Low-Cost, High-Strength Hollow Carbon Fiber for Compressed Gas Storage Tanks

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University of Kentucky Center for Applied Energy Research

DE-EE0009241
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Team Partners

Solvay Composite Materials	POC: Dr. Suzanne Crawford
Steelhead Composites Inc.	POC: Mr. Mike Stewart
Oak Ridge National Lab	POC: Mr. Bob Norris
Advanced Fiber Technologies Inc.	POC: Mr. Warren Schimpf
Strategic Analysis Inc.	POC: Dr. Cassidy Houchins

DOE H2@Scale
Topic 2: Advanced Carbon Fiber for Compressed Gas Storage Tanks
2024 Annual Merit Review and Peer Evaluation Meeting
Project ID: ST238

Project Goal

"Develop hollow carbon fibers which retain the tensile properties of T700S, but with a 12% CF cost reduction, a 29% decrease in system cost, and a 30% increase in gravimetric capacity"

Current SOA

Carbon Fiber (CF)

$22.19/kg*

Photo Credit: Izumi International

*Strategic Analysis, Inc.

Composite Overwrapped Pressure Vessel (COPV)

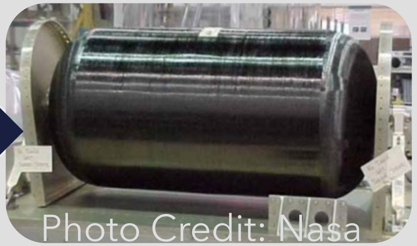


Photo Credit: Nasa

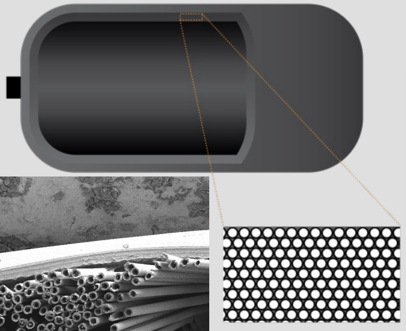
CF: 62% cost of COPV manufacture

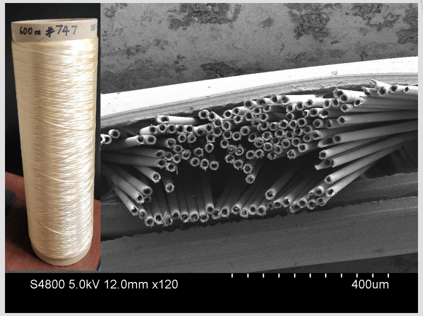
Hydrogen Fuel Cell Vehicle

High CF cost limits application

Project Goal

Incumbent T700S	**TARGET HCF**
4.9 GPa (711 ksi)	4.9 GPa (711 ksi)
230 GPa (33.4 Msi)	230 GPa (33.4 Msi)
2.1 % Strain	2.1 % Strain
1.8 g/cc	
Dia. = 7 μm	OD: 7 μm
	ID: 4.65 μm
	1.0 g/cc





-12% $/kg CF

-29% $/system

+30% kWh/kg

Overview

DE-FOA-0002229 Area 2
Advanced Carbon Fiber for Compressed Hydrogen and Natural Gas Storage Tanks

PHASE 1
1 October 2021 - 31 March 2024 (100% complete)

Phase 1 Budget as of 1/30/24

Total Project Budget:	$2,545,400
Total DOE Share:	$1,993,978
Total Cost Share:	$551,422 (22%)
Total DOE Funds Spent:	$1,769,027
Total Cost Share Funds Spent:	$551,422

PHASE 2
1 April 2024 - 31 March 2027 (3% complete)

Phase 2 Budget as of 3/8/24

Total Project Budget:	$3,527,260
Total DOE Share:	$2,821,808
Total Cost Share:	$705,452 (20%)
Total DOE Funds Spent:	$0
Total Cost Share Funds Spent:	$0

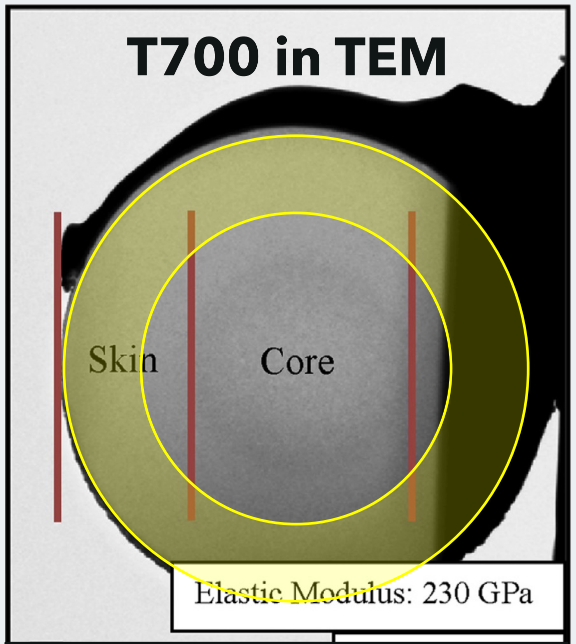
Barriers
A: System Weight and Volume
B: System Cost
G: Materials of Construction

Partner Organizations
Solvay Composite Materials – continuous thermal treatment, testing
ORNL – continuous thermal treatment, testing
Steelhead – prototype production & testing, and COPV reuse and recycling
Advanced Fiber Technologies – consulting toward high strength
Strategic Analysis – cost analyses

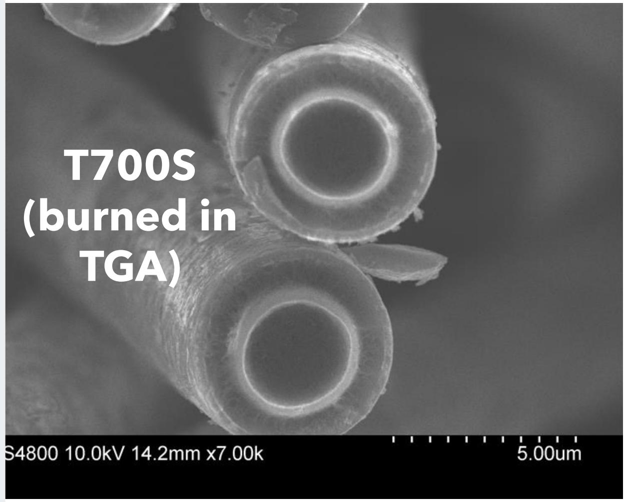
Relevance/Potential Impact - Advantages of hollow carbon fiber

Eliminate fiber core

- Disordered core contributes little to tensile strength

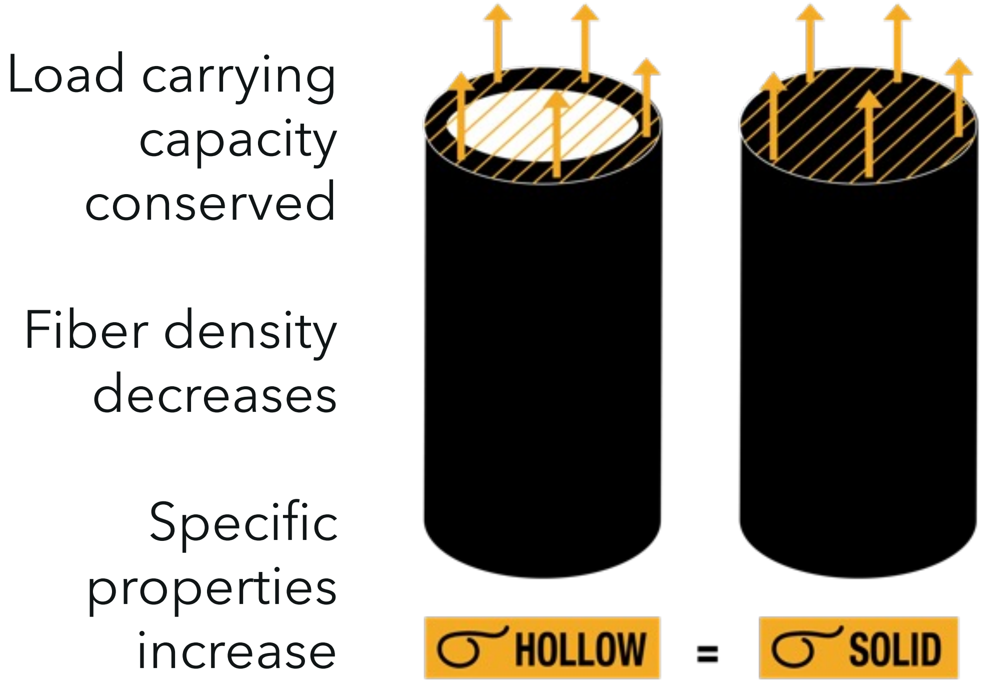


Overlay (yellow) of target HCF dimensions
7 µm OD, 4.65 µm ID



Maximize specific properties

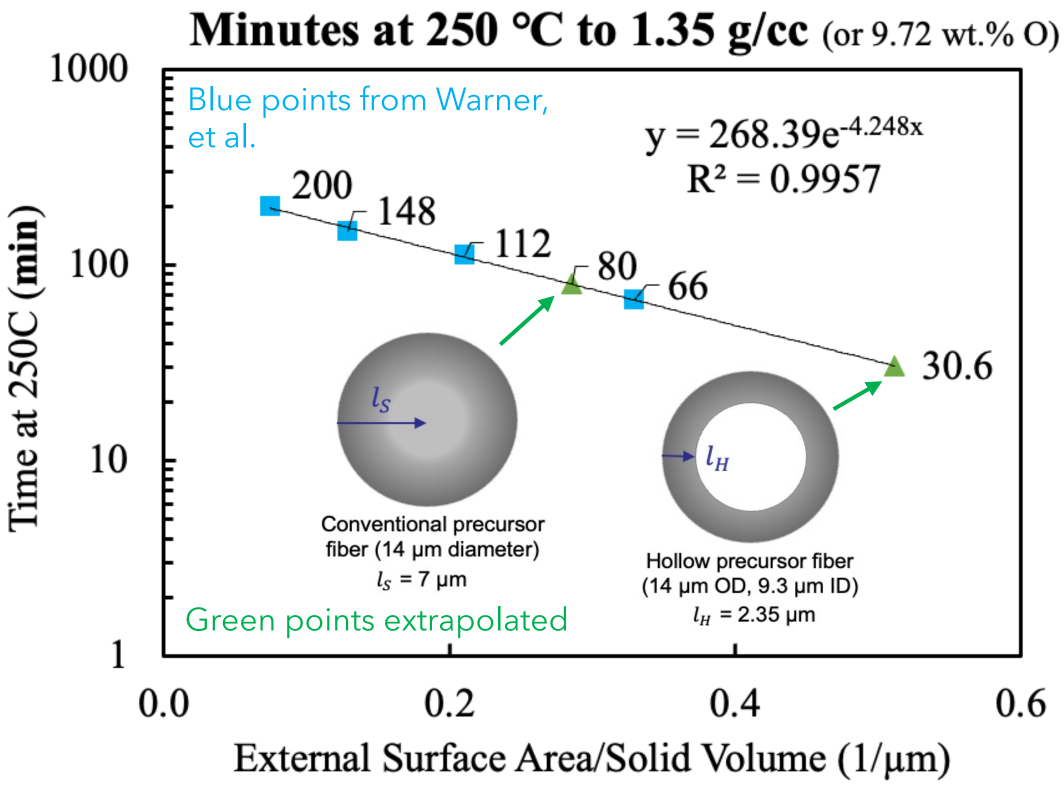
- Higher gravimetric capacity (kWh/kg)
- Less kg of HCF needed for same composite
- Lower tank cost ($/kWh)



Relevance/Potential Impact - Advantages of hollow carbon fiber

Faster oxidation

- Reduced oxygen diffusion distance
- Lower CF processing cost
- Hypothesized to arrive at target ox density in ½ the time



OVERALL PREDICTED COST AND PERFORMANCE ADVANTAGES

-12% $/kg CF

-29% $/system

+30% kWh/kg

Strategic Analysis, Inc.

Relevance/Potential Impact – Barriers and Goals

DOE EERE FCTO Program Goals

- Reduce onboard hydrogen storage from \$16/kWh, (with CF accounting for 62% of the total system cost) targeting **\$8/kWh**
- Reduce CF cost from \$22/kg* (T700S) targeting **\$13-15/kg**

Barriers	Impacts
A. System Weight and Volume	Hollow carbon fiber (HCF) COPV mass would be 30% less than T700S COPV, resulting in reduced system weight and a **30% increase in gravimetric capacity** (from 1.47 kWh/kg to 1.92 kWh/kg)
B. System Cost	A **\$19.51/kg cost of HCF** is expected (compared to \$22.19/kg* for T700S). Less kg of HCF is needed offering a **29% decrease in system cost**, from \$15.67/kWh to \$11.16/kWh
G. Material of Construction	The HCF capitalizes on efficient use of the ordered carbon to improve the specific properties of the fiber

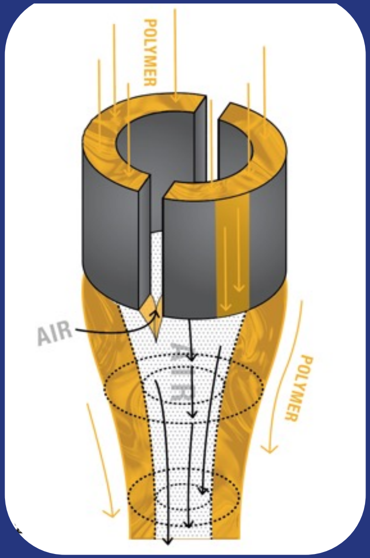
The project will further the goals of the DOE to:

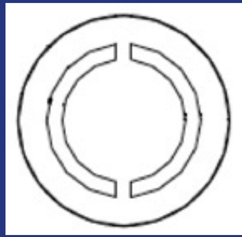
(a) Lower greenhouse gas emissions by encouraging the widespread adoption of fuel cell technologies
(b) Create good paying jobs in the US and strengthen US manufacturing through our domestic partners
(c) Improve progress toward the Hydrogen Shot goal of \$1 for 1 kg hydrogen in 1 decade by reducing the hydrogen storage system cost

* Strategic Analysis, Inc.

Overall Technical Approach

HF spinning method

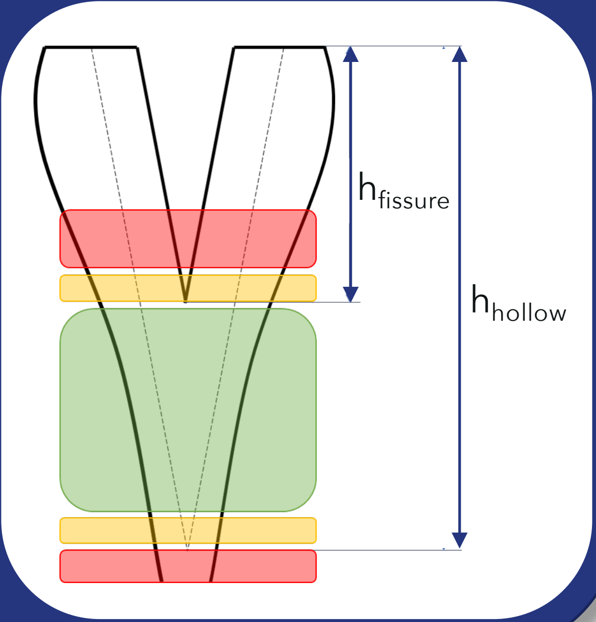




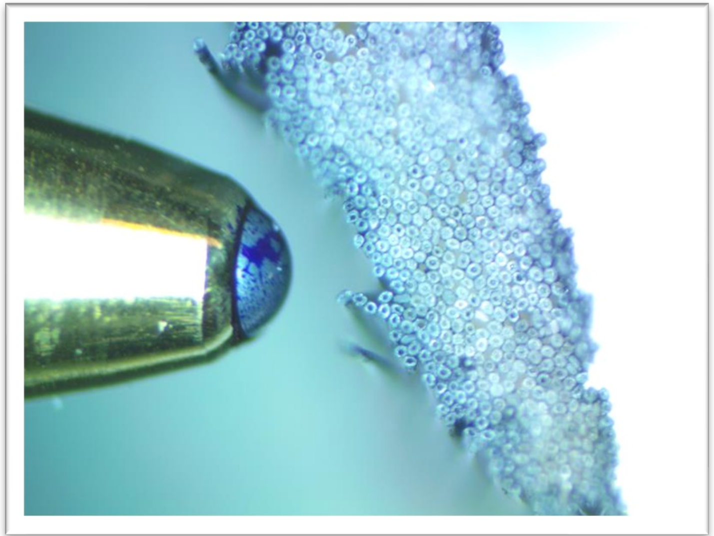
2C spinneret capillary

- Lumen supported by air entering through the heal points between the 2Cs
- 2Cs "heal" in the air gap to form a hollow filament

Effect of Air Gap Length



Batch and continuous oxidation and carbonization of multifilament solution spun HF



Coagulated, undrawn HF and ballpoint pen

Defect mitigation toward the production of HCF conserving the properties of T700S

Approach – Milestones for FY23 (BP2)

Milestones

1.1.3: Demonstrate the spinning of 100 filament HF precursor tow (100%)

2.1.1: Demonstrate the achievement of a target oxidized HF density in less time compared to a solid fiber (100%)*

4.2.1: Deliver a performance and cost analysis for HCF compressed gas storage tank production (100%)

Go/No-Go Review Points

GNG2: The decision to proceed into Budget Period 3 will be based on a down-select process as defined at the end of the SOPO, with only the project that meets all minimum required criteria and receives the highest score proceeding. The down-select criteria requires the production of at least 100 continuous meters of 100-filament tows of the project's best performing CF recipe. Scoring will be based on several properties measured by fiber characterization and laboratory-scale mechanical testing. DOE may require CF and composite samples be provided to an independent laboratory of DOE's choice for independent validation (100%)

We were not selected for Phase II based on our down-select score, but were selected to proceed on a modified Phase II SOPO

*proxied with thin films

Approach – PROPOSED* Milestones for FY24-25 (BP3)

Milestones

1.1.4: Design and place order for shaped spinnerets (100%)

1.1.5: Submit finalized plan for dust controlled spinning line assembly (0%)

2.1.2: Evaluate the times to target oxidized fiber density (1.34 to 1.38 g/cc) of current HF (25-30 μm OD) and solid fibers (11-14 μm and 25-30 μm) (0%)

Go/No-Go Review Point

GNG3: Demonstrate the spinning of HF precursor tow in a dust-controlled facility (0%)

*Phase II SOPO currently under negotiation

Approach - Safety Planning and Culture

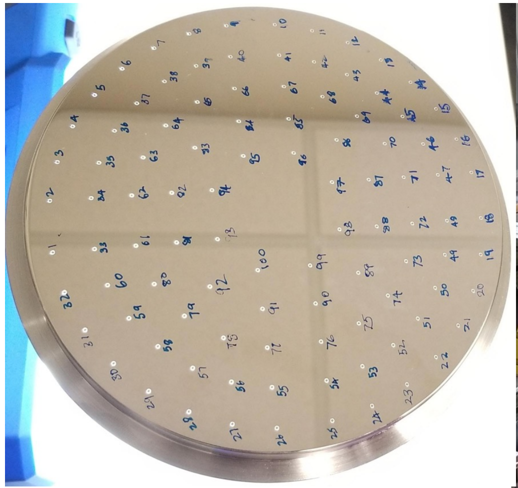
- This project was not required to submit a safety plan to the Hydrogen Safety Panel (HSP)
- The University of Kentucky Environmental Health and Safety Division maintains annual safety training, laboratory standards, SOPs, and compliance assistance, to name a few
- Safety culture is applied to this project by:
  - Prioritizing safety when using hazardous chemicals during solution spinning by employing appropriate PPE, including barrier gloves
  - Incorporating best safety practices when heat treating fibers to high temperature by following established SOPs
  - All employees are required to do annual refresher courses in chemical hygiene, hazardous waste, and fire extinguisher training

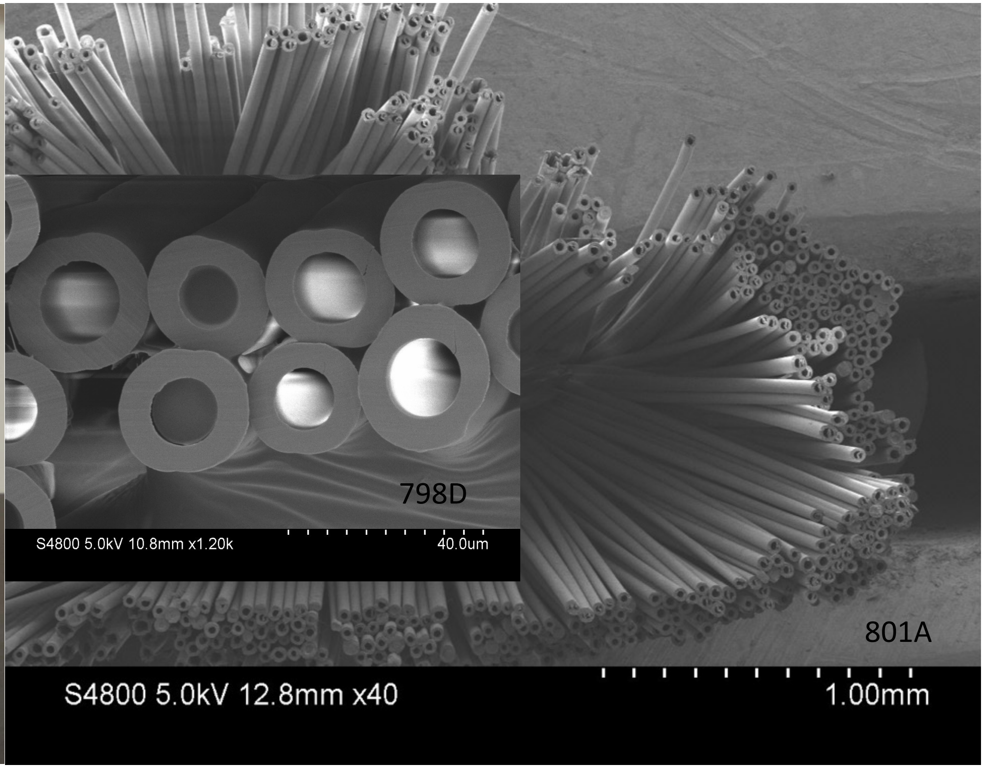
Technical Accomplishments Since 2023 AMR

ACCOMPLISHMENTS

✓ MILESTONE 1.1.3 Demonstrate the spinning of 100 filament HF precursor tow

- ✓ Achieved precursor dimensions: **25 µm OD, 14 µm ID**
- ➢ PHASE II target dimensions: **14 µm OD, 9 µm ID**





Technical Accomplishments Since 2023 AMR

ACCOMPLISHMENTS

- ✓ MILESTONE 2.1.1 Demonstrate the achievement of a target oxidized HF density in less time compared to a solid fiber
    - ✓ Extrapolated data from the literature (Warner, et al.) suggests HF should oxidize in ~1/2 the time compared to solid
    - ✓ Fiber oxidation proxied using thin films

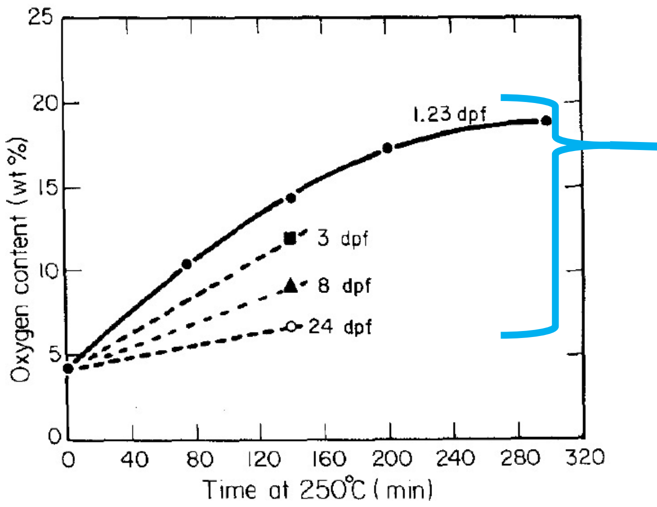
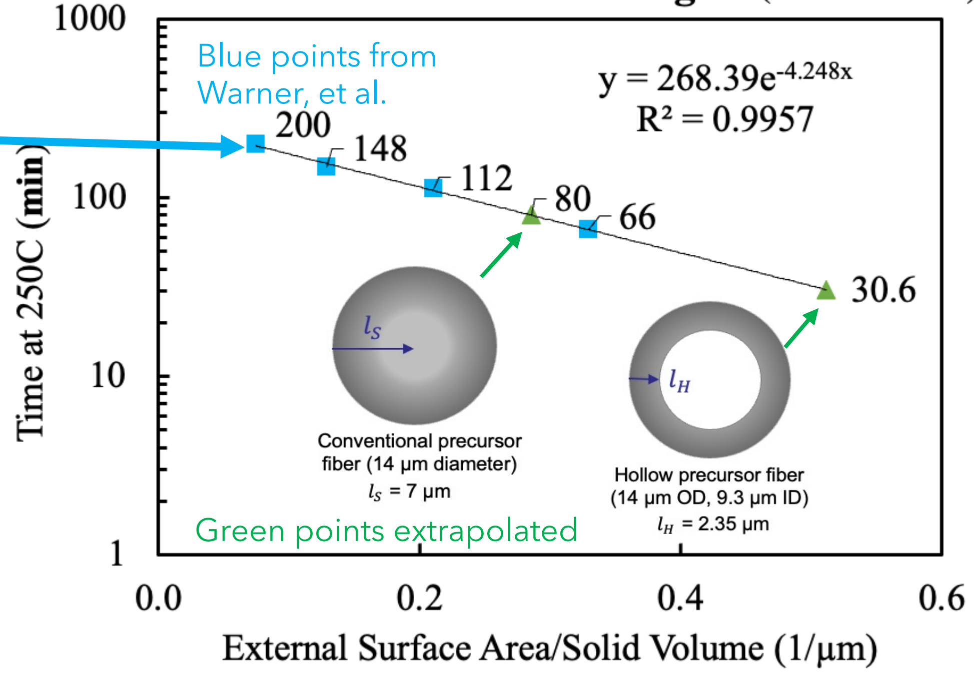


Figure 2 Oxygen uptake of various deniers of fibre N (obtained by varying the draw ratio) as a function of time at 250° C.

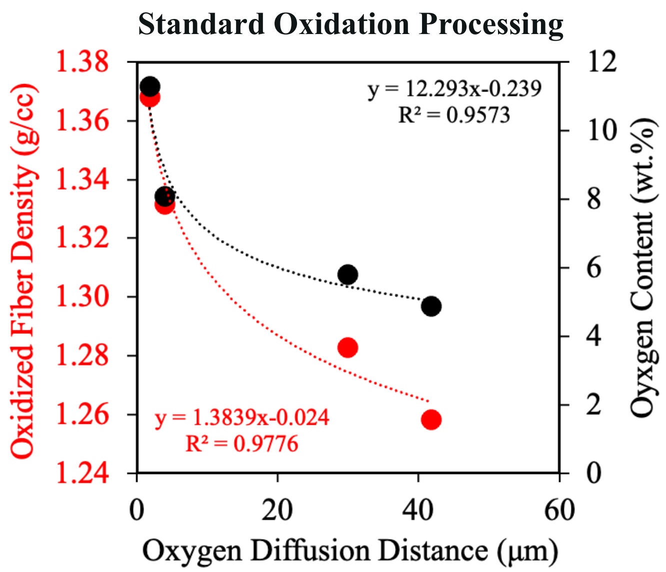
Warner, S. B., et al. *J. Mater. Sci.* **1979,** 14, (3), 556-564

Minutes at 250 °C to 1.35 g/cc (or 9.72 wt.% O)



Thin film oxidation results

Power law increase in O conc. and density as film thickness decreases



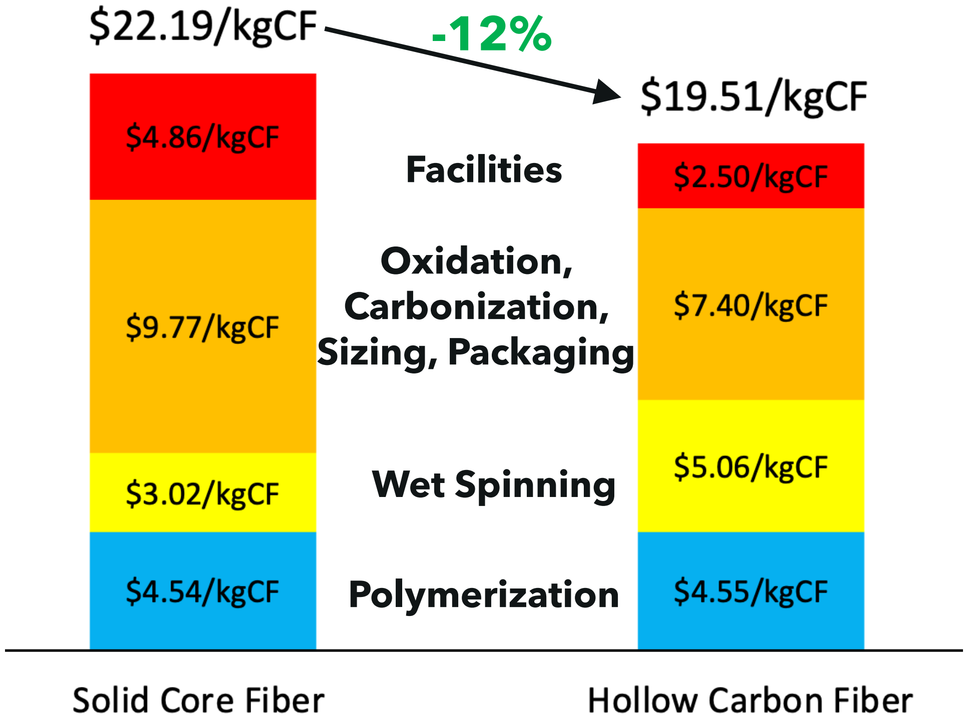
Technical Accomplishments Since 2023 AMR

ACCOMPLISHMENTS

✓ MILESTONE 4.2.1 Deliver a performance and cost analysis for HCF compressed gas storage tank production

These performance and cost analyses **will be realized** upon production of targeted HCF that:

- Conserves the tensile properties of T700S
- Achieves 7 µm OD and 4.65 µm ID
- Achieves target oxidation density in half the time compared to a solid fiber



System Cost

44% HCF open area

Solid fiber: ($994 BOP + $1925 tank) = $2919/sys

Hollow fiber: ($994 BOP + $1082 tank) = $2076/sys

-29% system cost

Gravimetric Capacity

44% HCF open area

Solid fiber: 67.1 kg fiber/sys

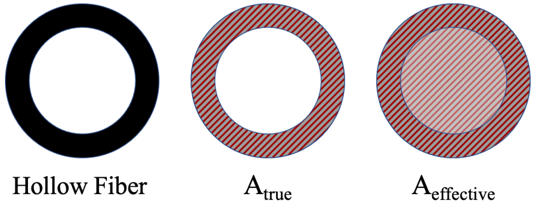
Hollow fiber: 37.6 kg fiber/sys

Solid fiber total system mass: 126.8 kg

Hollow fiber total system mass: 97.3 kg

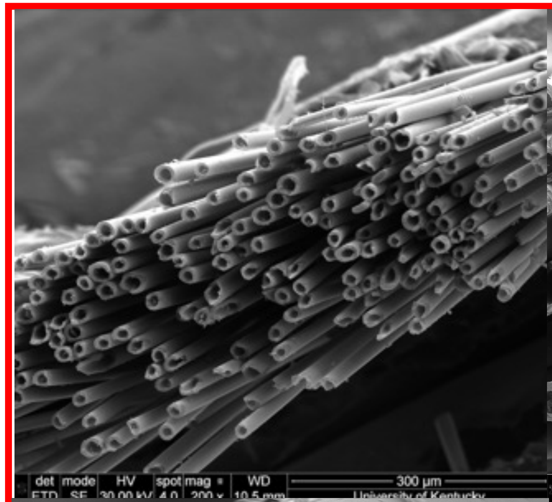
+30% gravimetric capacity

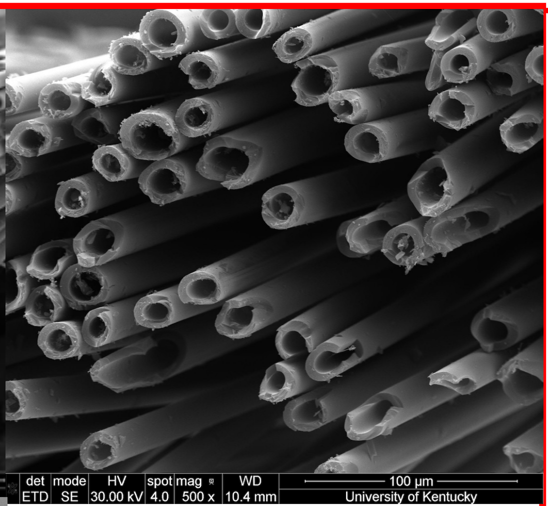
Technical Accomplishments Since 2023 AMR

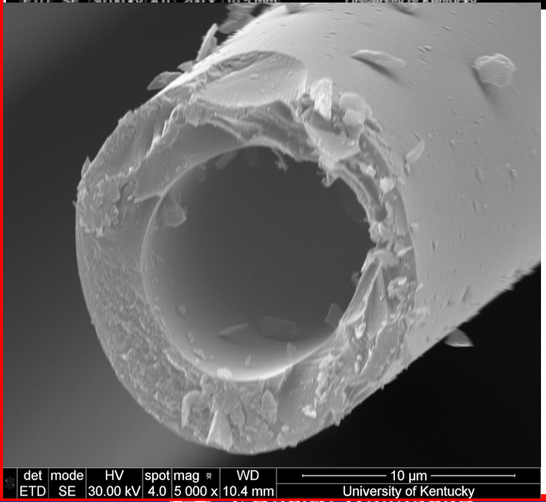


ACCOMPLISHMENTS

- ✓ HCF with 18 µm OD, 10 µm ID
- ✓ Single filament HCF tensile properties







HCF 290

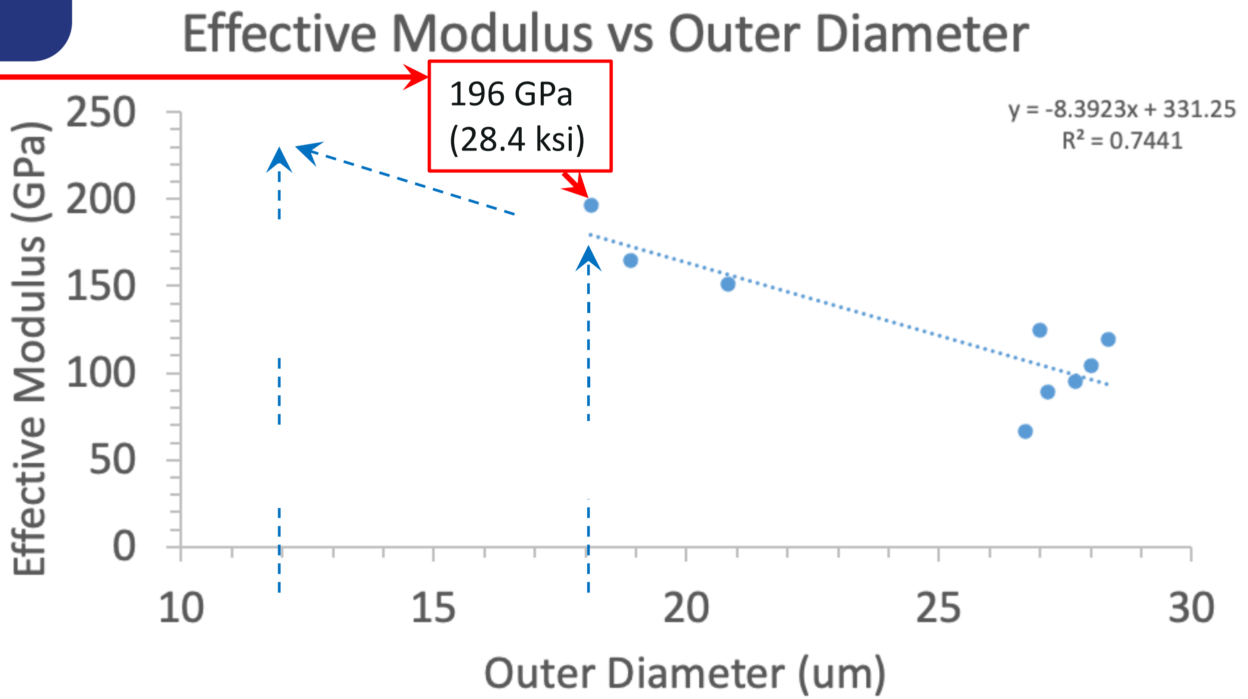
18.1/10.2 µm OD/ID

31% Open Area

Effective Modulus: 196 GPa (28.4 Msi)

Effective Density: 1.23 g/cc

Effective Strength: 1236 MPa (179 ksi)



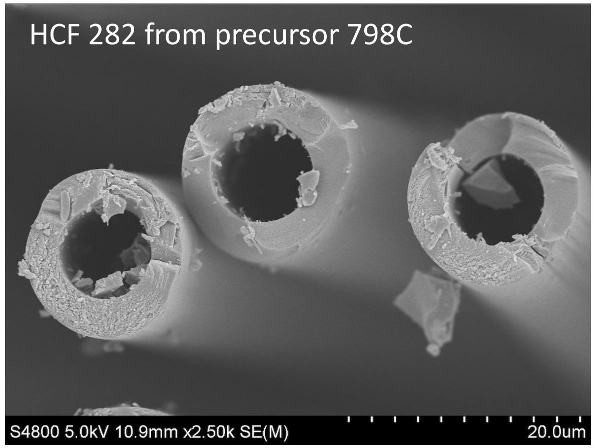
- **Current HCF conserves specific modulus of T1000**
- Trend demonstrates effective modulus increases with decreasing OD
- We hypothesize strength will improve with decreasing OD

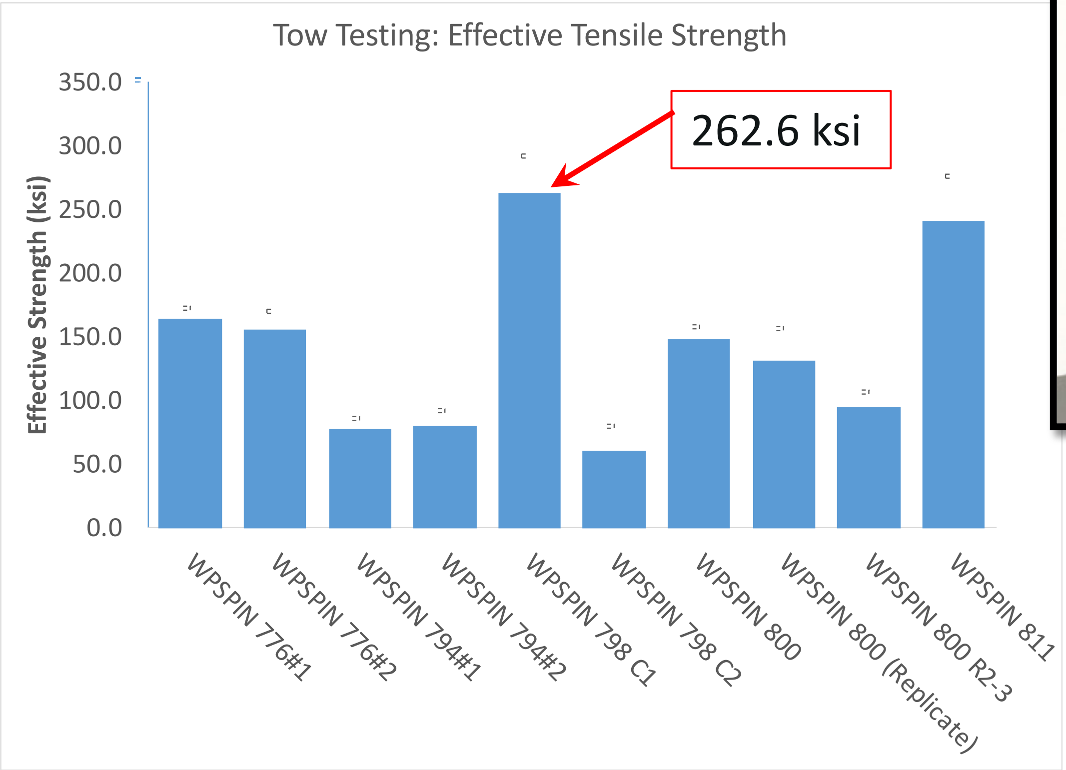
Technical Accomplishments Since 2023 AMR

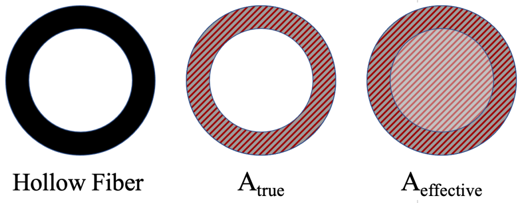
ACCOMPLISHMENTS

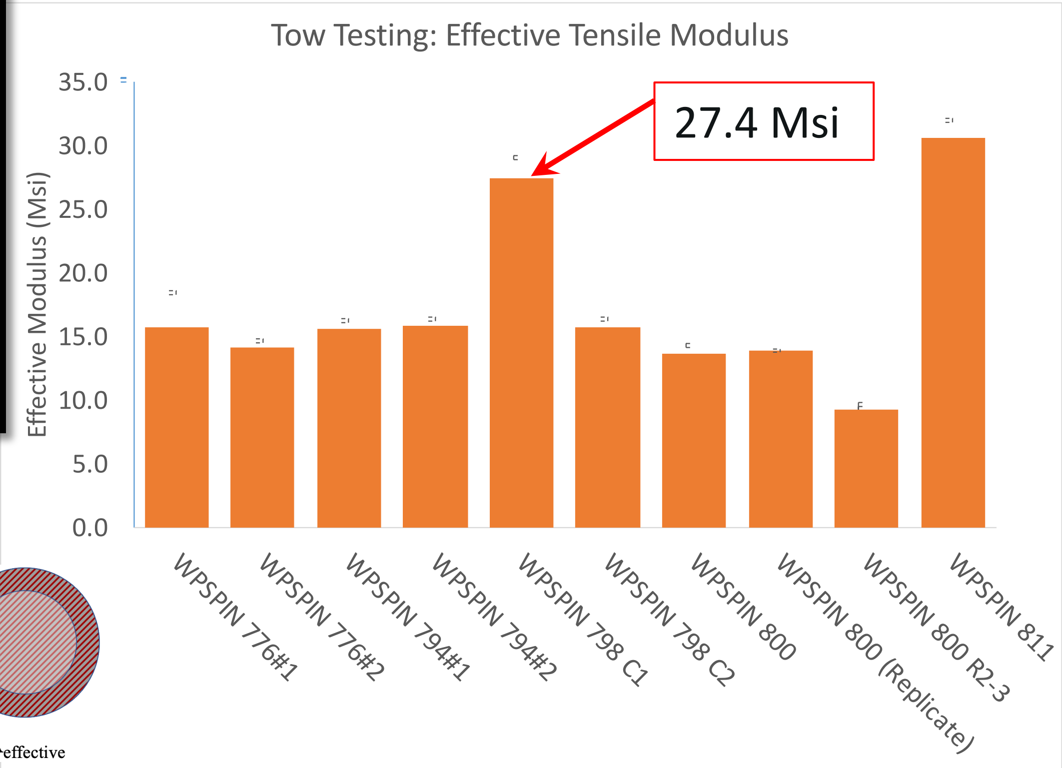
- ✓ Successful thermal conversion (ORNL) of 100 filament continuous tow (> 100m)
- ✓ Resin impregnated tow testing performed by Solvay on continuous tow HCF

OD = 15.68 μm
ID = 8.89 μm
% open area = 32









Responses to Previous Year Reviewers' Comments

This project was not reviewed at the 2023 AMR

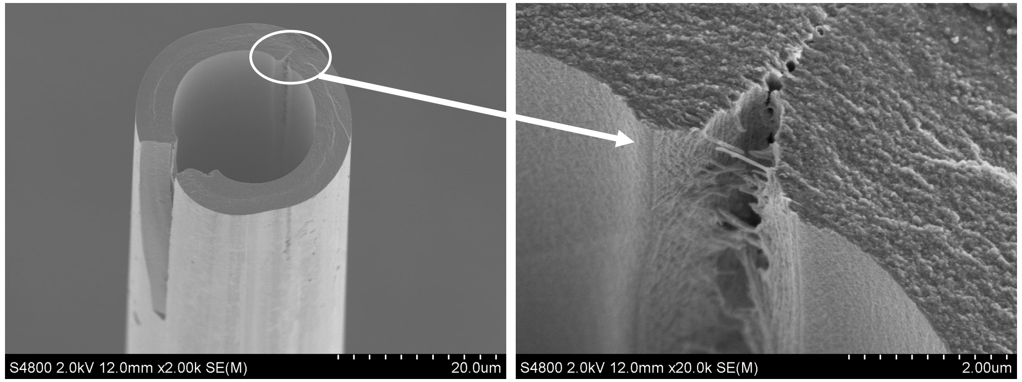
A Collaborative Project (Phase 1 and Phase 2)

University of Kentucky Center for Applied Energy Research PRIME	▪ Prime recipient; serves as lead institution ▪ 100 filament HF spinning scale up, batch oxidation and carbonization, and aiding in cost analysis ▪ Flaw analysis and mitigation ▪ Morphology, physical and chemical property analysis at all stages
Solvay Composite Materials Industry, Subrecipient	▪ Continuous oxidation and carbonization ▪ Resin impregnated tow testing ▪ Flaw analysis
Oak Ridge National Lab Subrecipient	▪ Continuous oxidation and carbonization ▪ Resin impregnated tow testing
Strategic Analysis Inc. Industry, Subrecipient	▪ Collaborate with all team members to provide periodic cost analyses throughout project ▪ Provide cost analyses including projections for HCF production and HCF tank manufacture: projected costs ($/kWh) and gravimetric capacity (kWh/kg)
Advanced Fiber Technologies Industry, Vendor	▪ Provide consulting and expertise through duration of project toward the production of high tensile strength and modulus HCF
Steelhead Composites Industry, Subrecipient (PHASE 1 ONLY)	▪ End-of-life reuse and recyclability of COPVs

Remaining Challenges and Barriers for FY24

Challenges

1. Structural issues exist in the HF as a result of non-fully merged sections during spinning
   - ➢ Spinneret design and control of spinning parameters is key



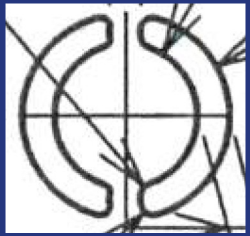
2. Further HCF diameter reduction needed to achieve cost metrics
   - ➢ Reduce HF precursor diameter through reduced spinneret capillary dimensions, reduced dope solids, improved fiber drawing methods, all leading to reduced HCF dimensions

3. The ability to oxidize in 50% of the time for a HF compared to a solid fiber
   - ➢ To accurately evaluate this, HF and solid fiber of the same outer diameter should be spun under similar conditions (a non-trivial task) and then oxidized

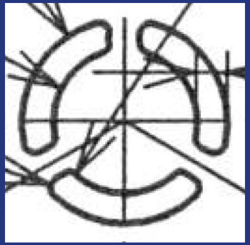
4. Improvements in HCF tensile properties needed to achieve T700S targets
   - ➢ HCF tensile properties will continue to improve with reduced fiber dimensions (less volume in which defects can exist)

Proposed Work for Phase II

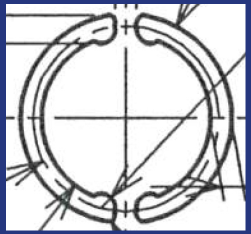
New smaller dimension spinnerets designed and ordered (12 total)



2C

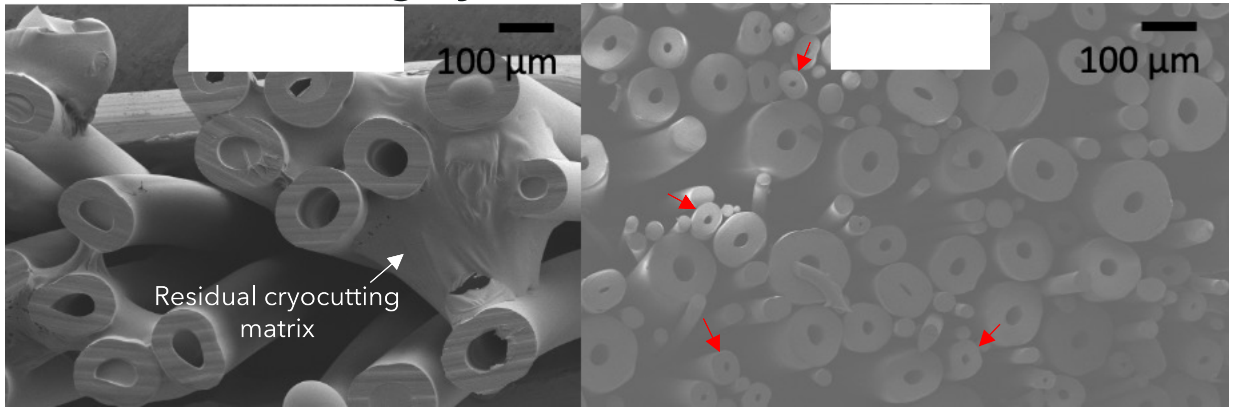


3C



2C and 3C with "feet"

Ultra-high jet drawn (UHJD) fiber



Presence of HF ~1/3 diameter of typical warrants further investigation

Spinning line and batch oxidation in dust-controlled environment (class 10,000 clean room)

- ✓ Clean room use increases tensile properties[1]
- ✓ Particulate control is considered "best practice" in high strength CF manufacture

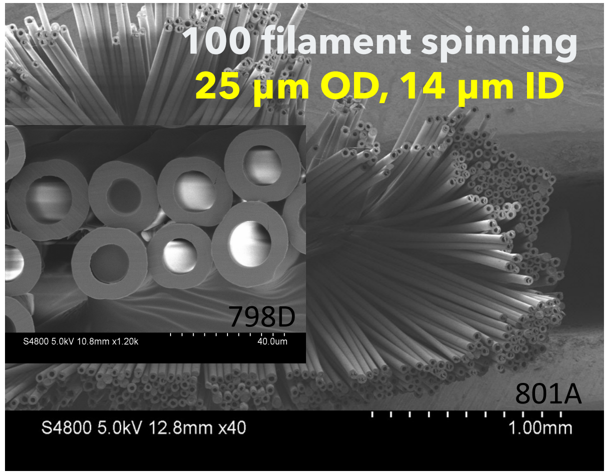
Higher HCF modulus observed with improved oxidation/carbonization method

- ➢ Recent experiments indicated a 45% increase in HCF modulus with further optimized oxidative stabilization and carbonization method
- ➢ The resulting HCF achieved the same specific modulus as T1100 CF

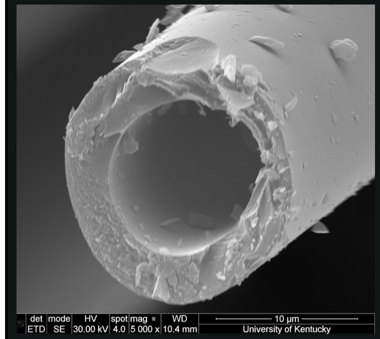
[1]Moreton, R.; Watt, W. Carbon 1974, 12, 543-554.

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

Summary – Project Accomplishments



Thermal conversion (ORNL) of 100 filament continuous tow (> 100m)



Single filament tensile properties (HCF 290)

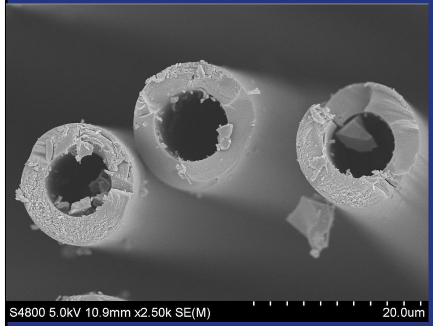
18.1/10.2 μm OD/ID

31% Open Area

Effective Modulus: 196 GPa (28.4 Msi)

Effective Density: 1.23 g/cc

Effective Strength: 1236 MPa (179 ksi)



Resin impregnated tow testing (HCF 282)

15.7/8.9 μm OD/ID

32% Open Area

Effective Modulus: 186 GPa (27 Msi)

Effective Density: 1.22 g/cc

Effective Strength: 1806 MPa (262 ksi)

OVERALL PREDICTED COST AND PERFORMANCE ADVANTAGES

-12% $/kg CF

-29% $/system

+30% kWh/kg

Modified Phase II awarded!