Novel Plasticized Melt Spinning Process of PAN Fibers Based on Task-Specific Ionic Liquids

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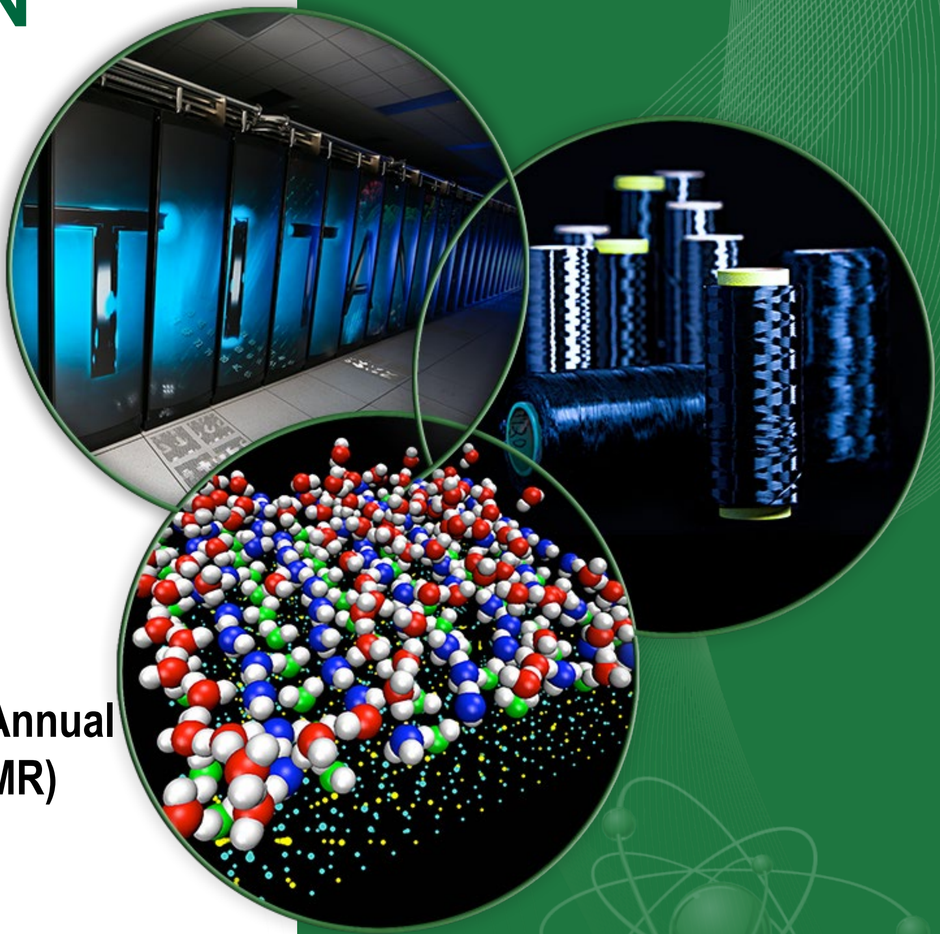


2019 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting (AMR)

May 01, 2019 **Project ID: ST148**

Overview

Timeline

- Project Start Date: 10/01/17
- Project End Date : 9/30/20
- Percent Complete: 58%

Barriers

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

Budget

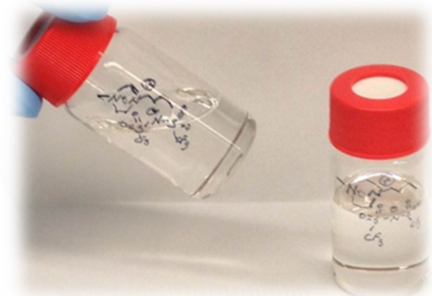
- Total task funding
  - $900k
- $257k in FY18
- $322k in FY19
- $321k in FY20

Partners

- Project Lead: ORNL
- Interactions/Collaborations
  - 525 Solutions

Relevance

- Objective: The overarching goal of this proposal is to develop a novel plasticized melt-spinning process to replace the current solution spinning process based on nonvolatile task-specific ionic liquids (ILs). The four underpinning research tasks we aim to accomplish in our project are:
  - to investigate how the molecular structures of ILs dictate plasticizing interactions with PAN for controlling glass transition temperatures and rheological properties of PAN-IL composites,
  - to study how the chemical interactions of ILs with PAN can be used to control the cyclization degree in intermediate ladder structures
  - to integrate the information gained from the above two tasks to develop IL-assisted melt spinning systems
  - demonstrate considerably enhanced production efficiencies and improved structural properties of PAN fibers.
- Relevance to Barriers and Targets
  - The ability to melt-spin the PAN into fibers has been identified as a significant cost-driver for high strength carbon fiber production.
  - The fiber production has a direct correlation to the costs of a hydrogen storage system where the carbon fiber cost is 75 % of the total system cost
  - To replace the current solution spinning process with a novel plasticized melt-spinning process based on nonvolatile task-specific ionic liquids (ILs)



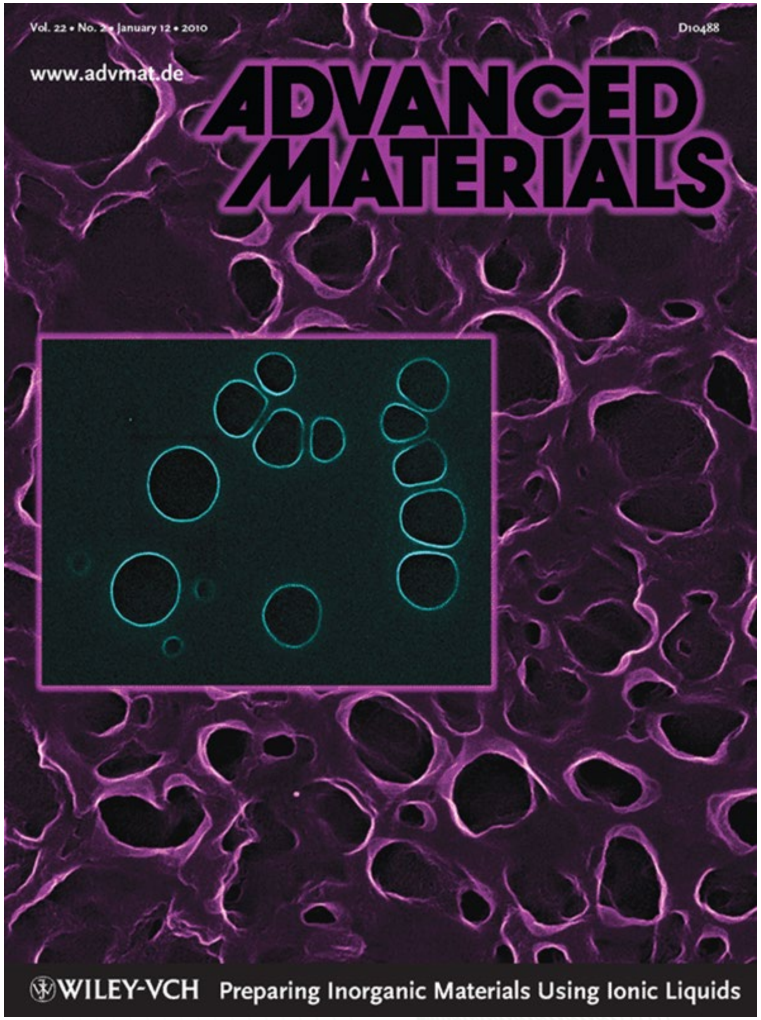
Approach

Why Ionic Liquids?

Ionic systems consisting of salts that are liquid at ambient temperatures can act as solvents for a broad spectrum of chemical species.

- *Ionicity*
- *Nonvolatility*
- *Thermal Stability*
- *Nonflammability*
- *Tunable Hydrophobicity*
- *Wide Liquid-Phase Temperature* (-100^{0}C to around 300^{0}C)
- *Wide Electrochemical Window*
- *Tunable Lewis Acidity*

Ideal as plasticizers and designer solvents

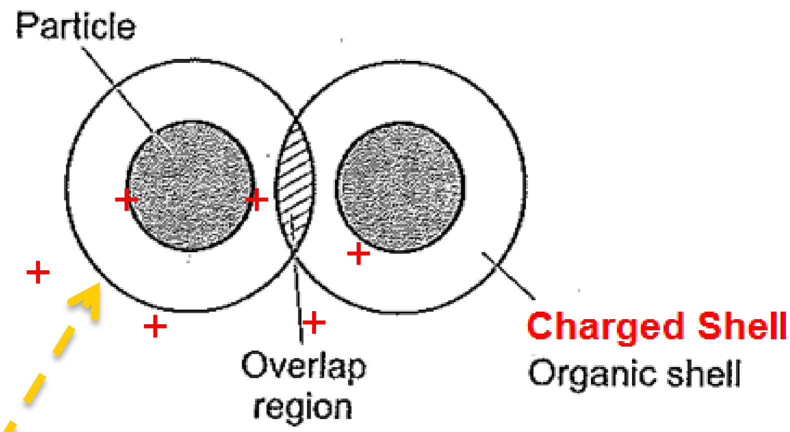


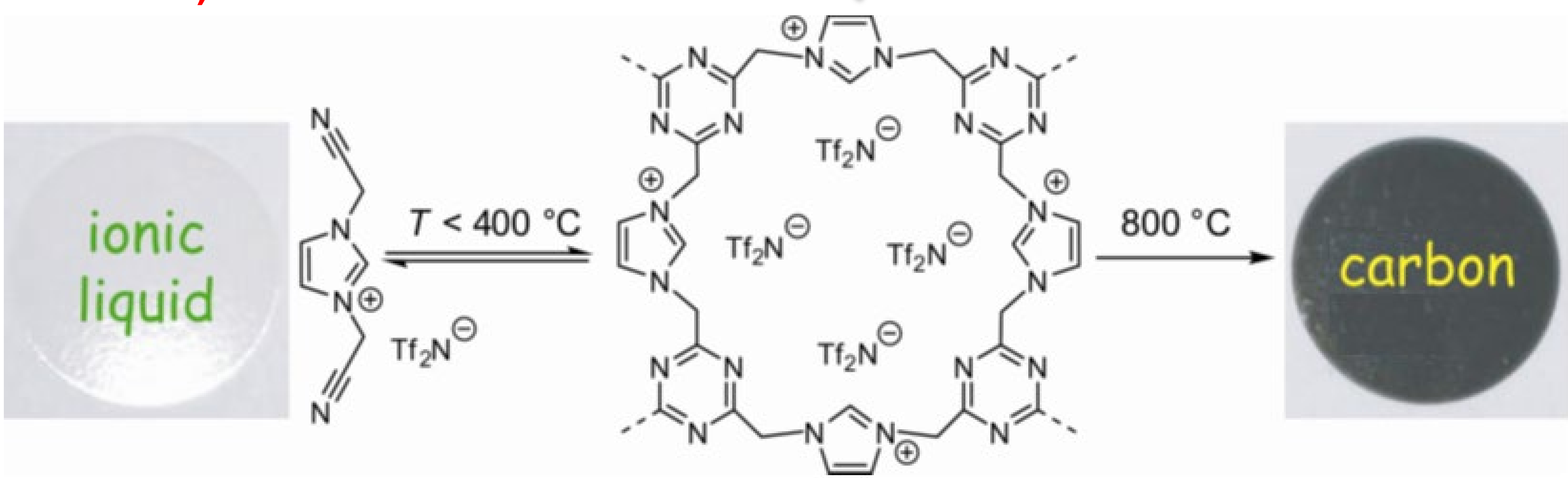
Ma, Yu, Dai, *Adv. Mater*. 2010, *22*, 261

Approach: Ionic-Liquid Strategy to Nonpolymeric Liquid Precursors for Formation of Carbons under Ambient Pressure

Key Features

- Nonpolymeric but negligible vapor pressure
- Polymerization strategy toward highly charged and crosslinked polymers
- Liquid precursors for N-doped carbonaceous materials (types of N-dopants and other elements)





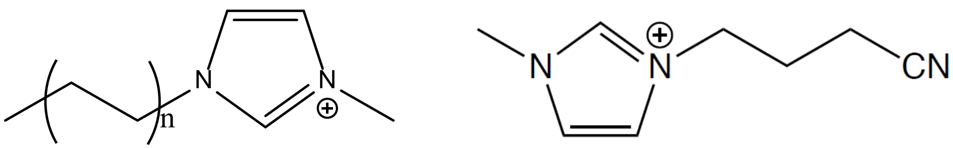
J. Lee, X. Wang, H. Luo, G. A. Baker, S. Dai, *J. Am. Chem. Soc.*, 2009, *131*, 4596.
X. Q. Wang, S. Dai, *Angew. Chem. Int. Ed.* 2010, *49*, 6664.

Approach: Project Milestones

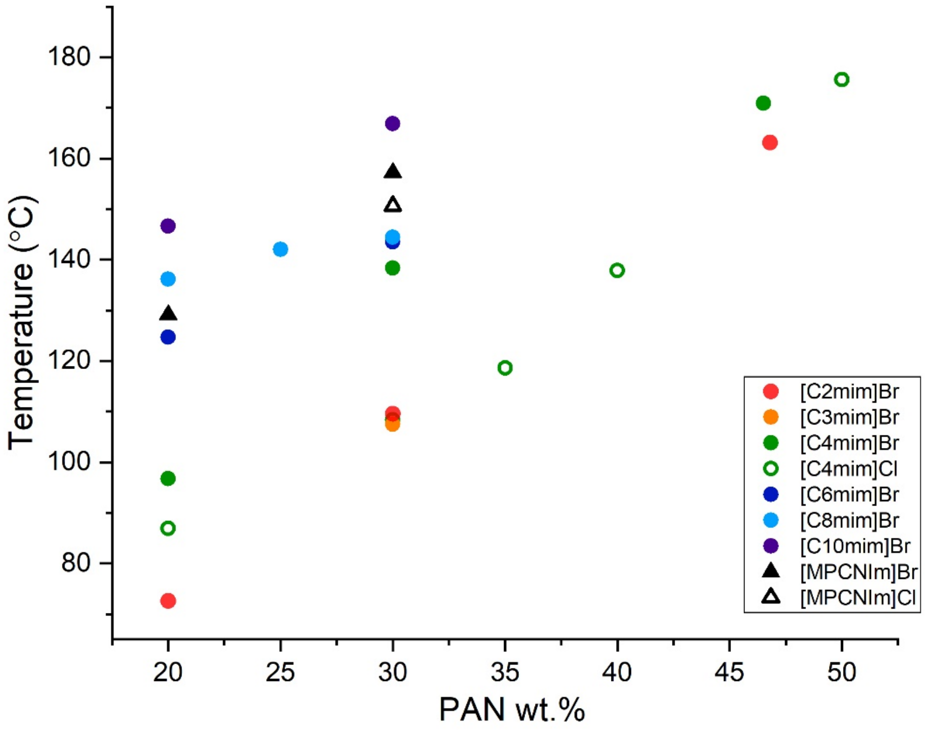
	% Accomplished
• Milestone 1: Investigate how the molecular structures of ILs dictate plasticizing interactions with PAN (FY 17-18)	
– 1.1 Demonstrate > 30 wt% IL solubility in PAN	100%
– 1.2 PAN-IL synthesis with carbon yield > 50%	100%
– 1.3 Demonstrate > 10 °C decrease in PAN melt temperature	100%
– Go/No-Go Point #1: Demonstrate > 15 °C decrease in PAN melt temperature	100% Go
• Study chemical interactions of ILs with PAN to control cyclization of degree (FY18-19)	
– 2.1 Down selection of IL for plasticization	50%
– 2.2 Demonstration of melt spinning of PAN fibers based on ILs	75%
– 2.3 Technoeconomic analysis for scale-up of the IL production	25%
– Go/No-Go Point #2: Demonstration of tensile properties of resultant fibers	50%Go
• Integrate the information gained form the above two tasks to develop IL-assisted melt spinning systems (FY19-20)	
– 3.1 Preliminary analysis of scale-up	0%
– 3.2 Scale-up IL to >1 kg production for IL to realize anticipated decreased cost	0%
– 3.3 Maintain melt viscosity for at least 10 minutes during spinning trials	40%
– 3.4 Demonstration of filament diameter of ~20 micrometer after carbonization	0%

Accomplishments and Progress: Demonstrate >15 °C decrease in PAN melt temperature

- Ionic liquids as a plasticizer to suppress the melting temperature of PAN
  - Melting temperature for PAN-IL composites are greater than 100 °C lower than neat PAN (~325 °C)
- Generally, for a given PAN wt.% as the carbon chain length is increased for $[C_n mim]^+$ the melting temperature is increased.
- Chloride anions suppresses the melting temperature greater than bromide anions for a given cation
- As the PAN concentration is increased the more energy it takes to disrupt the crystalline phases of the polymer chains

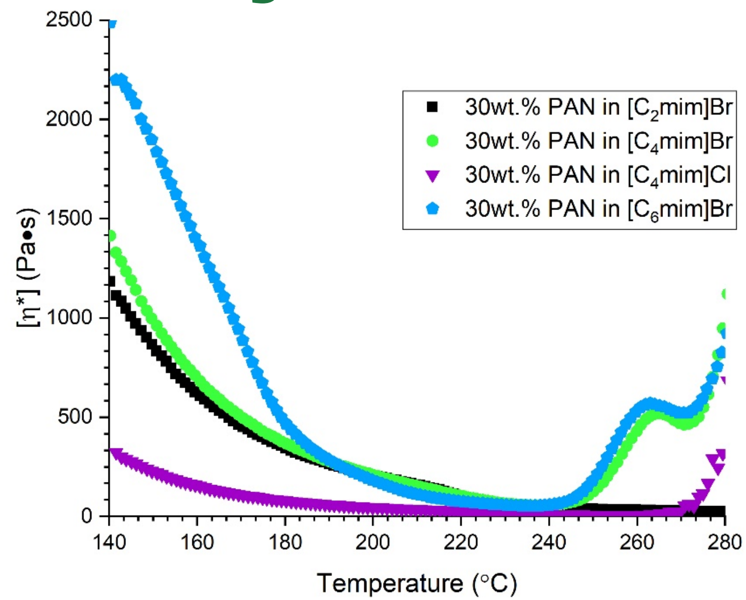


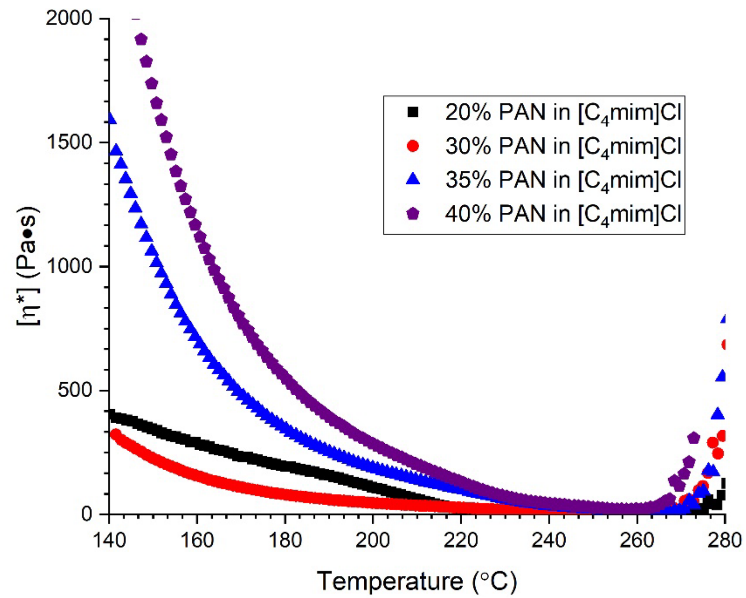
$[C_n mim]^+$ $[MPCNIm]^+$



Accomplishments and Progress: Demonstration of melt viscosity of PAN-IL composites

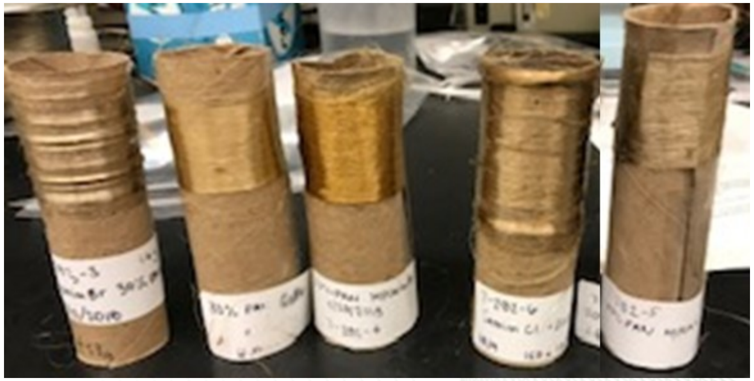
- Rheological properties of the PAN-IL composites can determine the "melt spinnability"
- Viscosity curves are a superposition of two different effects
  - Viscosity first decreases when the molecular activity is increased.
  - Viscosity increases when PAN begins to crosslink/cyclizes.
- As the carbon chain length is increased the initial viscosity is also increased.
- As the PAN concentration is increased for a given IL the viscosity also increases.





Accomplishments and Progress: Demonstration of Melt Spinning PAN Fiber

- Fiber spinning experiments were performed on a melt extruder
- Melt extruder is ideal for small sample sizes
  - 3-5 total grams of material
- Initial testing parameters are:
  - Rotor ≈ 150-160 °C
  - Header ≈ 150-170 °C
  - Rotational speed ≈ 90 RPM
  - Take up speed ≈ 60 ft/min
- 30 wt.% PAN in 5 different IL
  - [C_3mim]Br, [C_4mim]Br, [MPCNIm]Br, [C_4mim]Cl, [MPCNIm]Cl



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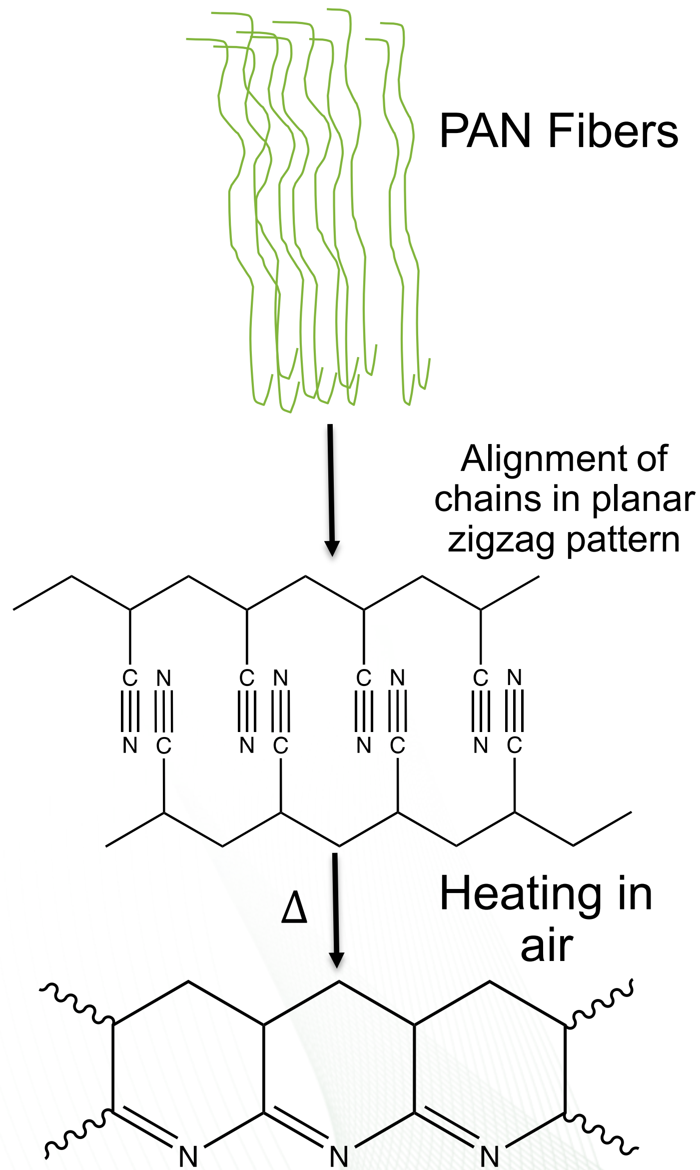
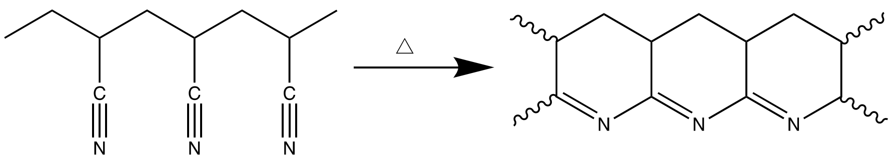
Understanding the Stabilization Process for PAN Fibers

- Stabilization of PAN fibers is the most time and cost consuming step for carbon fiber production.
- Stabilization utilizes a heat treatment in an oxidative environment with temperatures ranging from 200°C to 300°C.
- During stabilization, the washed PAN fiber undergoes a structural transformation where the linear polymer transitions into a rigid, thermally stable ladder structure.
  - Washing the PAN fibers removes the residual ionic liquid from the PAN.
  - Washing can remove and recover up to 80 wt.% of the original amount of ionic liquids.
- Stabilization has a strong influence on the mechanical properties of the resultant carbon fibers.

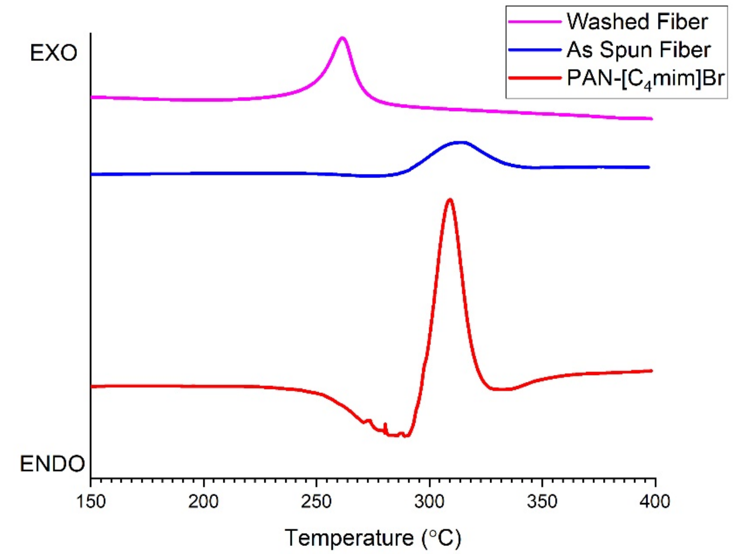


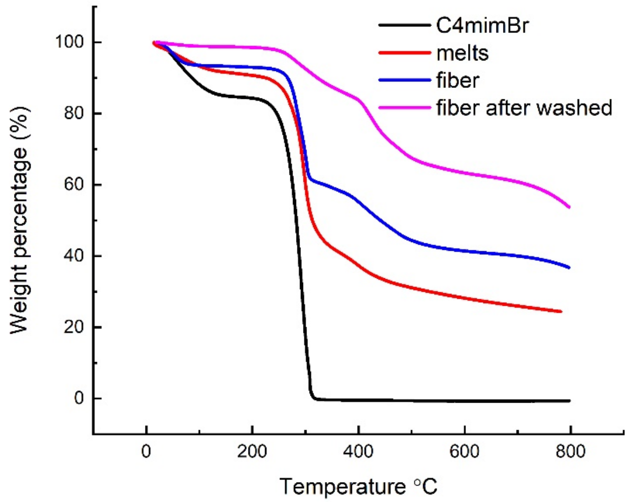
Accomplishments and Progress: Thermophysical Properties of PAN Fiber Precursors

- Stabilization process results in crosslinking and cyclization reactions that form a ladder-type structure.



- Cyclization of PAN macromolecules occurs at amorphous region first, then progresses to the crystalline phase.
  - Overlapping exothermic reactions
- DSC curves for the PAN fiber show a reduction in heat and widening of the distribution of heat emission which reduces oxidative destruction of the fibers
- Carbon yield increases from the melt to over 50 wt.% during stabilization.

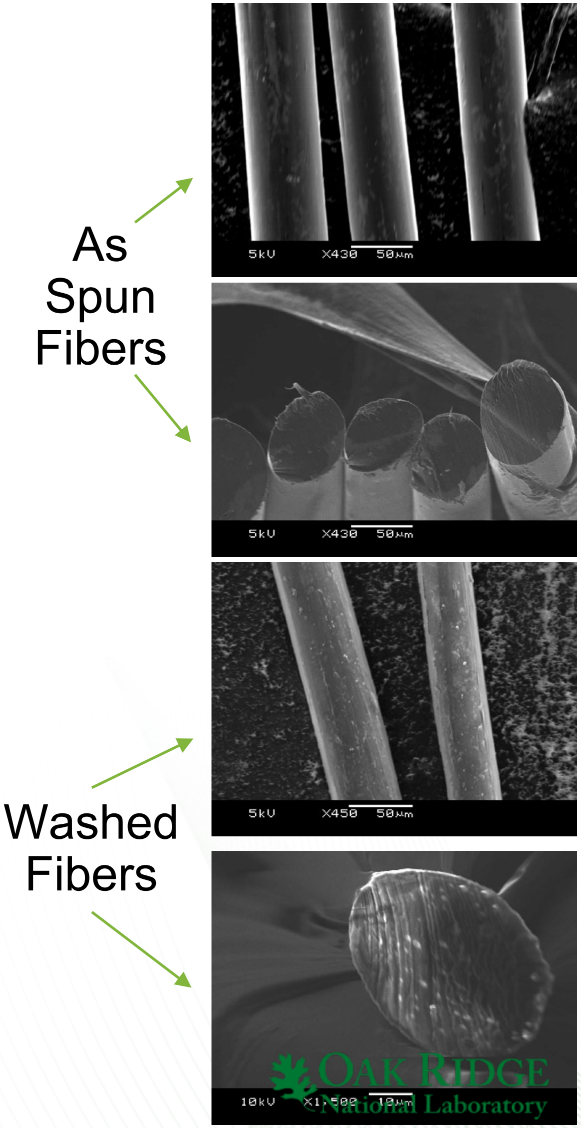




Accomplishments and Progress: Morphology of PAN Fiber Precursor

- Fiber from 30wt.% PAN in $[C_4mim]Br$

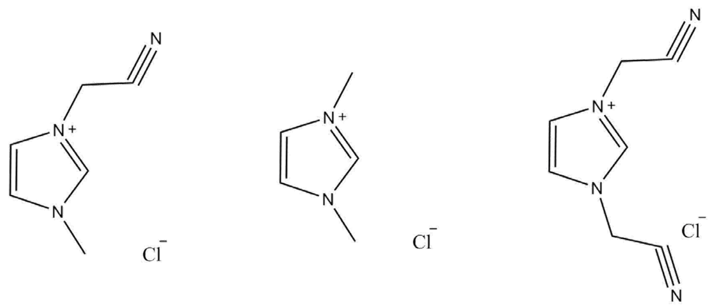
- Fiber drawing is not only responsible for the chain alignment but for the morphology of the fiber.
- Both surface and sub-surface morphology can affect the tensile strength.
- Surface of fibers are relatively smooth and the cross sections do not reveal any voids or defects.
- Diameters for as spun fiber precursors are comparable to literature values
- Commercial CF has a diameter range of 5-20 μm.



Ionic liquid	PAN (%)	As Spun Diameters (μm)	Washed Fiber Diameters (μm)
$[C_3mim]Br$	30	56.2 +/- 0.16	53.4 ± 7.6
$[C_4mim]Br$	30	56.8 +/- 0.20	45.6 ± 7.9
$[C_4mim]Cl$	30	54.7 +/- 0.08	45.3 ± 8.7
[MPCNIm]Br	30	59.6 +/- 0.25	47.9 ± 14.1
[MPCNIm]Cl	30	53.4 +/- 0.17	48.6 ± 10.4

Scale-up of the IL production
Initial cost assessment

- ILs as plasticizers will still dominate the global IL market[1]
  - Key driver: low production cost
- Statistical mixtures of best performing IL(s) advantages:[2]



  - Prepared *in situ* from aqueous, readily available, cheap raw materials
  - Increase of nitrile functionality sites, which could enhance the plasticization effect
  - Potential environmental benefit (reducing the use of VOCs)
  - Cost advantage: \$3.5/kg / \$1.62/lb (for the IL statistical mixture shown here)

IL statistical mixture synthesis	Raw material	Cost per metric ton	Cost per kg
One pot synthesis	Formaldehyde (37% aqueous solution)	\$400 (Alibaba)	\$0.251
	2-chloroethylamine	\$450 (Alibaba)	\$0.271
	Methylamine (40% aqueous solution)	\$1,935 (molbase)	\$1.166
	Hydrochloric acid (37% aqueous solution)	\$88 (ICIS)	\$0.535
	Glyoxal (40% aqueous solution)	\$1,000 (Alibaba)	\$1.122
Purification (optional)	Ethyl Acetate	\$978 (molbase)	\$1.210
Nitrile functionalization	Sodium cyanide	\$2,450 (Kemcore)	\$0.171
Total			**\$3.516**

1. "Technology Advancement in Ionic Liquids", Frost and Sullivan February 2016.
2. Rogers, R. D.; Daly, D. T.; Gurau, G. Methods for Dissolving Polymers using Mixtures of Different Ionic Liquids and Composition Comprising the Mixtures PCT Int. Appl. (2011), WO 2011056924 A2 20110512, US 2019/0040209 A1.

Responses to Previous Year Reviewers' Comments

This project was not reviewed last year.

Collaboration and Coordination

Project Team

Dr. Sheng Dai
Oak Ridge National Laboratory
Ionic liquids, carbon materials, and their energy-related applications, responsible for the overall project.

Dr. Huimin Luo
Oak Ridge National Laboratory
Responsible for synthesis of Ionic liquids and prepare of PAN melts

Dr. Halie Martin
University of Tennessee-Knoxville
Postdoctoral Research Associate responsible for polymer characterization and melt spinning

Dr. Richard T. Mayes
Oak Ridge National Laboratory
Carbon materials and their energy-related applications

Dr. Amit Naskar
Oak Ridge National Laboratory
Carbon materials and their energy-related applications

Dr. Gabriela Gurau
525 Solutions, Inc.-subcontract
responsible for technoeconomic analysis and scale-up



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Remaining Challenges and Barriers

- Investigation how the molecular structures of ILs dictate plasticizing interactions with PAN.
  - Ionic liquids with higher nitrile component lead to increased plasticizing interactions with PAN
    - New targeted anions including ($C(CN)_3^-$)
- Study how the chemical interactions of ILs with PAN can be used to control the cyclization degree in unique ladder structures
  - Demonstrate and understand the mechanical properties of as-spun fibers and fibers washed with water.
- Integrate the information gained from the above tasks to develop IL-assisted melt spinning systems.
  - Increase in the PAN concentration for melt spinning will lower the cost and increase mechanical properties

Proposed Future Work

- Remainder of FY19
  - Demonstrate tensile properties of the PAN fibers (ORNL)
  - Investigate alternate sources of PAN and synthesize new ionic liquids (ORNL)
  - Perform technoeconomic analysis of IL production to identify synthetic inefficiencies and cost drivers (525 Solutions)
- Into FY20
  - Maintain melt viscosity for at least 10 minutes during spinning trials (ORNL)
  - Demonstration of filament diameter of ~20 micrometer after carbonization (ORNL)
  - Perform technoeconomic analysis of scale-up (525 Solutions)
  - Scale-up IL to >1 kg production for IL to realize anticipated decreased cost (ORNL)
- Commercialization: Highly engaged with potential licensees; high likelihood of technology transfer because of significant cost reduction benefits and equipment compatibility.

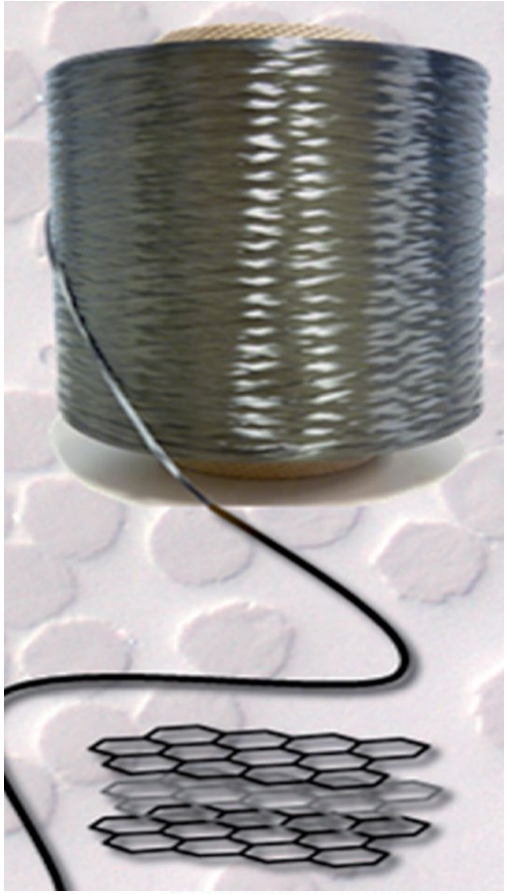
Any proposed future work is subject to change based on funding levels

Technology Transfer Activities

- The patent “Melt Spinning Process of PAN Fibers Based on Task-Specific Ionic Liquids” in preparation.
- Because significant cost reduction benefits and equipment compatibility of this project, potential licensees are highly engaged which may result in likelihood of technology transfer.

Summary: Progress and Accomplishments

- The melting temperature of PAN has been demonstrated to be suppressed by over 100 °C by the addition of ionic liquids.
    - Ionic liquids containing chloride anions had a greater effect on the decrease in melting temperatures.
    - Lower production temperatures decreases cost of carbon fiber production.
- Demonstrated the ability to successfully melt spin uniform and homogeneous PAN fibers.
    - Utilizing benchtop melt extruders allows us to determine the processability before scaling up.
    - Surface of fibers are smooth and without defects.
- Preliminary experiments show that the PAN fibers can be stabilized at lower temperatures with carbon yields > 50 %.



Angew. Chem. Int. Ed. **2014**, *53*, 5262 – 5298

Acknowledgements

U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE) (Program Manager: Bahman Habibzadeh)