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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

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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 August 2020*
Percent Complete: 30%

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

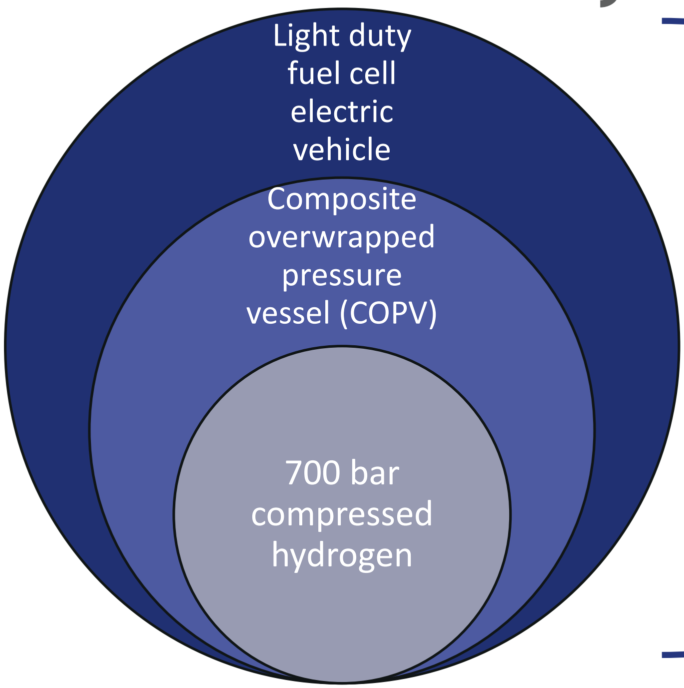
Budget

Total Project Budget:	$1,122,042
Total Cost Share:	$137,217 (12%)
Total Federal Share:	$984,826
Total DOE Funds Spent as of 3/31/18:	$201,409

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

*project continuation and direction determined annually by DOE

Relevance – Hydrogen Storage Materials



Carbon fiber accounts for 62% of the COPV system cost

COPV

Manufactured using a wet filament winding process using **Toray T700S carbon fiber** (CF), or equivalent, as a standard. CF strength is a vital driver for COPVs

Current Cost

COPV 700 bar hydrogen storage system equates to a cost of **$15/kWh of stored hydrogen**

Target

DOE interim target is **$10/kWh** of stored hydrogen to enable widespread commercialization of FCEVs

T700S CF cost: **$29.40/kg**

T700S CF properties

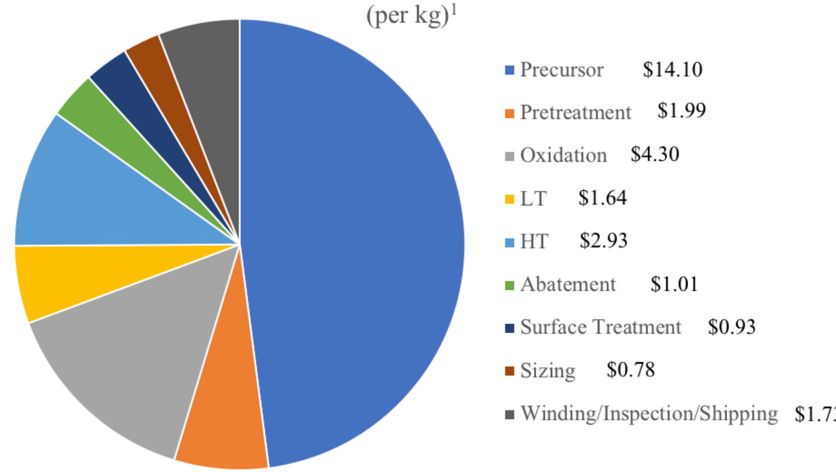
4.9 GPa tensile strength
230 GPa tensile modulus
2.1% strain
1.80 g/cm^3 density
7 μm filament diameter

Highest costs in production of CF

- ✓ Precursor manufacture
- ✓ Fiber Oxidation/Carbonization
- ✓ Wastewater treatment (wastewater treatment not accounted for in ORNL model)

DOE Target CF cost: **$12.60/kg**

Current Aerospace Grade (T700S or similar) CF Cost Breakdown (per kg)[1]



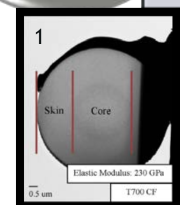
[1]Warren, C. D. *Development of low cost, high strength commercial textile precursor (PAN-MA)*; ORNL: 2014

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)

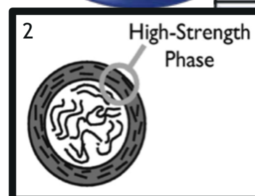
- Proprietary PAN polymer
- Skin-core carbon fiber structure
- Slow oxidation
- Millions of gallons of solvent wastewater per day



HIGH COST
$29.40/kg

Proposed Work

- Non-exclusive, low cost, high quality PAN polymer **"TechPAN"**
  CF Cost impact: -13.8%
- Hollow carbon fibers forego core structure, improve specific properties
  CF Cost impact: -15.4%
- Hollow fibers oxidize up to 35x faster
  CF Cost impact: -29.3%
- Water minimization and solvent recovery using activated carbon
  CF Cost impact: -5.2%



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

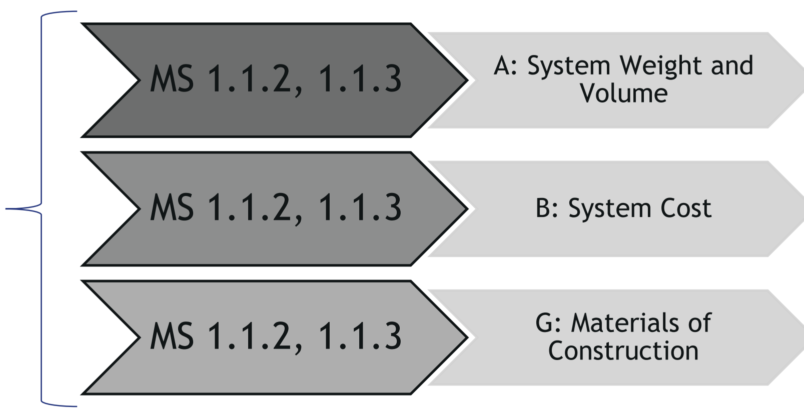
Relevance – April 2017 to April 2018

<u>**Objectives (April 2017- April 2018)**</u>

- Prove validity of TechPAN low cost PAN polymer for the production of air gap spun, high quality precursor fiber - 100% complete
  - MS 1.1.2 Demonstrate the air gap stability of nascent fiber jets for >10 min
  - MS 1.1.3 Demonstrate continuous multifilament air gap spinning, collecting a spool >10 m length and <12 micron in fiber diameter
- Develop efficient strain-controlled thermal conversion, optimize oxidation time/temperature pathway, decreased temperature carbonization optimization - 90% complete
- Design and acquire shaped spinneret for hollow fiber precursor spinning - 100% complete
- Fabricate counter current wash bath system, select activated carbon for adsorption, and install AC modules - 100% complete
- Develop design of experiments for residual solvent vs residence time during fiber spinning, determine breakthrough time as a function of activated carbon mass, and DMSO concentration in outlet stream vs inlet stream - 30% complete

ALL WORK IS ON SCHEDULE

Milestones completed toward identified technical barriers



Overall Technical Approach

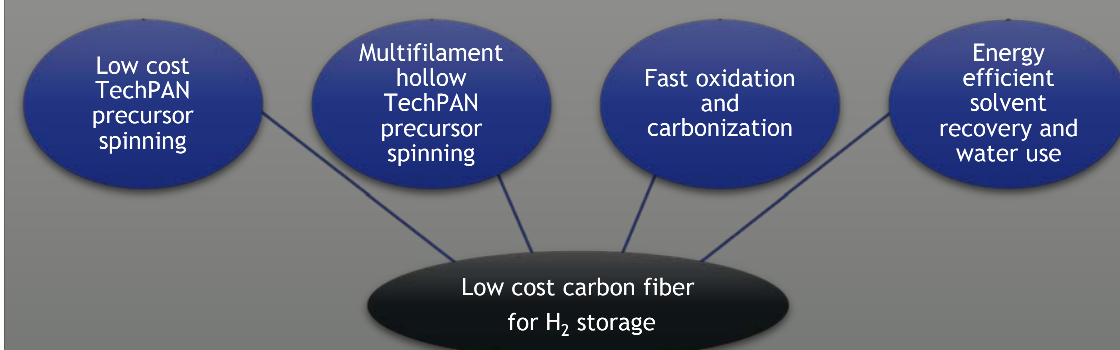
UNIQUE CAPABILITIES AT UK CAER

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

UNIQUE Approach

- ✓ Novel low cost TechPAN polymer
- ✓ Development of *hollow* precursor and carbon fiber
- ✓ Hollow fiber proposed to allow for faster oxidation, higher specific properties
- ✓ Utilize activated carbons as sorbents for solvent recovery (as opposed to commercially used energy-intensive distillation)

UK CAER multi-faceted method for producing low cost CF



Approach – Technical Barriers & Integration

DOE Technical Barriers and Impact

- **A: System Weight and Volume**
  - Designing and receiving the shaped spinneret for spinning of hollow fiber is the first step in achieving hollow carbon fiber with high specific strength properties compared to current state-of-the-art
- **B: System Cost**
  - Proving validity of low cost TechPAN polymer to produce high quality precursors lowers CF cost
- **G: Materials of Construction**
  - All milestones completed move toward the production of an aerospace quality carbon fiber at significantly reduced cost

Integration with research within the Hydrogen and Fuel Cells program

- UK CAER hosted the kickoff meeting of the 3 awardees of this FOA (UKY – M. Weisenberger, ORNL – S. Dai, Penn State, M. Chung)
  - Meeting facilitated collaboration between the awardees towards the final metrics of the FOA
- UK CAER is also working with ONRL – B. Norris, with LightMAT funding, to develop continuous thermal conversion of the TechPAN precursor, and generation of T700S properties

Approach – Planned Milestones FY18 & FY19

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FY18	**Milestones** 1.1.2: Demonstrate air gap stability of nascent fiber jets for > 10 min (100%) 1.1.3: Demonstrate continuous multifilament air gap spinning, spool >10 m length, <12 micron fiber diameter (100%) 1.2.2: Demonstrate batch stabilized fiber density between 1.35-1.37 g/cc via helium pycnometry and an aromatization index >0.7 via differential scanning calorimetry (DSC) (90%) **Go/No-Go Review Points** G1: 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. Deliver cost analysis showing a reduction of ≥10%, from \$29.40/kg to \$26.46/kg is possible via low cost polymer. (75%)
FY19	**Milestones** 2.1.2: Demonstrate coagulated fiber with hollow core, coalesced shell, and circular cross section (10%) 2.1.4: Demonstrate spooled HF with <100 um OD, <50 um ID (0%) 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 (50%) **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. (10%)
FY20	**Milestones** 2.1.6: Demonstrate spooled HF with <50 um OD, <25 um ID (0%) 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 (0%) 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. (0%)

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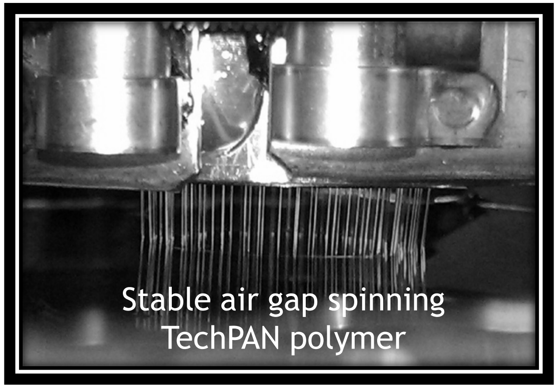
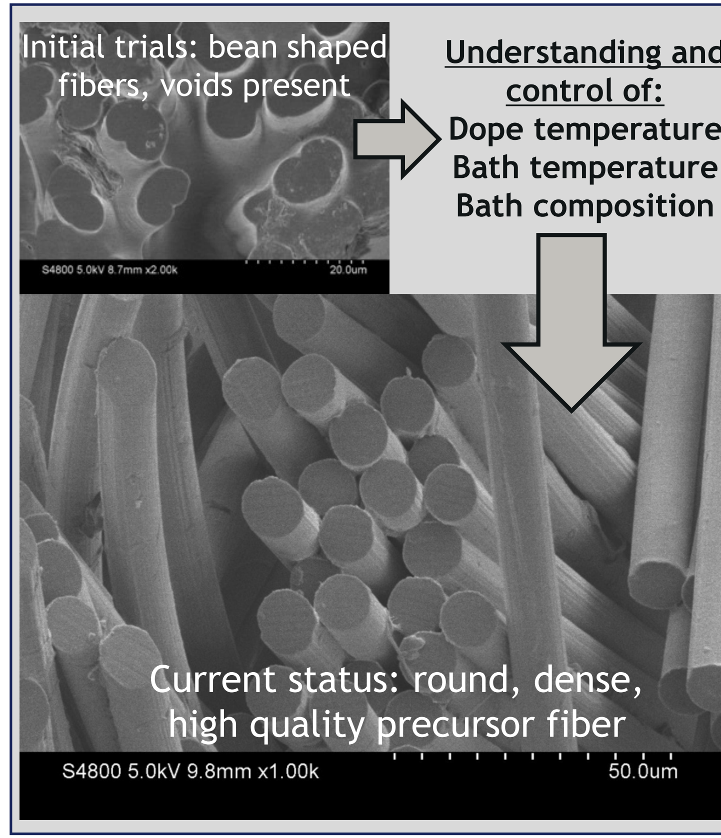
Technical Accomplishments and Progress
Air gap spun TechPAN and resulting carbon fibers



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



Relevant Completed Milestones

MS 1.1.2 Air gap spinning stable in the airgap for > 10 min.

MS 1.1.3 Continuous multifilament air gap TechPAN spinning, spool >10 m length, < 12 micron fiber diameter

Summary Statement

Low cost TechPAN polymer

- Spins well in DMSO
- Produces round cross section filaments
- Low void content
- High tensile properties

Current single filament precursor properties
(N=15, 25.4 mm gauge)

Tensile strength = 782 ± 66 MPa

Elastic modulus = 16.4 ±0.6 GPa

Elongation = 10.0 ± 0.7 %

Fiber diameter = 9.85 ± 0.26 μm

(Toray precursor tensile strength = 456 MPa[1,2])

[1] Morris EA, et al. Polymer. 2014;55(25):6471-82.

[2] Matsuhisa Y, Kibayashi M, Yamasaki K, and Okuda A. Carbon Fibers, Acrylic Fibers and Process for Producing the Acrylic Fibers. Toray Industries, Inc. US Patent No. 6,438,892 B2. 2002.

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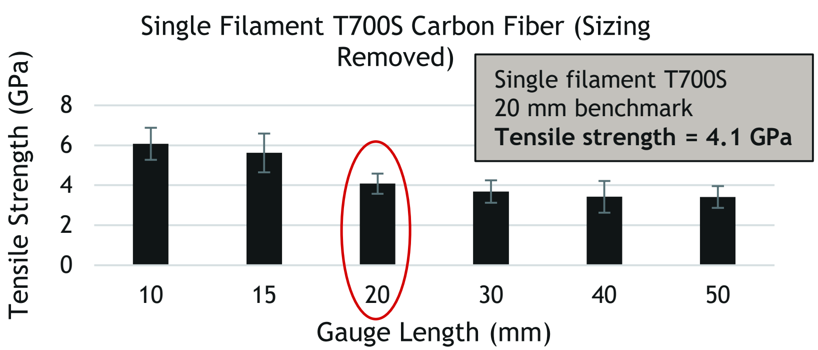
Technical Accomplishments and Progress
Air gap spun TechPAN and resulting carbon fibers

UK CAER

BATCH thermal conversion to CF

- Custom built strain control batch stabilization and carbonization system
- Minimizes amount of precursor fiber required to develop high quality CF



ORNL (supported by LightMAT)

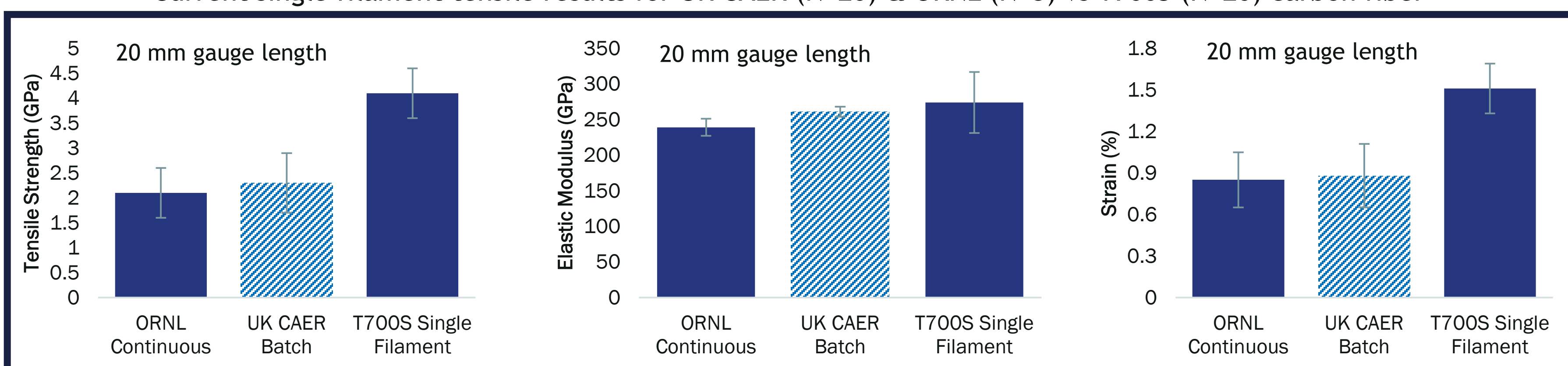
CONTINUOUS thermal conversion to CF

- Utilizes lab scale furnace systems
- Replicates current commercial conversion processes

Summary Statement

- T700S single filament strength shown to be slightly lower than reported tow tensile properties (4.1 GPa vs 4.9 GPa)
- UK CAER batch process currently producing CF with properties similar to ORNL continuous process
- UK CAER CF tensile strength currently at 50% that of T700S

Current single filament tensile results for UK CAER (N=20) & ORNL (N=5) vs T700S (N=20) carbon fiber



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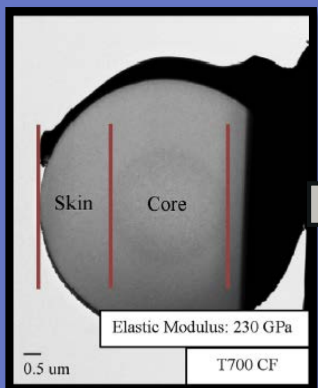
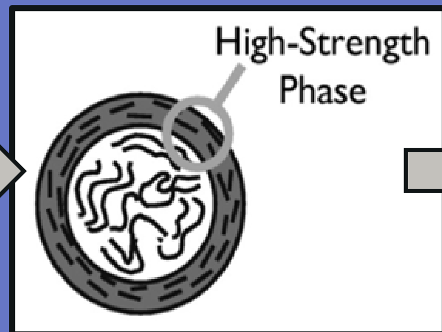
Technical Accomplishments and Progress
TechPAN *hollow* fiber spinning and resulting *hollow* carbon fiber

Background

Skin-core structure T700 CF[1]

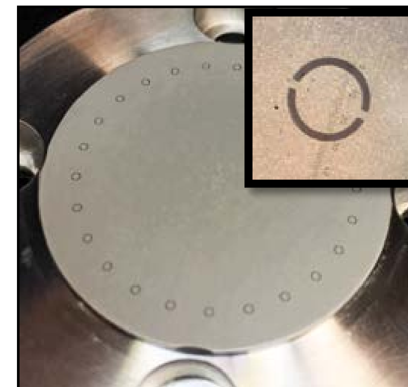


Skin-core model of PAN CF[2]



Large diameter (~190 um OD) PAN fiber by Zhang using two segmented-arc slip shaped spinneret[3]

Two-segment arc slip spinneret designed and acquired by UK CAER for multifilament hollow fiber spinning

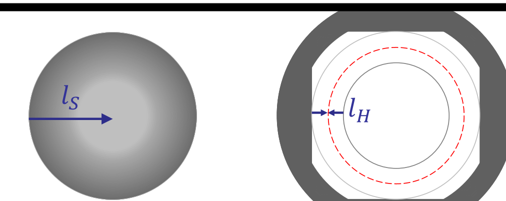


UK CAER approach:

- ✓ Eliminate fiber core
  - o Disordered core contributes little to tensile strength
  - o Removal of core increases specific properties of the fiber, reduces amount of polymer utilized
- ✓ Utilize segmented-arc slip shaped spinneret for multifilament, small diameter hollow fiber spinning
  - o Traditional solution spinning - bore fluid hollow fiber approach limits minimum diameter of fiber (~500 um OD for traditional hollow fiber)
  - o Multifilament bore fluid spinnerets are impractical for manufacture
- ✓ Hollow fiber proposed to oxidize up to **35x faster** than conventional solid fiber due to reduced oxygen diffusion length ($l_H << l_S$)

Summary Statement

- ➢ Hollow fiber spinneret designed and acquired
- ➢ Initial hollow fiber spinning trials beginning



Hollow precursor fiber (14 um OD, 9.3 um ID)

l_S = 7 um

l_H = 1.175 um

[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
[3] Zhang, X., et al., *J. Macromol. Sci., Part B: Phys.* **2008,** 47, (6), 1039-1049

Technical Accomplishments and Progress
Energy efficient solvent recovery and water use

Current commercial process

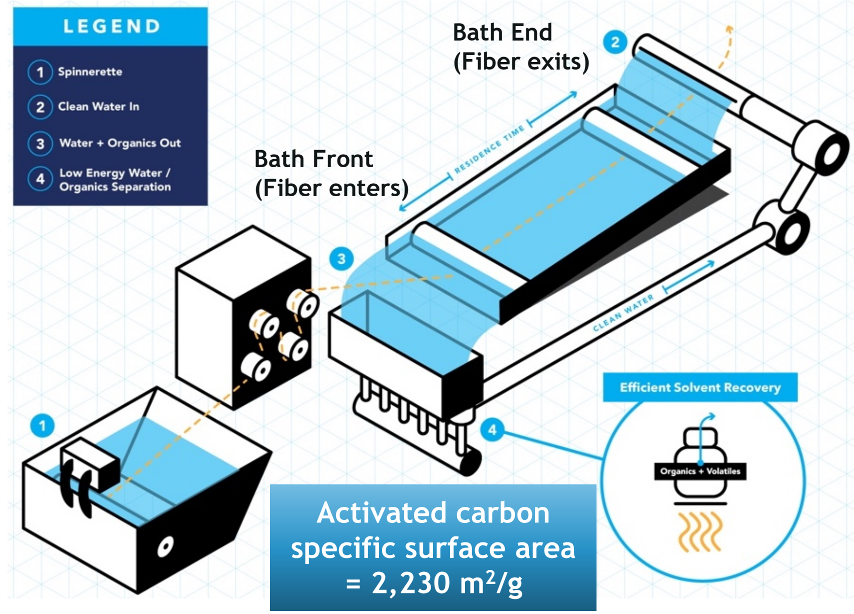
40 kg solvent/ water waste

6-line site
10 to 20 12k tows per line
100 to 400 m/min
24 hrs/day

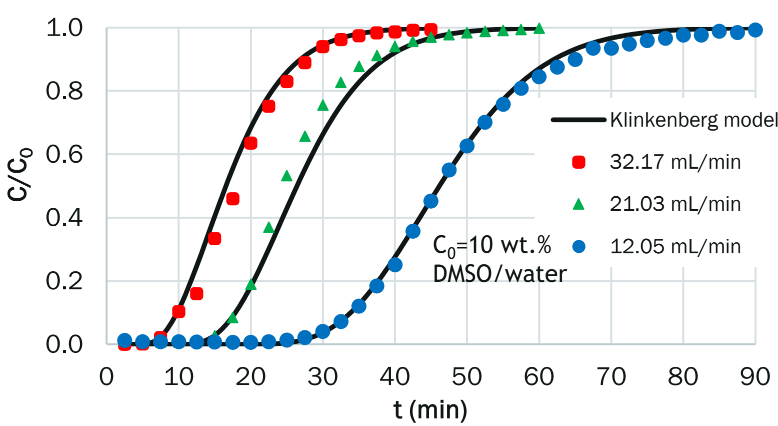
=

424,000 to 1,696,000 gal/day of wash water

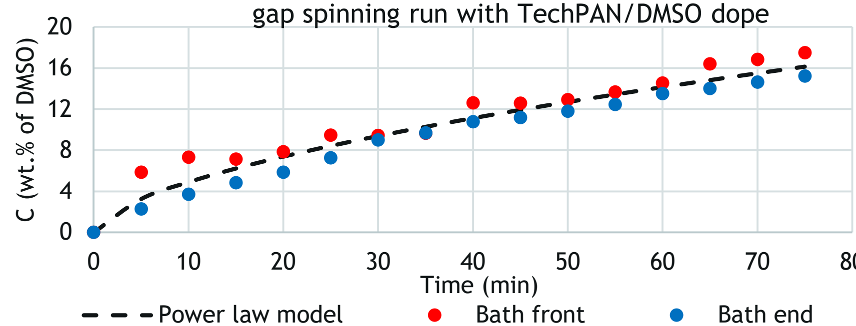
50% reduction in wastewater generated = 5% carbon fiber cost reduction



Breakthrough curves for 150 g of activated carbon (AC)



Buildup of solvent in 1st wash bath during typical air gap spinning run with TechPAN/DMSO dope

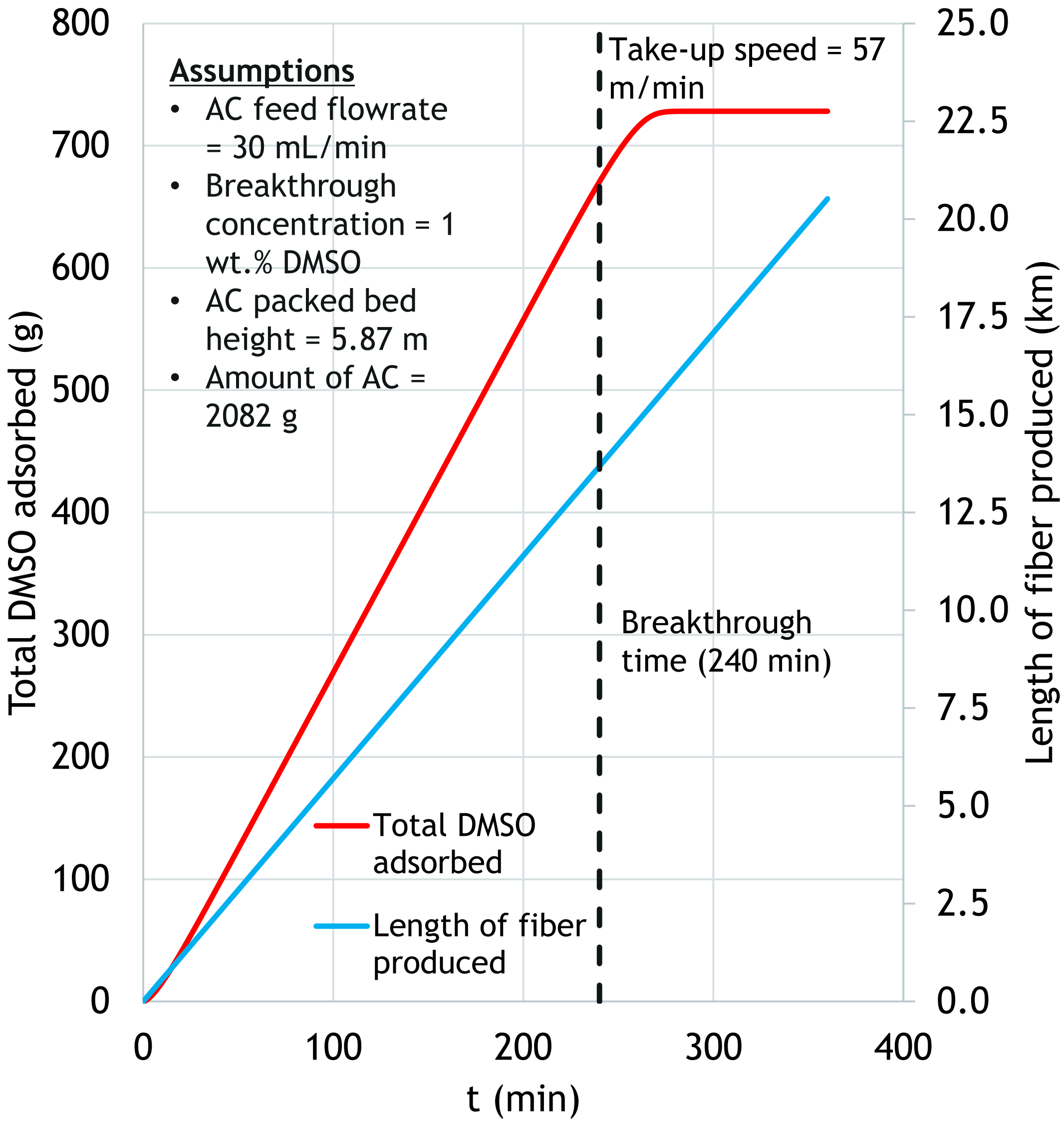


Summary Statement

- Breakthrough curves for activated carbon completed
- Solvent buildup during spinning fit with power law model

Technical Accomplishments and Progress
Energy efficient solvent and water use

Calculated total amount of DMSO adsorbed by the activated carbon versus length of fiber produced



Based on data so far, the use of activated carbon is estimated to reduce the amount of wastewater generated by 86% (>50% target set forth in proposal for 5% carbon fiber cost reduction)

Over 4 hour spin run

- WITHOUT AC → estimated to generate 7 L of DMSO wastewater
- WITH AC → estimated to recycle 1 L of water
- 13 km of continuous, 100 filament, fiber tow or ~100 g of fiber
- Initial experimental results predict 670 g of DMSO will be adsorbed by 2082 g of AC

Summary Statement

- Use of activated carbon estimated to reduce fresh water usage by 86%
- 3 g of the activated carbon is capable of absorbing 1 g of DMSO

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Responses to Previous Year Reviewers' Comments

This project was not reviewed last year

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

- ➢Utilizing their continuous stabilization and carbonization capabilities to convert UK CAER TechPAN precursor fiber to carbon fiber to prove TechPAN is capable of producing carbon fiber with tensile properties similar to T700S
- ➢Use as a comparison for the efficacy of UK CAER strain controlled batch system

Remaining Challenges and Barriers

Low cost TechPAN fiber spinning and thermal conversion

- Achieve T700S tensile properties with TechPAN fiber

Energy efficient solvent recovery and water use

- Achieve <1 wt.% residual solvent in fiber with minimum wash residence time
- Reduce the waste water burden by > 50% with activated carbon sorption
- Regenerate the used activated carbon with <15% loss in specific surface area

Multifilament, *hollow* TechPAN fiber and resulting *hollow* carbon fiber

- Demonstrate air gap spinning of *hollow* TechPAN fiber with OD < 100 um and ID < 50 um
- Demonstrate hollow carbon fiber properties approaching T700S
- Deliver analysis of specific strength of hollow carbon fiber pertaining to part weight consideration

Final Deliverable

- Cost analysis of precursor and carbon fiber with a cost potential of $12.60/kg carbon fiber

Proposed Future Work

Remainder FY2018

Validate

Low-cost TechPAN polymer as a precursor capable of achieving T700S carbon fiber properties for COPVs

- Focus on continued work with ORNL to develop time/temperature pathway for conversion to high quality carbon fiber
  - MS 1.2.2: Demonstrate batch stabilized fiber density between 1.35-1.37 g/cc via helium pycnometry and an aromatization index >0.7 via differential scanning calorimetry (DSC)
- TechPAN must be validated as a high quality polymer capable of producing fiber with T700S properties, while attempting to produce hollow carbon fibers with similar properties

Multifilament, hollow filament formation

- Focus on processing parameters (dope solids content, coagulation bath conditions, jet stretch, etc.) to produce hollow TechPAN fiber

Water minimization & low energy solvent recovery with DMSO selective activated carbon modules for conventional TechPAN solid fiber

- Begin spinning trials utilizing activated carbon modules of experimentally determined design (5.87 m height, containing 2000 g of AC for 4 hr spinning run)

FY2019

Develop

Multifilament, hollow filament formation

- Continue focus on producing hollow fiber (HF), utilizing air gap atmosphere control as necessary
- Focus on dimensional and concentricity control and downstream spinning optimization
  - MS 2.1.2: Demonstrate coagulated fiber with hollow core, coalesced shell, and circular cross section
  - MS 2.1.4: Demonstrate spooled HF with < 100 um OD, < 50 um ID

Activated carbon regeneration processing

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

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

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

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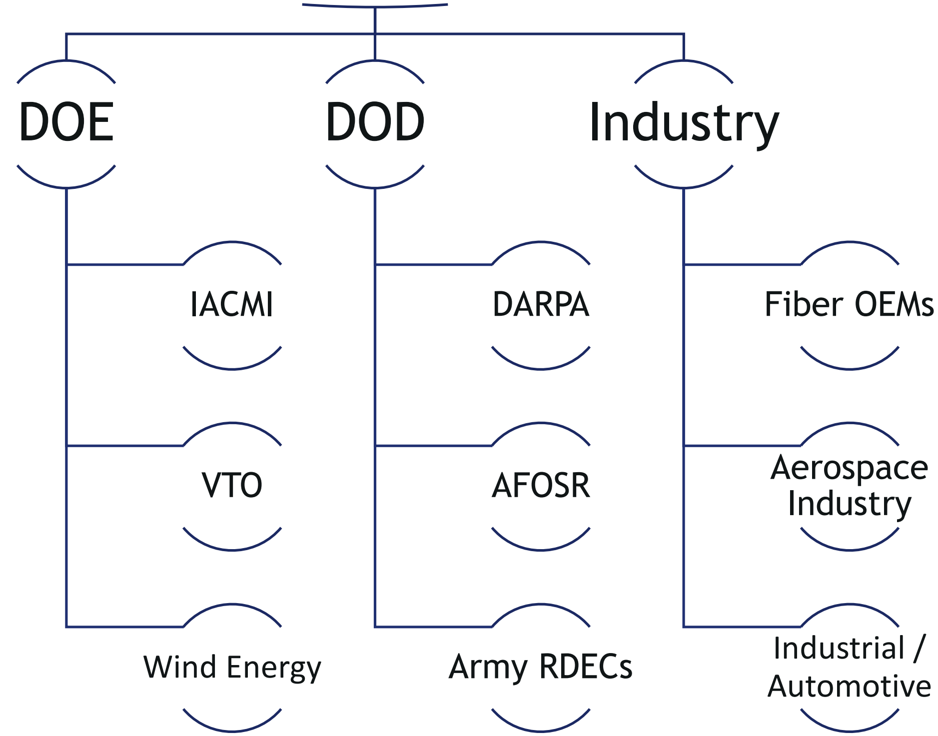
Technology Transfer Activities

Tech-to-Market Plan

Potential Future Funding



Patents/Licensing

To date, none to report

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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: Low cost TechPAN has been successfully spun into high quality precursor using a multifilament, air gap solution spinning approach and thermal conversion to CF with T700S properties is underway at both UK CAER (batch) and ORNL (continuous).

An arc slip shaped multifilament spinneret for producing hollow fiber has been designed and acquired, and initial hollow fiber spinning trials are under way.

Breakthrough curves for activated carbon (AC), as well as measurement of solvent buildup in the wash baths during spinning has been completed and the necessary AC module height determined to be 5.87 m, containing 2000 g of activated carbon, for a 1 wt.% DMSO breakthrough time of 240 min, hypothesized to reduce water usage during spinning by 86%.

Collaborations: UK CAER is assisted by ORNL (funded by LightMAT) in the continuous thermal conversion of UK CAER TechPAN precursor to carbon fiber.

Summary Table FY2018

Milestone #	Project Milestones	Type	Task Completion Date (Project Quarter)				Progress Notes
			Original Planned	Revised Planned	Actual	Percent Complete	
1.1.2	Demonstrate the air gap stability of nascent fiber jets for > 10 min.	Milestone	Q1		Q1	100%	Complete
1.1.3	Demonstrate continuous multifilament air gap spinning, collecting a spool >10 m length and <12 micron in fiber diameter.	Milestone	Q2		Q2	100%	Complete and improving
1.2.2	Demonstrate batch stabilized fiber density between 1.35-1.37 g/cc via helium pycnometry and an aromatization index >0.7 via differential scanning calorimetry (DSC).	Milestone	Q3		Q3	90%	Nearing completion
GNG 1	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. Deliver cost analysis showing a reduction of ≥10%, from $29.40/kg to $26.46/kg is possible via low cost polymer.	Go/No-Go	Q4		Q4	75%	Progressing well