

1. Demonstrate ≥10 filament, air gap, hollow fiber spinning of TechPAN precursor polymer with OD <100 um and ID <50 um with specific strength and modulus approaching 635 MPa/g/cc and 8.5 GPa/g/cc.
2. 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.
3. 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.