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

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Project ID # st146

Overview

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 December 2020*
Percent Complete: 85%

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 FY19 Received:	$286,801
Total Planned FY20:	$342,745
Total DOE Funds Spent as of 3/31/20:	$818,251

Partners

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

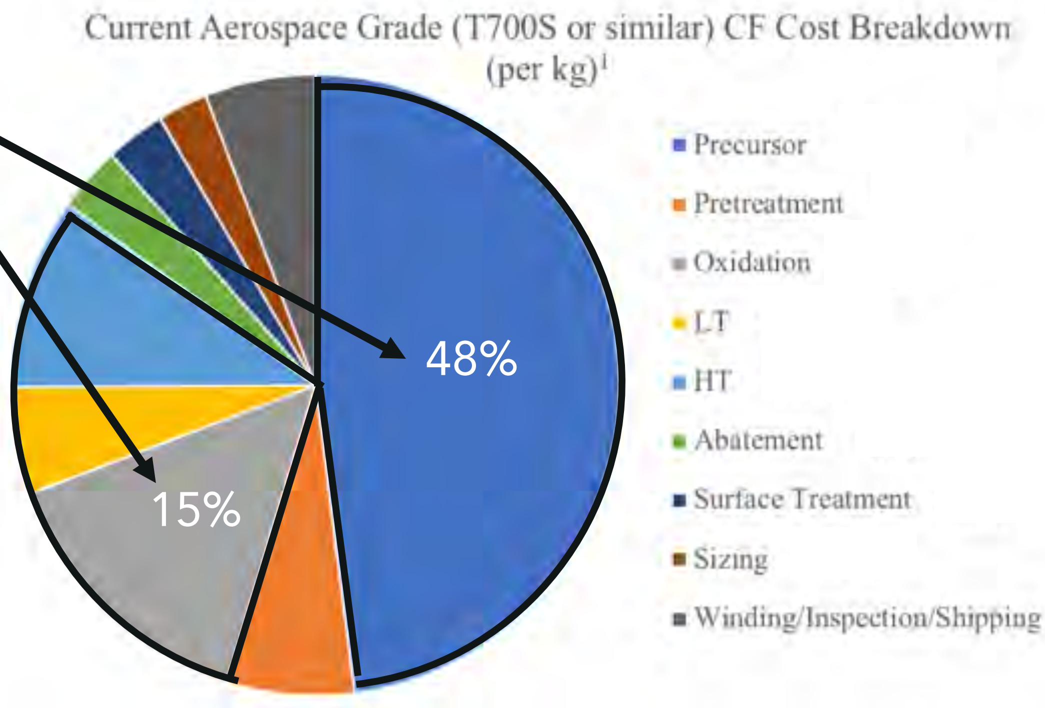
*project continuation and direction determined annually by DOE

Relevance – Hydrogen Storage Materials

Largest costs in CF production
- ✓ Precursor manufacture
- ✓ Fiber oxidation

Current T700S CF cost: $29.40/kg

DOE Target CF cost: $12.60/kg

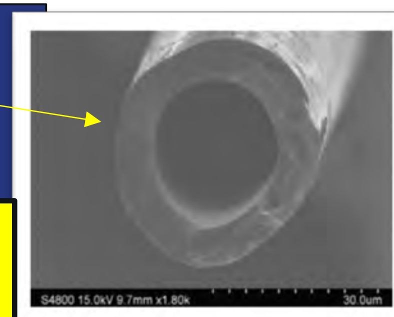


[1]Warren, C. D. *Development of low cost, high strength commercial textile precursor (PAN-MA)*; ORNL: 2014

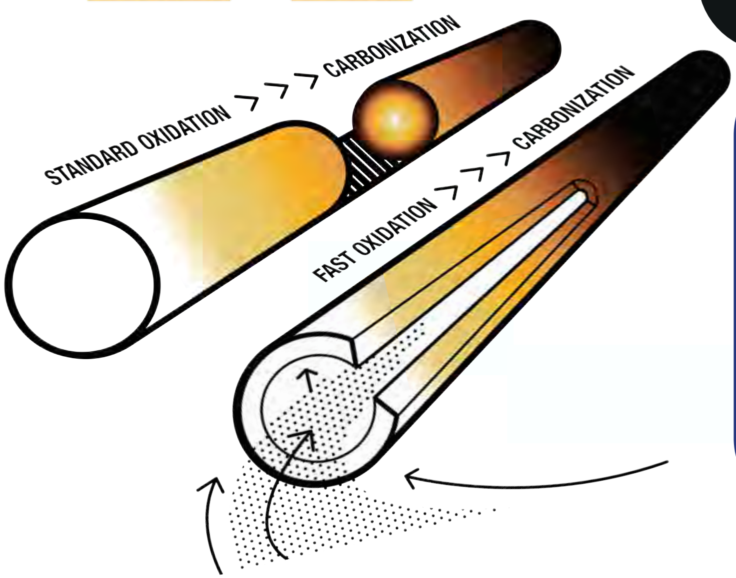
[2]Ordaz, G., C. Houchins, and T. Hua. 2015. “Onboard Type IV Compressed Hydrogen Storage System - Cost and Performance Status 2015,” DOE Hydrogen and Fuel Cells Program Record, https://www.hydrogen.energy.gov/pdfs/15013_onboard_storage_performance_cost.pdf

Relevance – Why *hollow* carbon fiber?

Objective (Life of Project)
Develop hollow fiber (HF) processing to demonstrate hollow carbon fiber (HCF) tensile properties similar to T700S approaching a cost potential of $12.60/kg



Cost reductions (from $29.40/kg CF T700S)



Carbon fiber manufacturer point of view:

- Low cost TechPAN precursor ($3/kg)
  - 9.0% cost reduction in $/kg CF: $26.77/kg HCF
- Fast oxidation due to reduced oxygen diffusion length into fiber walls from interior **and** exterior
  - Fourier analysis suggests 35x decrease in oxidation time
  - We estimate a more realistic 3.5x decrease in oxidation time, and commensurate cost reduction
  - 10.4% cost reduction in $/kg CF: $23.70/kg HCF

Composite manufacturer point of view:

- "Avoided costs" in COPV manufacture
- 7 µm OD 4.65 µm ID HCF with effective
  - Strength = 4.9 GPa
  - Modulus = 230 GPa
- 44% less HCF needed than for T700S
- 44% cost reduction in "effective" $/kg CF: **$13.27/kg HCF**
  - Reduced composite part weight (~30%)
- In sum, HCF offers 55% effective cost reduction in COPV CF cost by using less, and lower manufacturing costs

Relevance –HCF Detailed Cost Breakdown

(1) CF Manufacturing Costs Savings in \$/kg CF

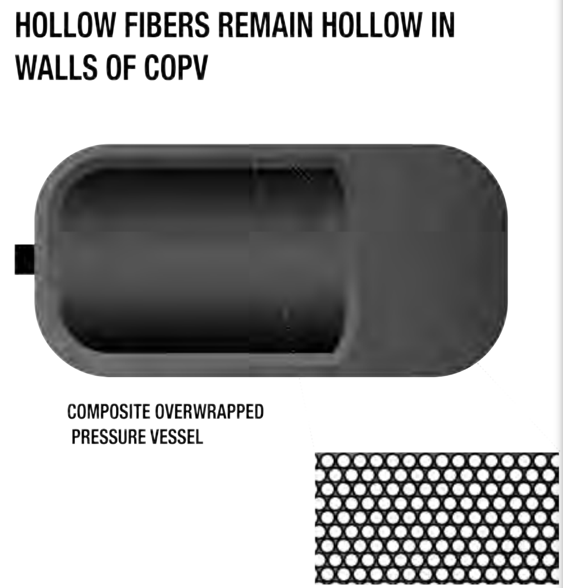
Savings

(a) Low cost TechPAN
(b) faster oxidation (assume 3.5x)

HCF manufacturing cost drops from \$29.41/kg to \$23.70/kg (-19.4%)

Process	T700S Cost (\$)/kg CF[2,3]	HCF Cost (\$)/kg CF
Precursor Polymer	9.24	6.60
Spinning	4.86	4.86
Pretreatment	1.99	1.99
Oxidation	4.30	1.23
LT Carbonization	1.64	1.64
HT Carbonization	2.93	2.93
Abatement	1.01	1.01
Surface Treatment	0.93	0.93
Sizing	0.78	0.78
Winding	1.73	1.73
Sum	29.41	23.70

(2) "Avoided CF Costs" in COPV manufacture



$$\frac{m_h}{m_s} = \frac{OD_h^2 - ID_h^2}{OD_s^2} = \frac{\text{area of annulus}}{\text{area of solid}}$$

COPV Manufacture

For 67 kg CF in COPV1, or 81 km of 12k CF tow

81 km of T700S = 67.0 kg
81 km of HCF = 37.5 kg

T700S cost in COPV:
(\$29.41/kg)(67.0 kg) = \$1970

HCF cost in COPV:
(\$23.70/kg)(37.5 kg) = \$889

HCF offers 55% effective cost reduction in COPV CF cost by using less, and lower manufacturing costs.

The effective HCF cost is \$13.27/kg

1 Adams, J., C. Houchins, and R. Ahluwalia. 2019. "Onboard Type IV Compressed Hydrogen Storage System - Cost and Performance Status 2019," DOE Hydrogen and Fuel Cells Program Record 19008, https://www.hydrogen.energy.gov/pdfs/19008_onboard_storage_cost_performance_status.pdf
2 Warren, C. D. Development of low cost, high strength commercial textile precursor (PAN-MA); ORNL: 2014
3 Choi, D.; Kil, H.-S.; Lee, S., Fabrication of low-cost carbon fibers using economical precursors and advanced processing technologies. *Carbon* **2019,** *142*, 610-649.

Relevance –Milestone Progress (Since Previous AMR)

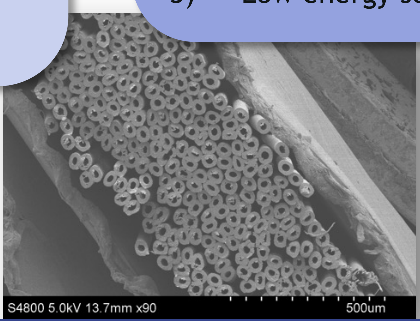
Completed milestones

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.
2.1.6: Demonstrate spooled HF with <50 um OD, <25 um ID
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.

COMPLETED GNG2: 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.

Barrier A:
System Weight and Volume

Successfully spun multifilament, spooled hollow PAN fiber and converted to hollow carbon fiber



Barrier B:
System Cost

Current cost reduction achievement:

1) Use of low cost TechPAN
2) Water minimization
3) Low energy solvent recovery

Barrier G:
Materials of Construction

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

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Overall Technical Approach

At the last AMR, we had successfully demonstrated multifilament, hollow PAN fiber production with outer diameters of ~150 μm

Desired Improvement	Technical Approach
Diameter of HF should be reduced to improve tensile performance and toward thinner walls to enable homogeneous fast oxidation	▪ Fibers were drawn using hot water and hot glycerol along the spinning line to reduce fiber diameters ▪ Using knowledge gained with the original spinneret, a new spinneret was designed and acquired with the hypothesis that the new dimensions would aid in reducing fiber diameter/wall thickness
Reduction in macrovoid content in as-spun precursor hollow fibers	▪ Increasing the polymer content of the spinning solution tempered instantaneous de-mixing during coagulation and reduced macrovoid formation
Thermal conversion of hollow precursor fiber to hollow carbon fibers	▪ Batch stabilization and carbonization trials were undertaken at UK CAER ▪ Continuous stabilization and carbonization trials were undertaken at ORNL (under LightMAT funding)

A multitude of characterization techniques are being used to understand hollow precursor and carbon fiber processing/structure/property relationships, including tensile analysis, SEM, EDX, FIB, TGA, DSC, gas pycnometry, etc.

Approach – Integration within the Hydrogen and Fuel Cells Program

- UK CAER has shared TechPAN polymer with Sheng Dai at ORNL for the formulation and spinning PAN fibers using their ionic liquid assisted melt spinning approach at ORNL
- UK CAER continues to work with ONRL (Bob Norris) under LightMAT funding
  - ORNL is utilizing their continuous continuous thermal conversion capabilities to convert hollow PAN precursors to hollow carbon fibers
  - Through this partnership, we can study the impact of continuous thermal conversion on:
    - Fiber oxidation, to determine if oxidation from the interior fiber lumen is possible for long continuous lengths of fiber common in commercial operations (1000s of m)
    - The potential for fiber collapse during commercial fiber processing
      - UK CAER has proven **precursor HF remain hollow** despite high tensions over small diameter rollers during fiber spinning
      - Data from ORNL has also proven that **oxidized HF and carbonized HF remain hollow**
      - As HF has no issues retaining hollow structure, particularly when still in a plastic state, **we hypothesize no issues retaining the hollow structure when HCF is filament wound to produce COPVs**, as the radius of curvature is much larger for the COPV compared to rollers encountered during spinning/thermal conversion

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 (100%)

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 (100%)

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. (100%)

FY20

Milestones

2.1.6: Demonstrate spooled HF with <50 um OD, <25 um ID (100%)

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 (100%)

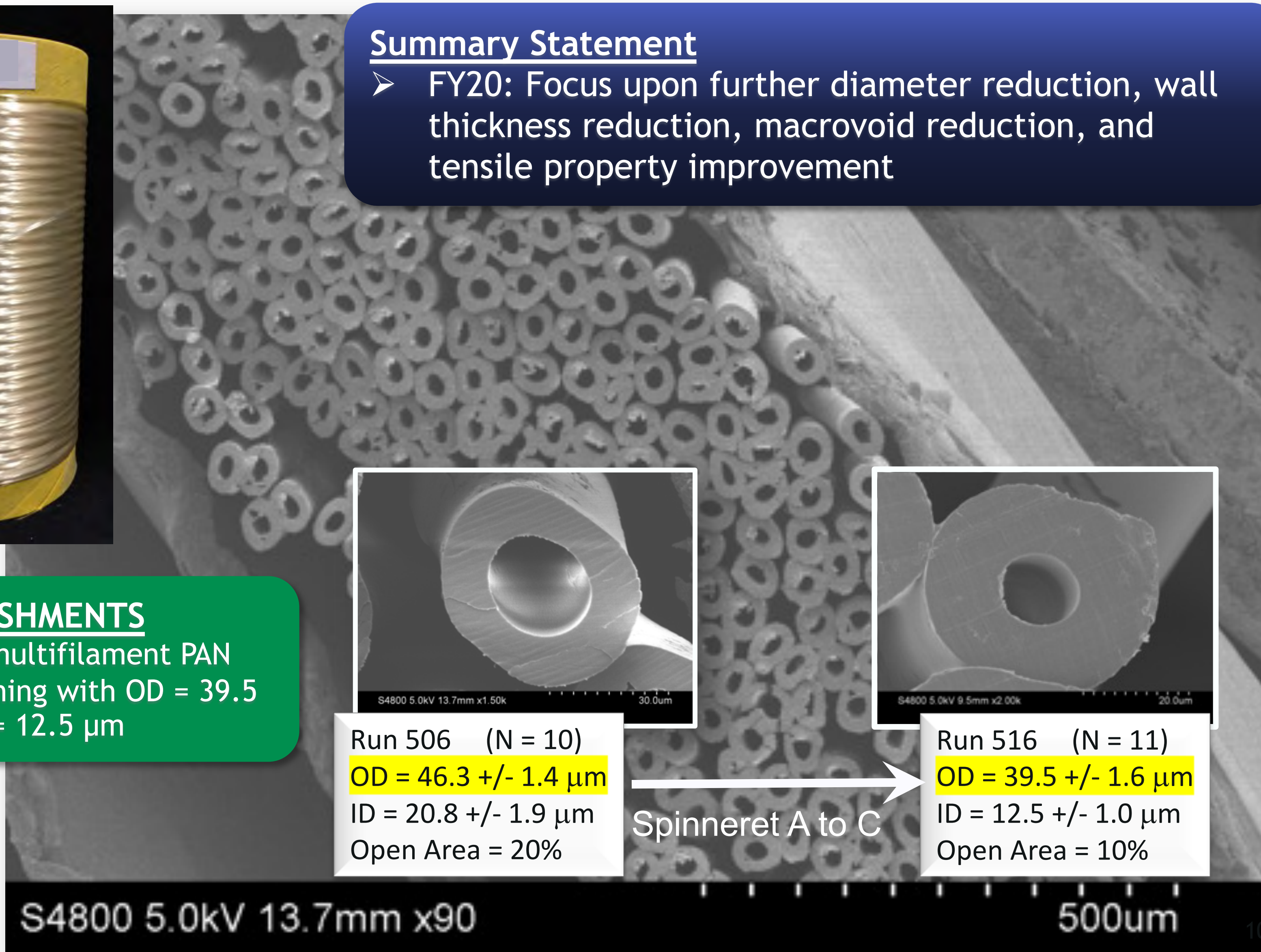
2.2.1: Demonstrate that ≥10x faster oxidation rate is possible for HF compared to solid fiber (50%)

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. (50%)

Technical Accomplishments and Progress From 2019 AMR to present

Summary Statement
- FY20: Focus upon further diameter reduction, wall thickness reduction, macrovoid reduction, and tensile property improvement



ACCOMPLISHMENTS
- Stable multifilament PAN HF spinning with OD = 39.5 μm, ID = 12.5 μm

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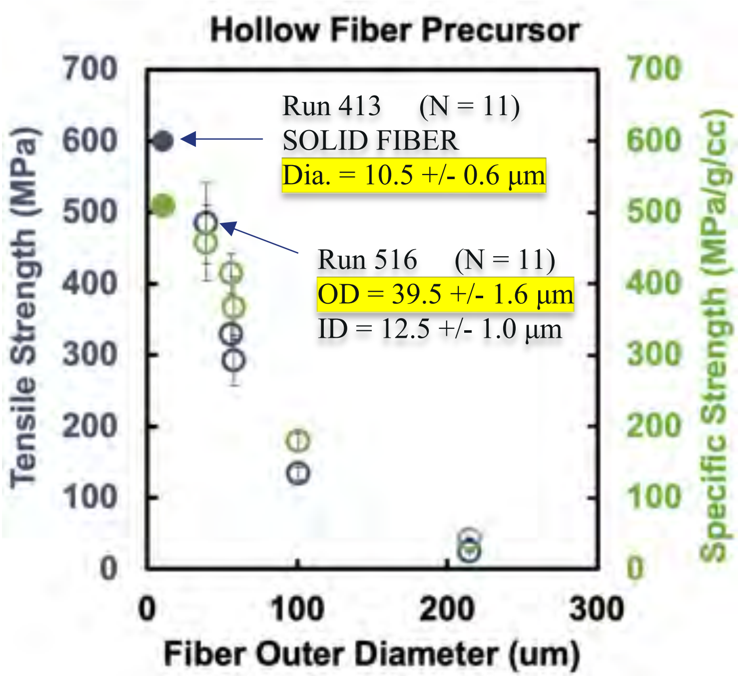
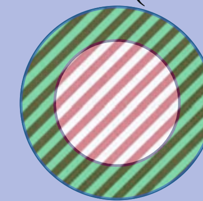
Technical Accomplishments and Progress from 2019 AMR to present



Area is outer diameter (OD) based

Stress = F/A_{OD}

Density = m/V_{OD}

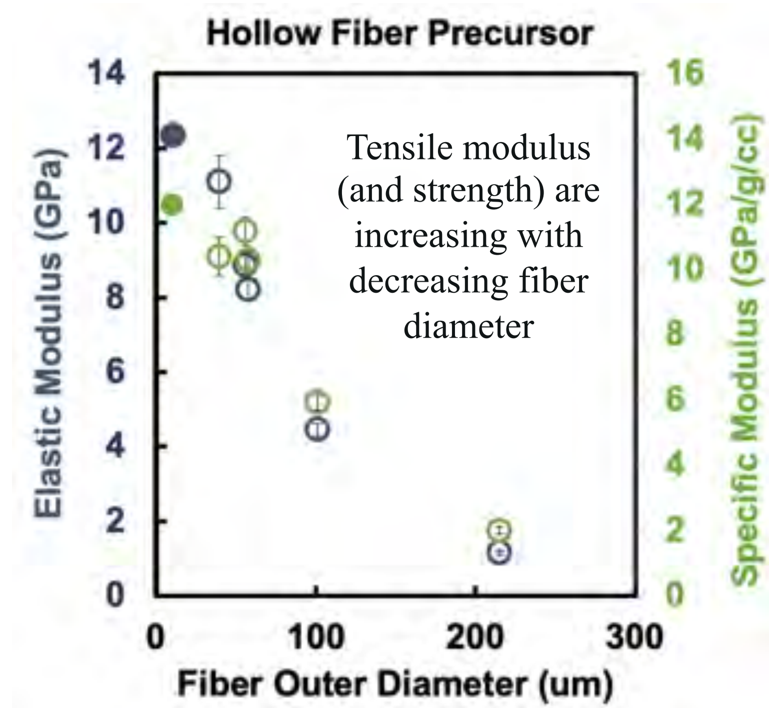


Fiber ρ_{OD} = ~ 0.75 g/cc

where ρ_{PAN} = 1.18 g/cc

Solid circles – solid precursor fiber baseline comparison

Open circles – hollow fiber samples



<u>Current HF precursor tensile properties (N=11)</u>

OD = 39.5 ± 1.6 µm, ID = 12.5 ± 1.0 µm

Tensile strength = 485 ± 56 MPa

Elastic modulus = 11.1 ± 0.7 GPa

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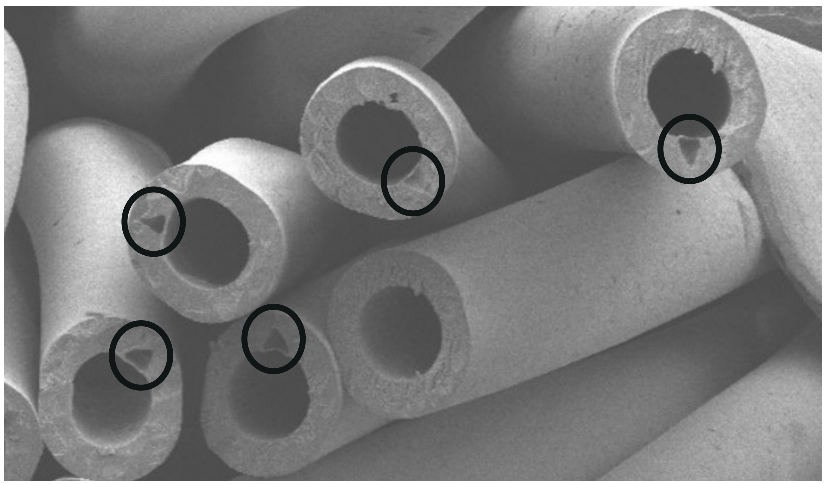
Technical Accomplishments and Progress from 2019 AMR to present

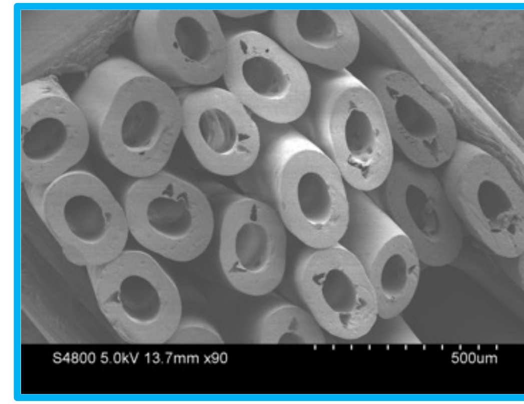
Reducing void content in the precursor fiber is **pivotal** to producing high quality carbon fiber

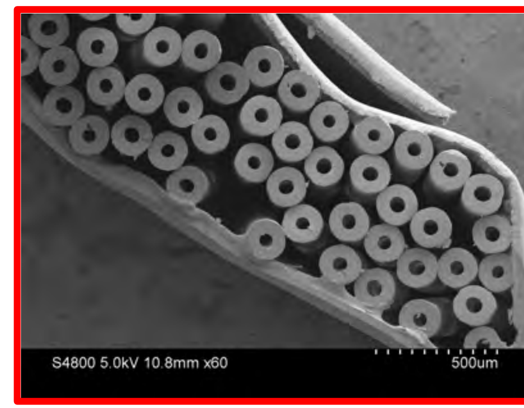
Coagulated into 100% DI water bath



58% macrovoid content

10% macrovoid content





Increasing dope polymer content successful in aiding void reduction

	Process	Effect on macrovoids
(1) % Polymer in dope	↑	↓
(2) Jet Stretch	↑	↓
(3) Dope temperature	↑	↑

Void content = ((# of voids)/(# of fibers))x100%

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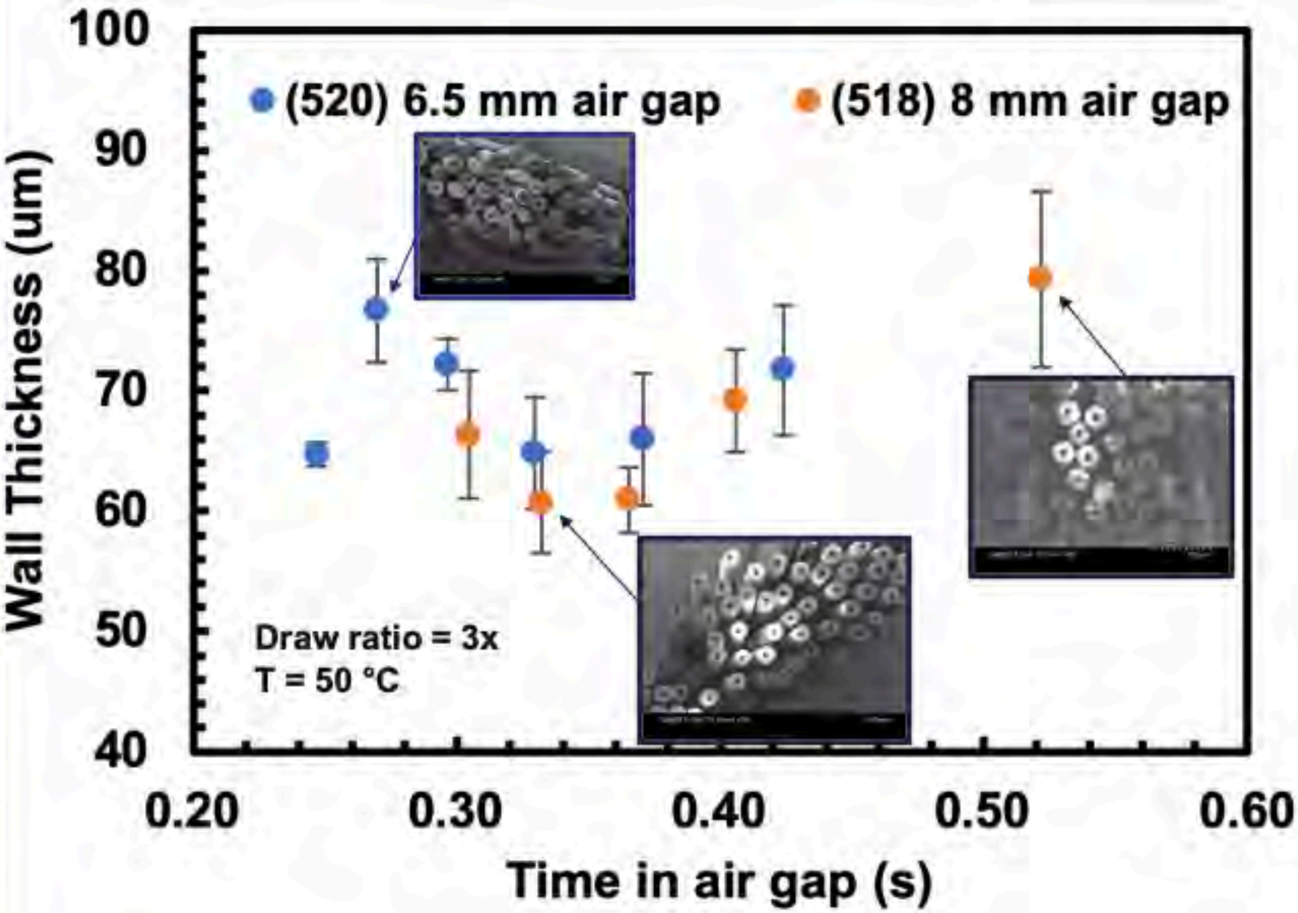
Technical Accomplishments and Progress from 2019 AMR to present

- The ability to control HF wall thickness is pivotal to improving oxidation rate
- Experiments indicate there is a characteristic time scale to achieve minimum wall thickness, based on the time the polymer solution (dope) spends in the air gap during spinning

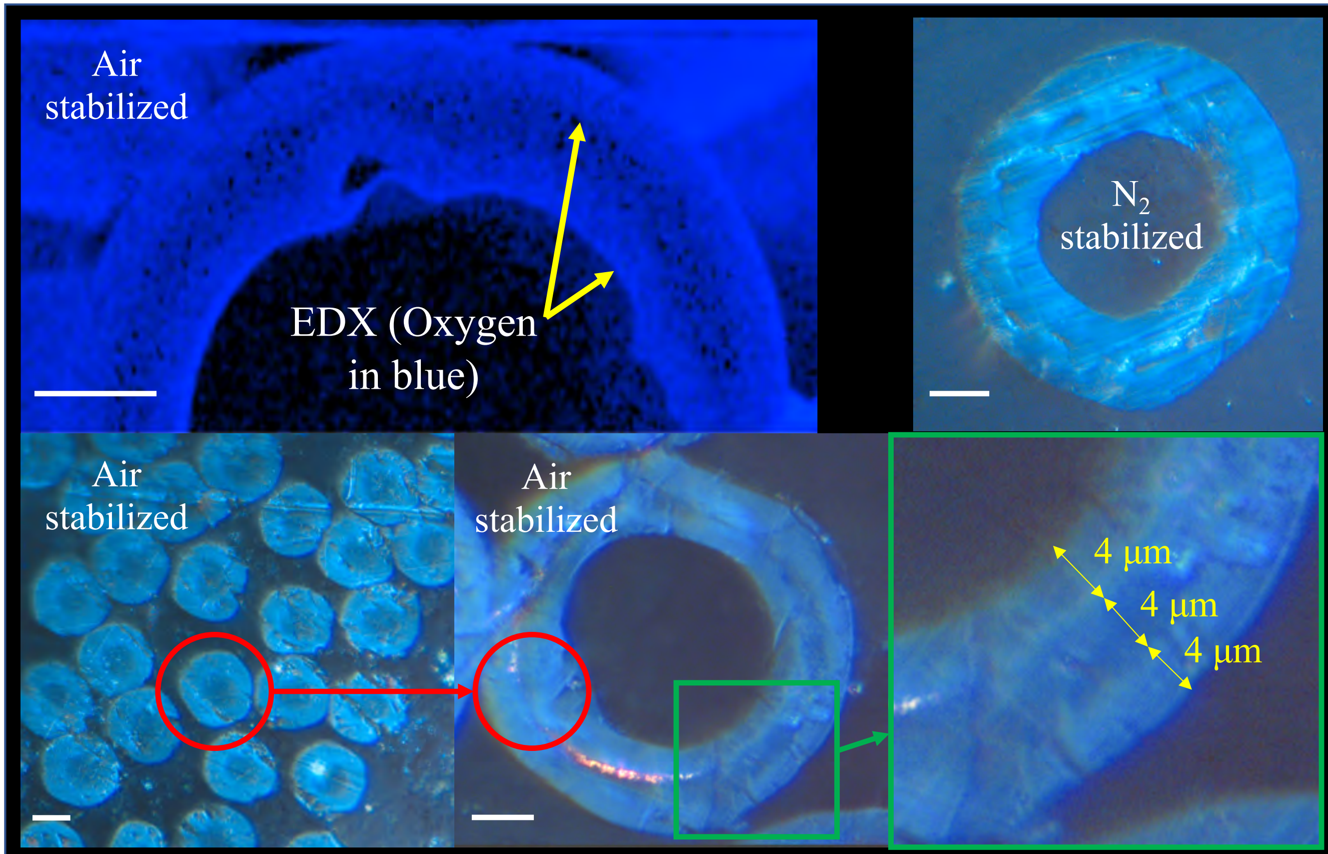
Characteristic time for HF formation (with minimum wall thickness) is ~0.33 s

(for draw ratio = 3x and T = 50 C)



Technical Accomplishments and Progress from 2019 AMR to present

Batch oxidation results indicate oxygen diffusion occurs from both the exterior AND interior of the HF



HF stabilized in N_2 polarized optical microscopy (POM) does not show contrast differences

HF stabilized in air (oxidized fiber) shows contrast differences, indicating oxygen diffusion from the interior **AND** exterior

Solid precursors with diameters similar to the wall thickness of the HF were oxidized, and show skin-core structure.
Results indicate thinner walls will enable faster oxidation
These results are being verified using continuous oxidation (as opposed to batch oxidation)

*calibration bars are 10 μm

Technical Accomplishments and Progress from 2019 AMR to present

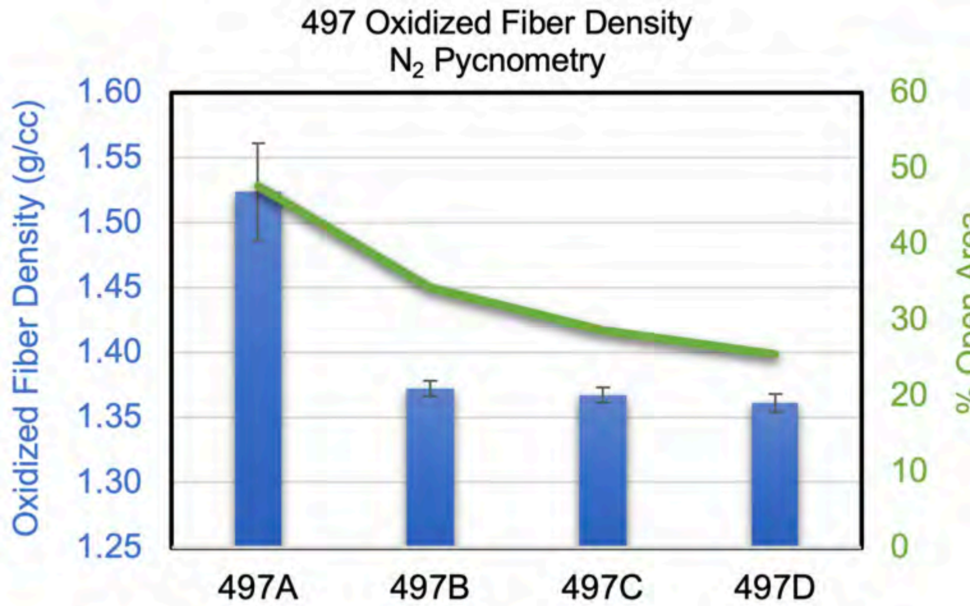
Oxidized fiber density is an important metric in the development of high-quality carbon fiber and is used as an indicator of oxygen content

Target oxidized fiber density is 1.34 to 1.39 g/cc[1]

Precursor fibers drawn at different draw ratios

497A: 1.4x
497B: 3.7x
497C: 8.1x
497D: 9.7x

Fibers batch oxidized (6 m length) simultaneously (fixed length)



Higher oxidized fiber density suggests that HF with higher percent open area oxidized faster

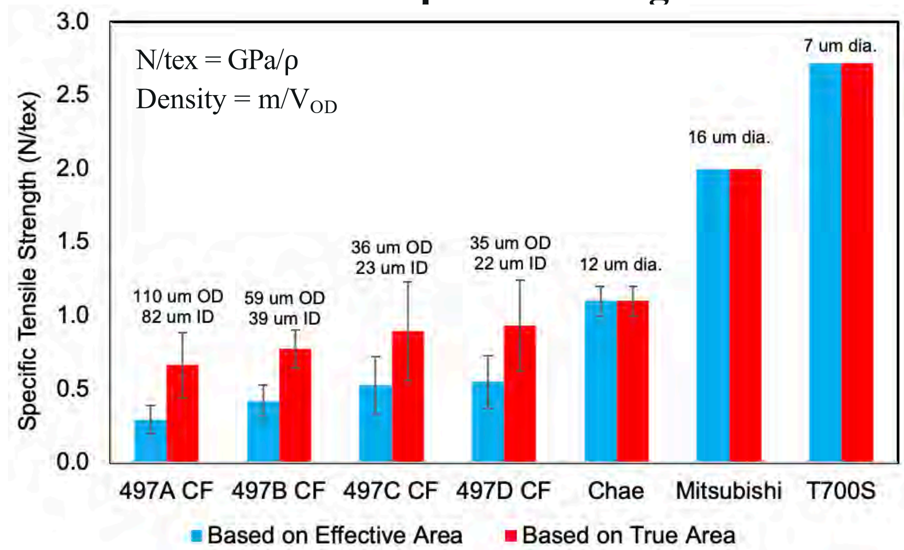
N_2 pycnometry used, in dry room maintained at 0.3% humidity, 10 measurements/sample

[1]Takaku, A., T. Hashimoto, and T. Miyoshi, Tensile properties of carbon fibers from acrylic fibers stabilized under isothermal conditions. Journal of applied polymer science, 1985. 30(4): p. 1565-1571.

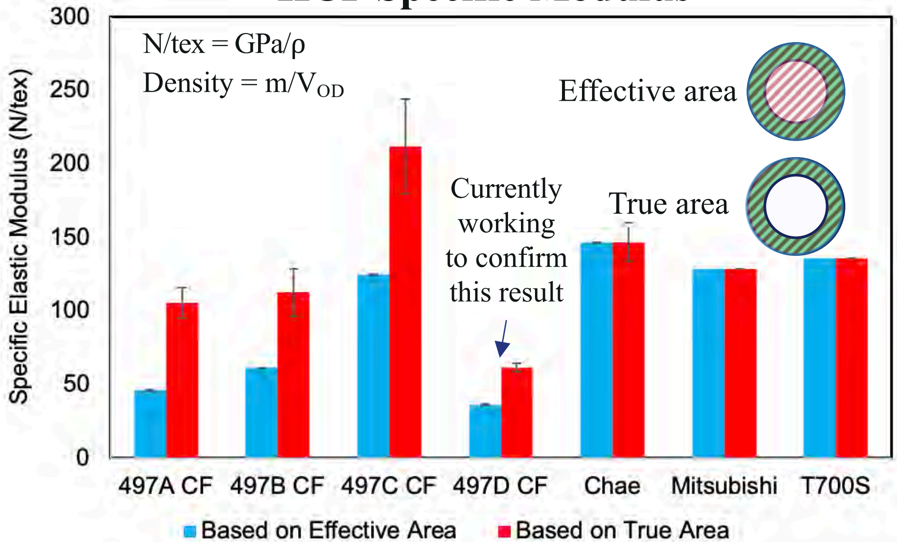
Technical Accomplishments and Progress from 2019 AMR to present

- Specific tensile properties of **hollow carbon fiber** samples (497A, B, C, D) were compared to "large diameter" CF values found in the literature and the incumbent T700S
- Specific tensile strengths are improving with reduced outer diameter. HCF studied here are still quite large (35 μm OD) and suffered from higher than desired void content and fusion issues. Smaller OD HF precursor, with reduced voids and fusion, are being carbonized and are currently under study
  - Further improvements in tensile strength are achieved as defects in precursor fibers are reduced
  - **High quality precursors are necessary to produce high quality CF**
- Specific modulus values are approaching those of T700S and other large diameter CF

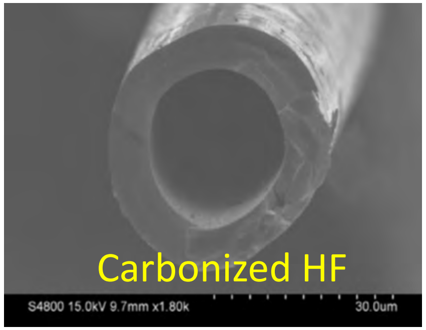
HCF Specific Strength



HCF Specific Modulus



~55% reduction in carbon fiber effective density



Fiber remained hollow despite high tensions during thermal conversion

Chae, H. G., Minus, M. L., Rasheed, A., & Kumar, S. (2007). Stabilization and carbonization of gel spun polyacrylonitrile/single wall carbon nanotube composite fibers. *Polymer, 48*(13), 3781-3789.

(Mitsubishi) Shinmen, Y.; Hirota, N.; Nii, T. Carbon-fiber-precursor fiber bundle, carbon fiber bundle, and uses thereof. U.S. Patent 10,233,569, 2019.

Responses to Previous Year Reviewers' Comments

Comment	Response
Project focused on fiber spinning, less discussion or emphasis on the approach to achieve high performance hollow fiber	In order to produce high-performance CF, high quality precursors (targeted diameters, low void content, etc.) are necessary. We understand the urgency, however, in the need to demonstrate hollow carbon fiber, and have presented results here on our initial hollow carbon fiber
Another item not addressed is fiber buckling or collapsing on bending	We have demonstrated that fiber remains hollow during spinning and thermal conversion, in which high tensions are applied and HF is passed around rollers 3 inches in diameter. But measuring compressive properties of the fibers is not directly inside the scope of this project.
Weaknesses include a reliance on a non-commercial grade of precursor, the lack of industrial participation, assumptions on oxidation rate and ability to achieve diameter and spinnability, and reliance on tensile properties	We have utilized TechPAN polymer (non-commercial grade precursor) due to its low cost and ability to produce fibers with T700S properties. It can also serve as a non-proprietary polymer for use by multiple spinning operations, rather than being tied to one commercial CF manufacturer. However, the technology developed with this project may be utilized with a commercial manufacturers proprietary polymer, if they so wish. We maintain contact with a number of commercial CF manufacturers, and given the success of the project thus far, a CF manufacturer has expressed interest in collaborating on future research projects to produce hollow carbon fiber at commercial scale. Assumptions regarding the impact of oxidation rate on cost have been revised from 35x (theoretical) to a more conservative 3.5x, and experimental determination of oxidation rate is underway. Based on knowledge gained throughout the project, we believe that attaining a 14 μm OD hollow precursor may not be necessary in order to achieve the desired tensile properties. We hypothesize that we may be able to produce larger OD fibers with a targeted wall thickness (<10 μm), which will retain solid fiber tensile properties.
Although this is correctly focused on the gas storage application, something should have been mentioned about suitability of hollow fibers for other applications.	While this was not mentioned during the previous AMR, the success of this project stands to greatly impact the CF market at large, as the use of HCF may allow for lower density fibers at the same tensile performance in composites. HCF offers higher specific tensile properties. Therefore, the HCF stand to improve all applications where lightweight composite structures are required.

Collaboration

Oak Ridge National Lab (ORNL)

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

Importance to project objectives

- ➢ORNL is utilizing their lab-scale continuous continuous thermal conversion capabilities to convert hollow PAN precursors to hollow carbon fibers
- ➢Through this partnership, we can study the impact of continuous thermal conversion on:
  - ➢ Confirmation that fast oxidation of HF is possible (or not)
  - ➢ Fiber oxidation, to determine if oxidation from the interior fiber lumen is possible for long continuous lengths of fiber common in commercial operations (1000s of m)
  - ➢ The potential for fiber collapse during commercial fiber processing
- ➢UK CAER has proven HF precursor remain hollow despite high tensions over small diameter rollers during fiber spinning
- ➢Data from ORNL has also proven that oxidized HF and carbonized HF remain hollow

Remaining Challenges and Barriers

Challenge: COVID-19

COVID-19 pandemic resulted in the closure of non-essential UK research beginning 17 March 2020. Plans to begin re-opening are being discussed for June 2020

Response: Researchers are using this time to conduct in-depth literature reviews, design experiments, write publications, and analyze previously gathered data related to this DOE project and are fully prepared to swiftly resume laboratory experiments upon deployment of university-wide restart plans. However, delays in laboratory research may hinder our ability to meet our remaining milestones:

2.2.1: Demonstrate faster oxidation in HF compared to solid fiber

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

Other challenges:

- Achieving T700S tensile properties (in particular tensile strength)

Proposed Future Work

Remainder FY2020

Demonstrate

Faster oxidation in HF compared to solid fiber (MS 2.2.1)

- We have some evidence, for example, the oxidized fiber density results on slide 15, which suggests that HF is oxidizing faster with larger percent open area (resulting in higher density)
- Experiments will be run wherein HF and solid fiber are oxidized concurrently and the resulting fiber density studied to determine if HF reaches the target ox density faster than solid

Demonstrate

(End of project goal) 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, and deliver a cost analysis of the precursor and carbon fibers with a cost potential of $12.60/kg.

- Current HCF specific tensile strength (based on effective area) is **20%** that of T700S
- Current HCF specific modulus (based on effective area) is **92%** that of T700S
- To improve strength, diameter reduction and defect reduction are key, both of which are progressing well

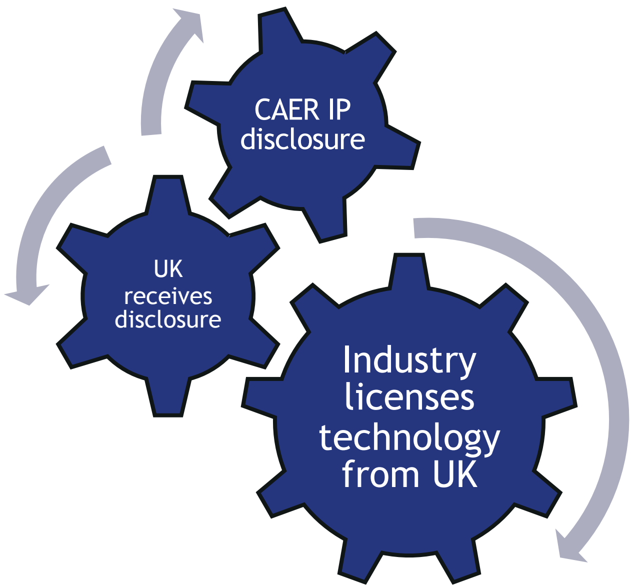
Risk Mitigation

- We have identified new spinneret designs which should help us achieve diameter and macrovoid reduction, which should improve tensile strength
- We are performing oxidation on 100s of m of continuous fiber tow with ORNL to determine if oxidation proceeds from the interior far from the fiber ends

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

Technology Transfer Activities

Tech-to-Market Plan



Patents/Licensing

To date, none to report

Manuscript

Manuscript preparation nearing completion for submission to peer-reviewed journal

Potential Future Funding

- **Proposal submitted** to DOE-FOA-0002229 Topic 2: "Low-Cost, High-Strength Hollow Carbon Fiber for Compressed Gas Storage Tanks"
- $8.4M over 60 months
- Partnering with multiple highly-esteemed industrial companies and laboratories
  - Including a CF manufacturer and COPV manufacturer

Summary – Progress and Accomplishments

- Hollow carbon fiber (HCF) offers a path to significant cost reduction
  - Lower manufacturing costs
  - Significant "avoided" kg of CF needed for COPV manufacture
    - Lighter weight COPVs
  - Together, these offer a 55% reduction in effective CF costs from $29.41/kg to $13.27/kg
- We have achieved world's smallest hollow precursor fiber (via segmented arc spinneret) in multifilament continuous tow
  - Utilizing segmented arc spinneret technology is drop-in replaceable at existing CF manufacturer plants (no complex bi-component spinning)
- We have demonstrated oxidation from the interior of the HF
  - All else equal, the degree of oxidation was observed to have advanced further for HF with greater percent open area, supporting faster oxidation of HF
- The tensile properties of the HCF are improving
  - Current HCF specific tensile strength (based on effective area) is 20% that of T700S
  - Current HCF specific modulus (based on effective area) is 92% that of T700S
  - To improve strength, diameter reduction and defect reduction are key, both of which are progressing well

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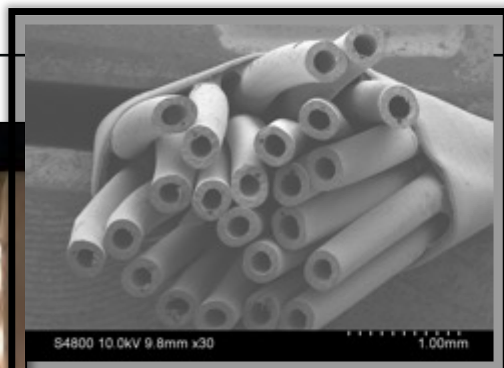
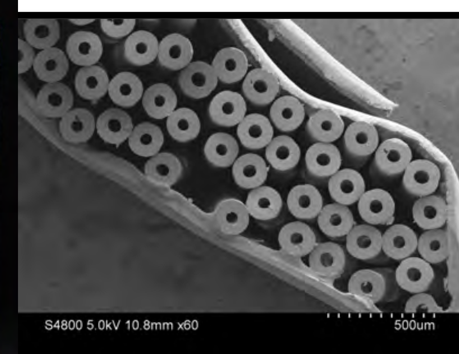
Summary Table
FY19 Results vs Current FY20 Results

FY19 Results	Current FY20 Results

○ Consistently producing multifilament, continuous, drawn TechPAN hollow filaments
○ The use of activated carbon (AC) 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
	• HCF offers a path for a 55% reduction in effective CF costs from \$29.41/kg to \$13.27/kg
	• We have achieved world's smallest hollow precursor fiber (via segmented arc spinneret) in multifilament continuous tow
	    • Utilizing segmented arc spinneret technology is drop-in replaceable at existing CF manufacturer plants (no complex bi-component spinning)
	• We have demonstrated oxidation from the interior of the HF
	    • All else equal, the degree of oxidation was observed to have advanced further for HF with greater percent open area
	• The properties of the HCF are improving with decreasing diameter





Summary Table - Remaining Targets

Remaining Technical Targets for FY20
MS 2.2.1: Faster oxidation in HF compared to solid fiber **G3: (End of Project Goal)** 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, and deliver a cost analysis of the precursor and carbon fibers with a cost potential of $12.60/kg.