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

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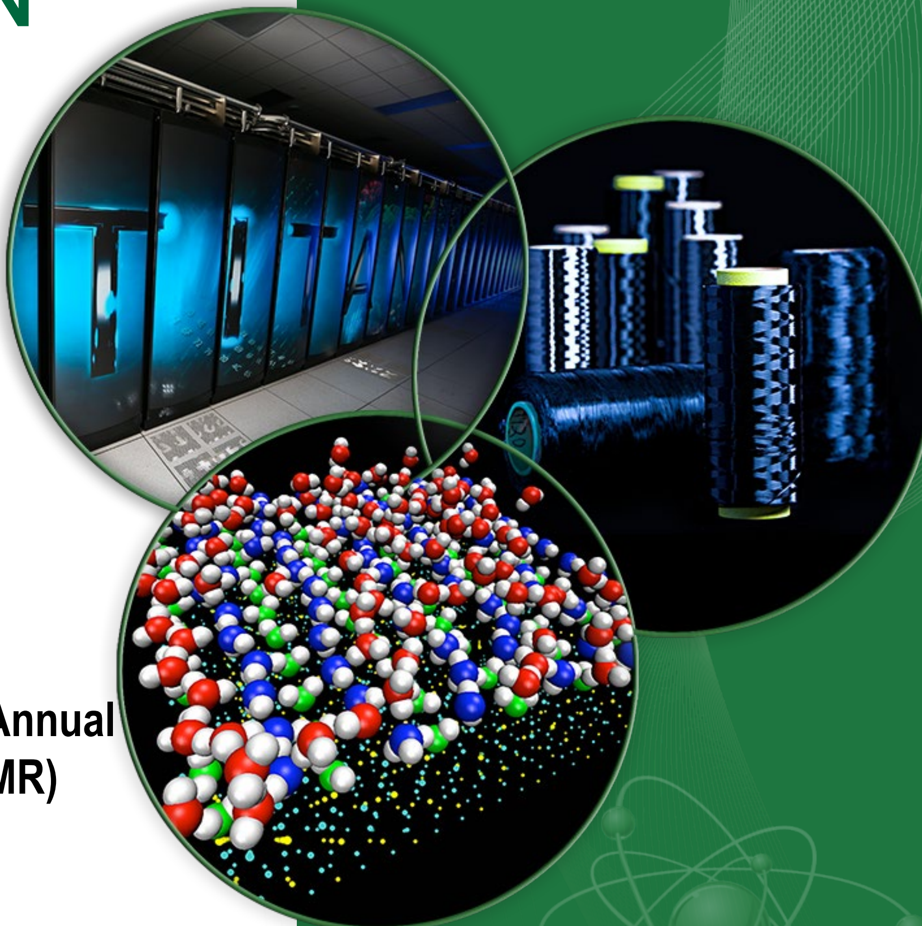

2020 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting (AMR)

May 21, 2020 **Project ID: ST148**

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Overview

Timeline

- Project Start Date: 10/01/17
- Project End Date : 9/30/20
- Percent Complete: 78%

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

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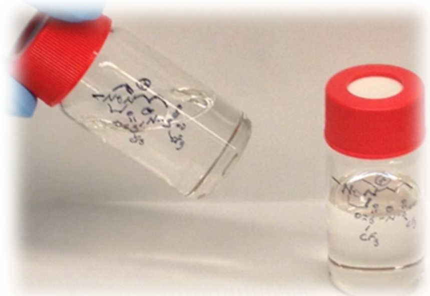
Relevance

- Main 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). During the second year of this project (current reporting year), we have accomplished:
  - Down selection of IL for plasticization
  - Demonstration of melt spinning of PAN fibers based on ILs
  - Technoeconomic analysis for scale-up of the IL production

- 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)



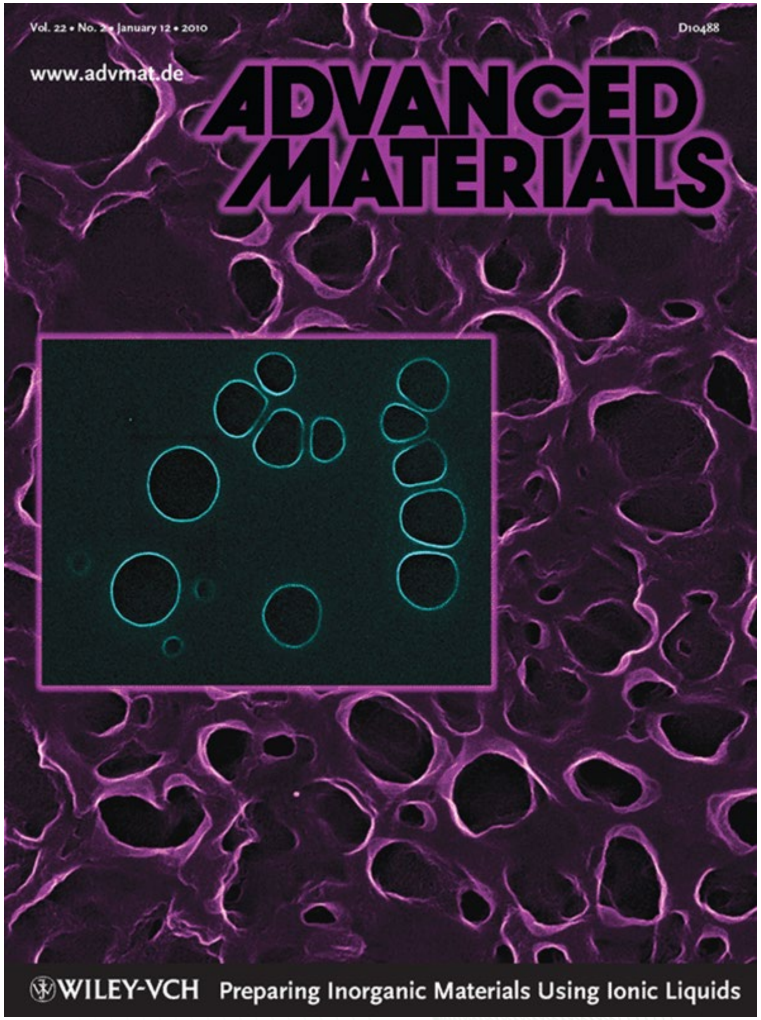
Approach

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

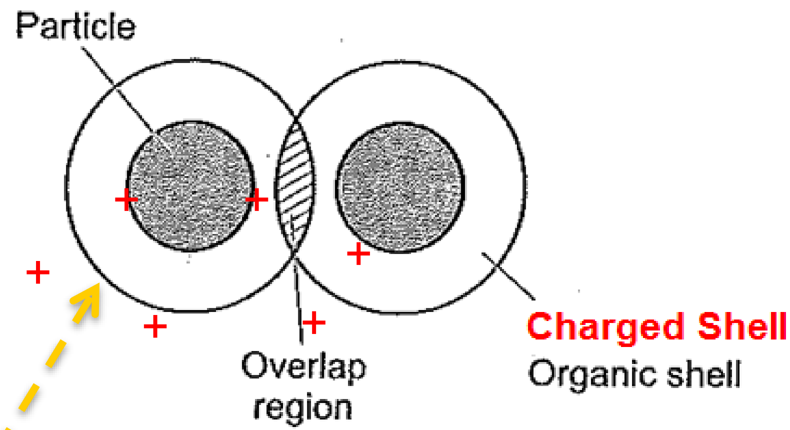


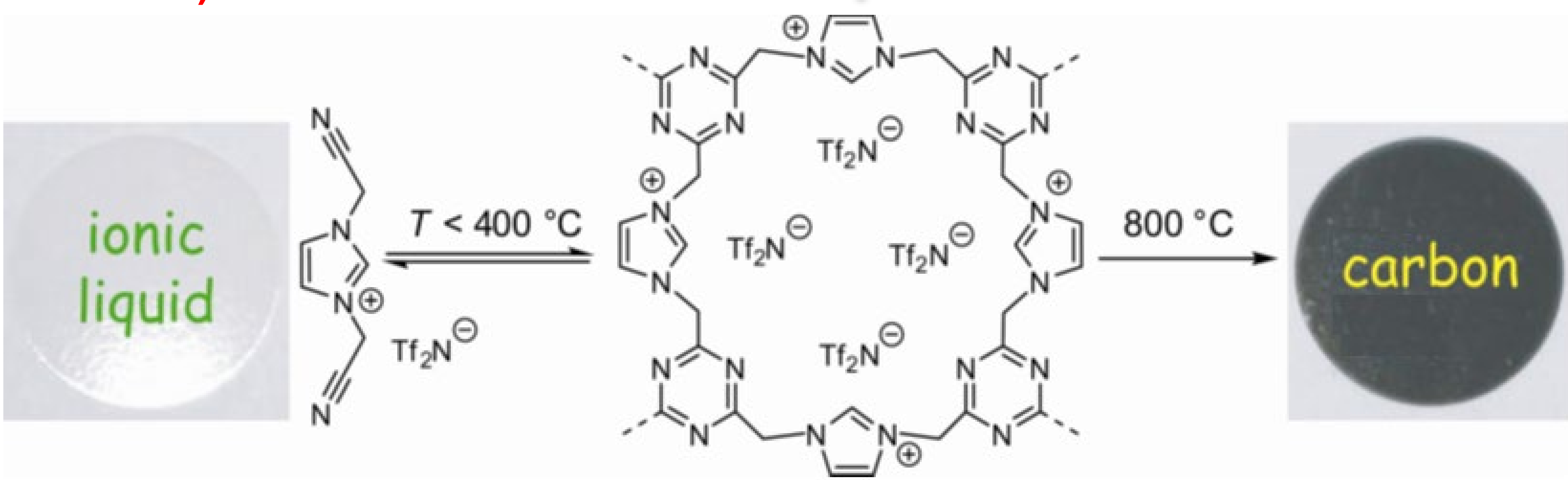
Ma, Yu, Dai, *Adv. Mater*. 2010, *22*, 261

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. M. Luo, G. A. Baker, S. Dai, *J. Am. Chem. Soc.*, 2009, *131*, 4596.

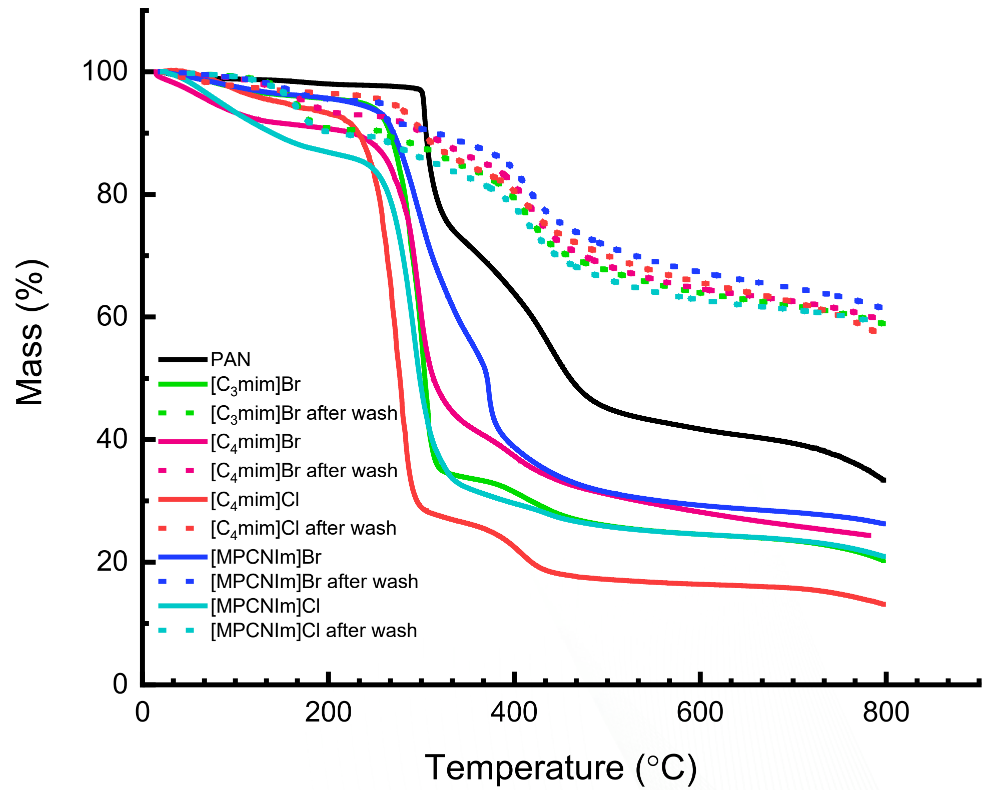
X. Q. Wang, S. Dai, *Angew. Chem. Int. Ed.* 2010, *49*, 6664.

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	100%
– 2.2 Demonstration of melt spinning of PAN fibers based on ILs	100%
– 2.3 Technoeconomic analysis for scale-up of the IL production	100%
– Go/No-Go Point #2: Demonstration of tensile properties of resultant fibers	100%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	50%
– 3.2 Scale-up IL to >1 kg production for IL to realize anticipated decreased cost	50%
– 3.3 Demonstration of filament diameter of ~20 micrometer after carbonization	60%
– 3.4 Demonstration of melt spinning with recycled ionic liquids	0%

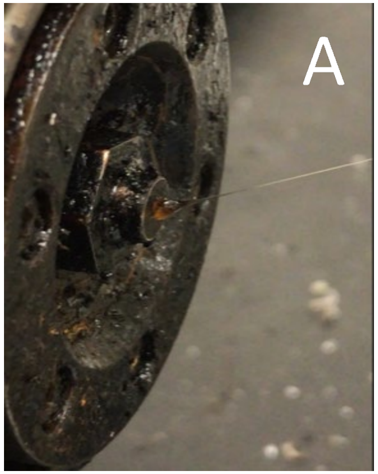
Accomplishment: Down selection of IL for plasticization

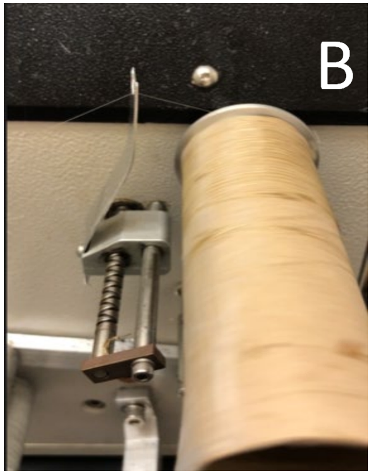
- PAN-IL composites were investigated by TGA.
  - Illustrates the thermal stability
  - Quantifies carbon yield
- Adding ILs to PAN originally decreases the carbon yield.
  - Proves IL disrupts PAN chain alignment
- Recycling or Removal of ILs results in the increase of carbon yield and likely linked to the crosslinking pathway change.
- ILs containing bromide anions have higher carbon yields.

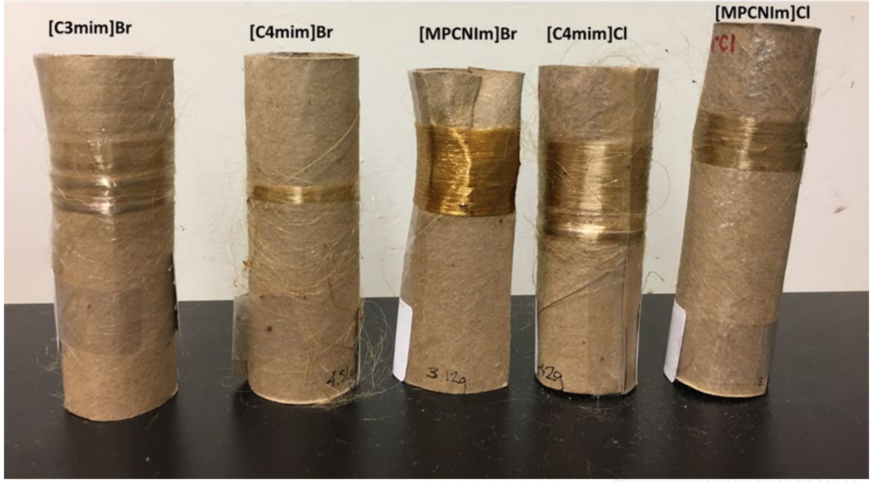


Accomplishment: Demonstration of Melt Spinning PAN Fiber Based on ILs

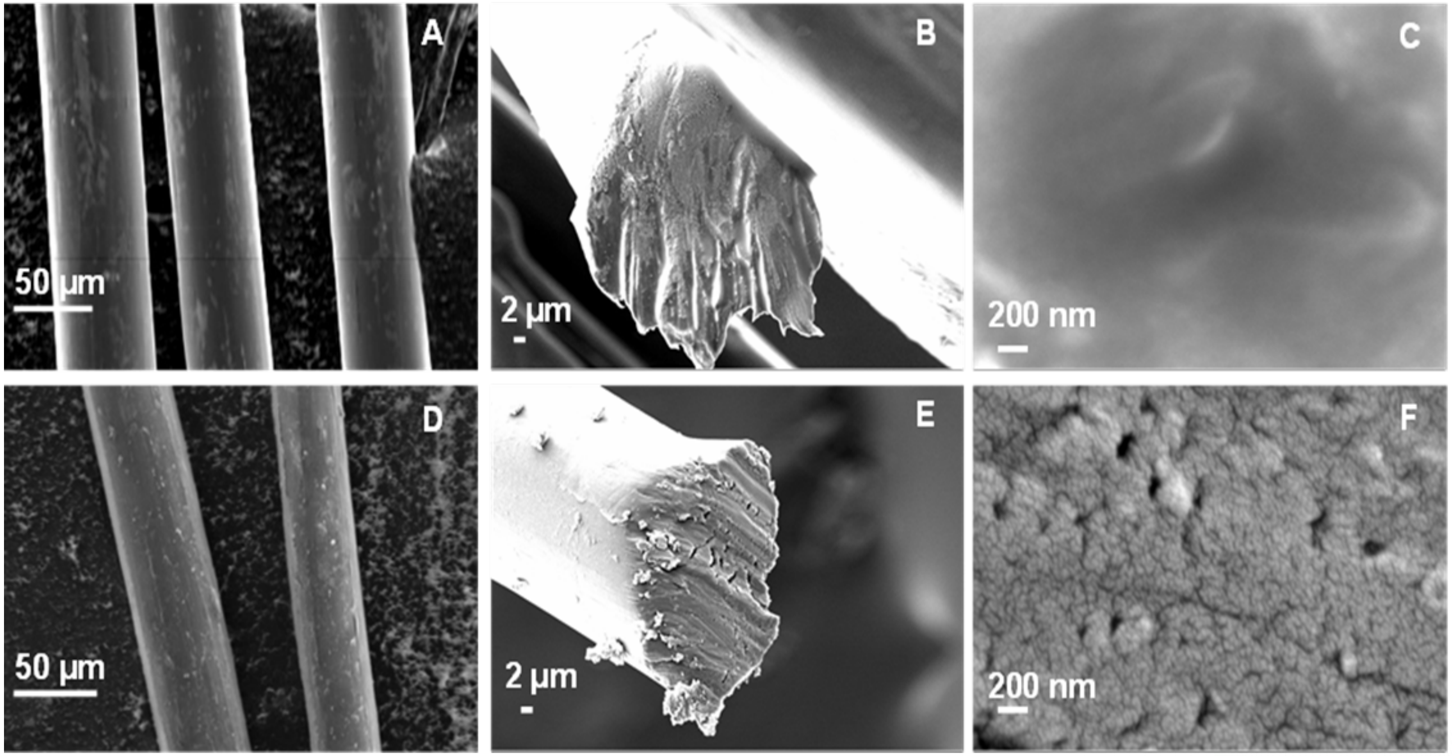
- Fiber spinning experiments were performed on a melt extruder
- Melt extruder is ideal for small sample sizes
  - 3-5 total grams of material
- Initial testing parameters are:
  - Rotor ≈ 150-160 °C
  - Header ≈ 150-170 °C
  - Rotational speed ≈ 90 RPM
  - Take up speed ≈ 60 ft/min
- 30 wt.% PAN in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







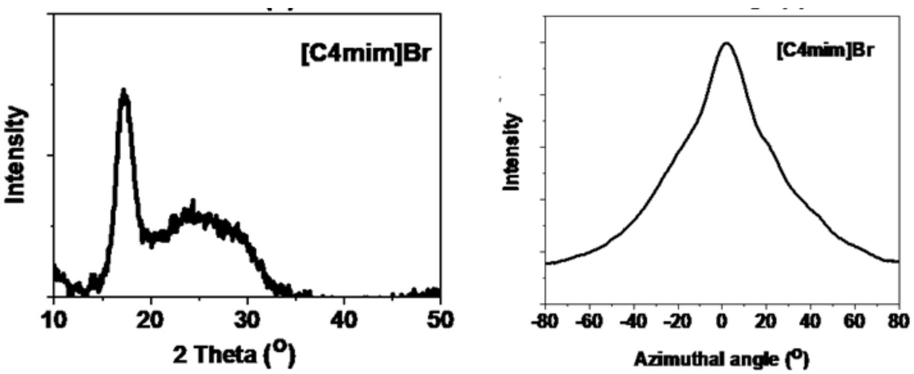
Accomplishment: Morphology/Size of PAN Fiber Precursor (SEM)



High resolution SEM images of A) as spun PAN fiber from PAN-[C_4mim]Br composite, B, C) cross section of as spun fiber, D) PAN fiber after washing, and E, F) cross section of washed fiber

Accomplishment: Morphology/Size of PAN Fiber Precursor (XRD)

Fiber Sample	Crystallinity (%)	Crystal size (nm)	Crystalline orientation (%)
[C_3mim]Br	63.4	11.45	74
[C_4mim]Br	63.1	7.86	78
[C_4mim]Cl	49.3	7.11	70
[MPCNIm]Br	38.9	8.08	81
[MPCNIm]Cl	61.9	9.66	75

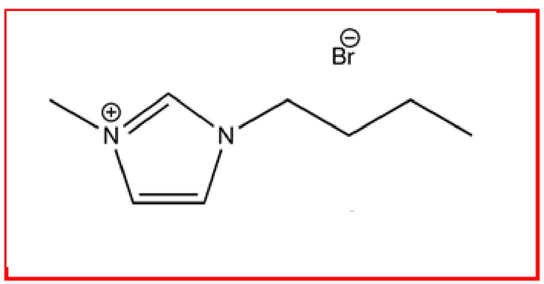


XRD results of as-spun PAN-[C_4mim]Br

- The XRD patterns and calculated structural data (crystallinity, crystal size and crystalline orientation) of the as-spun PAN-IL fibers containing [C_3mim]Br, [C_4mim]Br, [MPCNIm]Br, [C_4mim]Cl, and [MPCNIm]Cl have been performed and results are summarized in above table. One example with [C_4mim]Br is shown in above figure.
- The crystallinity order: [C_3mim]Br ≈ [C_4mim]Br > [MPCNIm]Cl > [C_4mim]Cl >[MPCNIm]Br
- The crystal size order: [C_3mim]Br > [MPCNIm]Cl > [MPCNIm]Br > [C_4mim]Br > [C_4mim]Cl
- Thus, the PAN-[C_4mim]Br fiber showed the almost highest crystallinity and the second smallest crystal size.

Accomplishment: Comparison of 30% PAN in $[C_4mim]Br$ melt spun fiber properties resulting from Atlas and the single-shot apparatus with 100 µm die

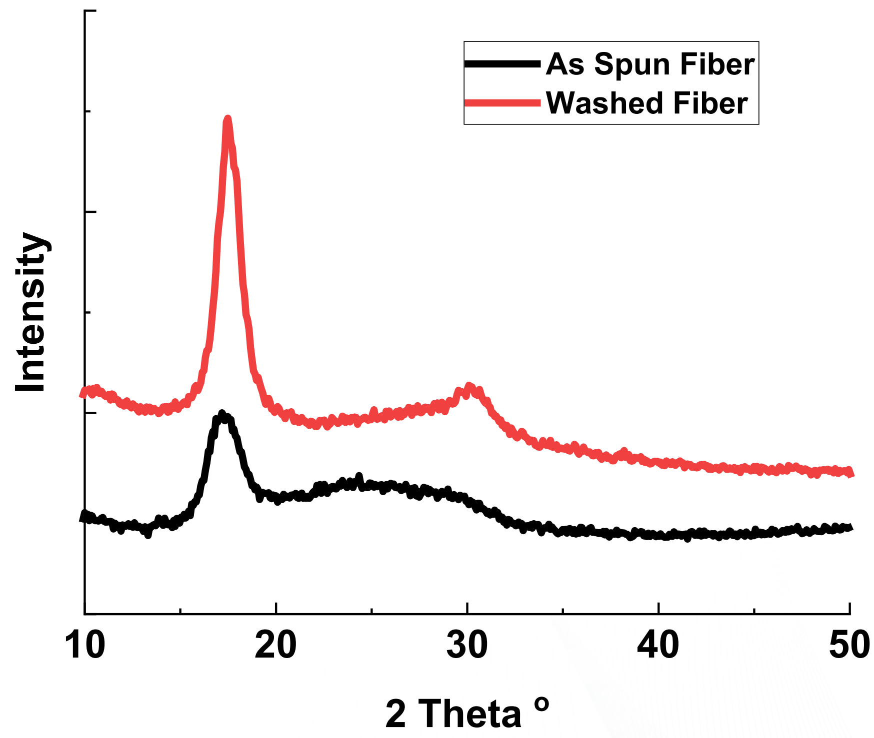
A single-shot extruder based on simple plunger and barrel assembly (Alex James & Associates Fiber) appointed with a 100 µm aperture is used to melt spin PAN/$[C_4mim]Br$ composite . The melt was pressurized through the 100 µm die by a screw-driven press. The resulting monofilament was taken up on an analogue winding unit. Winder unit take up speed was increased until the fiber became unstable and broke, then slightly reduced in speed to stability and maintained for the duration of the extrusion. The as-spun fibers were then subjected to a post-spinning draw and washing step using a set of two rollers and a draw ratio of 2x ($V_{r2}=2V_{r1}$) which stretched the fibers through a boiling DI water bath.



30% PAN in C4mimBr	As-spun fiber		Washed fiber	
	Atlas (1/8 inch)	100 micron die	Atlas (1/8 inch)	100 micron die
Ultimate tensile strength (MPa)	68	88.3	110	248
Elastic modulus (MPa)	2700	2100	6000	8900
Extension (%) at break (mm/mm)	75	87.4	45	12.7
Diameters (µm)	56.8	36.8	45.6	22.0

Accomplishment: Morphology/Size of PAN Fiber Precursor (XRD)

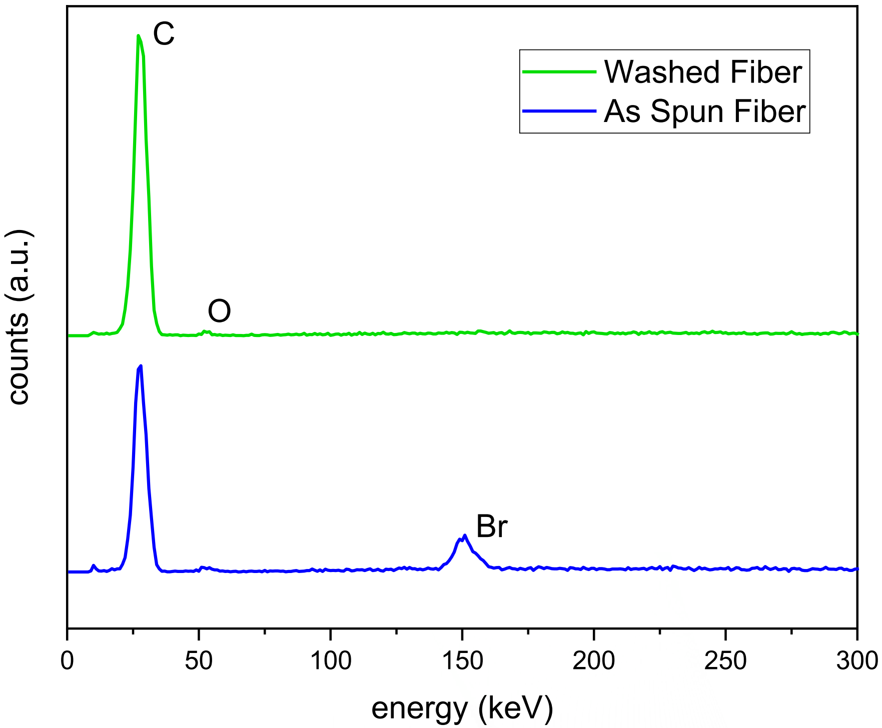
- Structures of the as-spun PAN-[C_4mim]Br and washed fibers produced with single-shot apparatus (100 µm die) were investigated by XRD.
- The removal of ILs slightly influences the crystallinity and crystal size of the PAN fibers. The as-spun fiber showed 43.9% crystallinity with 8.8 nm crystal size. Washing increased crystallinity to 69.9% and crystal size to 9.5 nm.

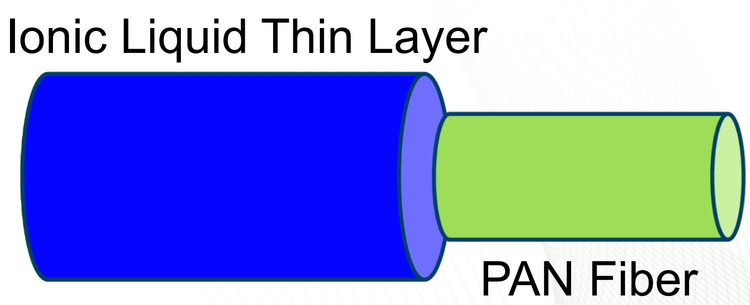


XRD results of as-spun PAN-[C_4mim]Br and washed fibers

Accomplishment: Elemental Composition of PAN Fiber Precursor Surface by EDS

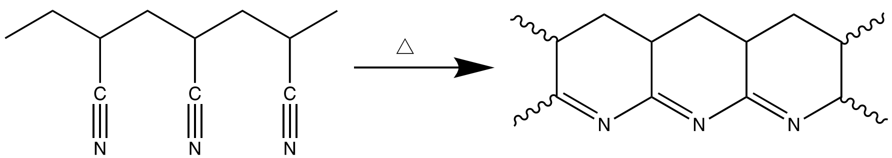
- EDS characterizes the elemental composition of the surface of the fibers.
- As spun fiber have a thin coating of ionic liquids on the surface.
  - Denoted by a bromide or chloride elemental response.
- Washed fibers show no evidence of IL on surface
  - Accounts for the smaller fiber diameters.

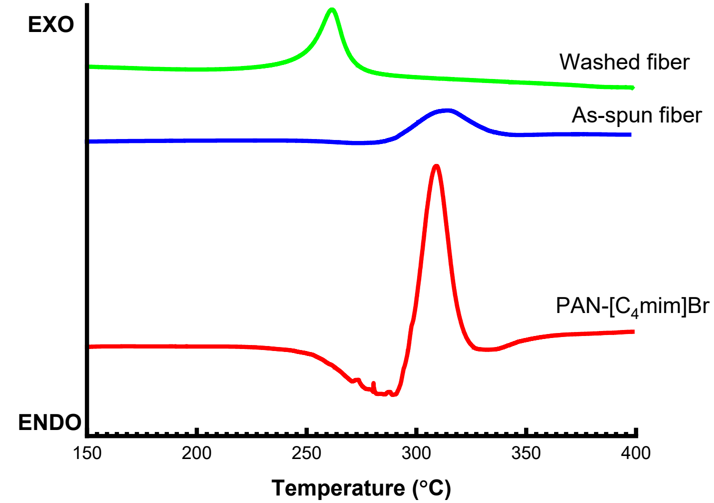




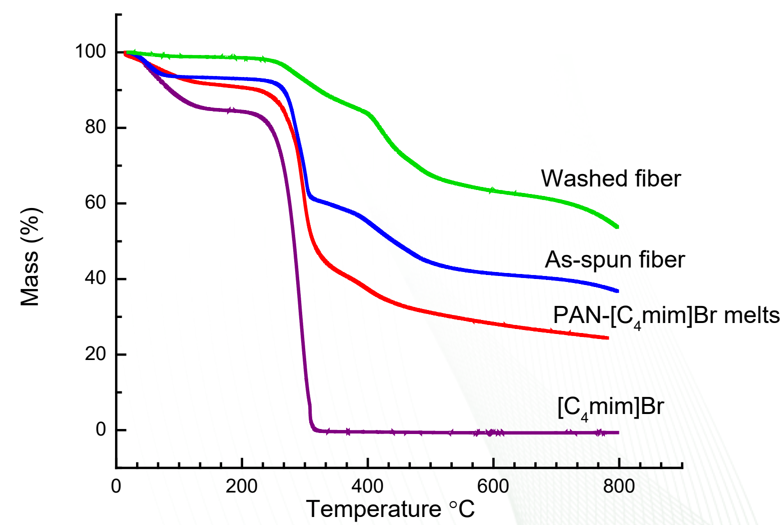
Accomplishment: PAN Fiber Precursors Characterization

- DSC shows the as-spun fiber exhibits a smaller, wider exotherm compared to composite.
  - DSC of washed PAN fibers elude to stabilization process





- Carbon yield increases from the melt to over 50 wt.% for the washed PAN fibers.
  - Higher carbon yield indicates an increase in crystallinity
  - Weight loss intervals correspond to stabilization process and low temperature carbonization



Ionic liquid	PAN (%)	Carbon yield (%)		
		Melt	As Spun Fiber	Washed Fiber
PAN	100	33.4	31.4	----
C_3Br	30	20.6	44.4	53.7
C_4Br	30	24.4	36.8	53.8
C_4Cl	30	13.1	29.3	45.0
CNBr	30	26.5	38.4	58.5
CNCl	30	21.0	33.1	52.2

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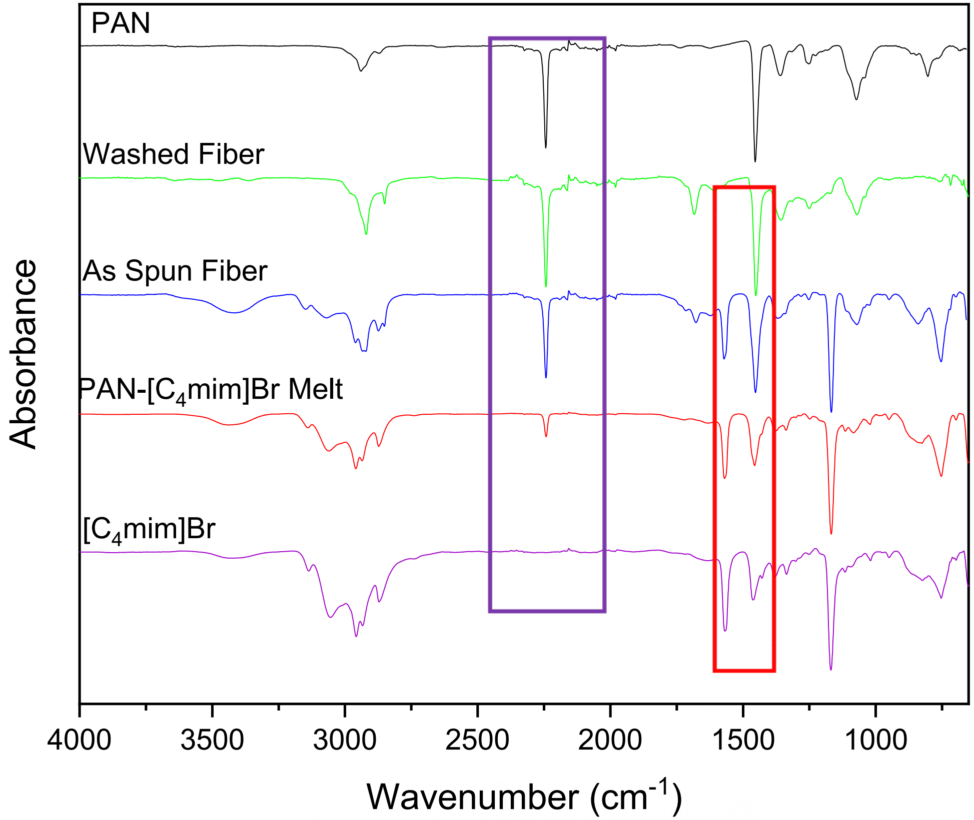
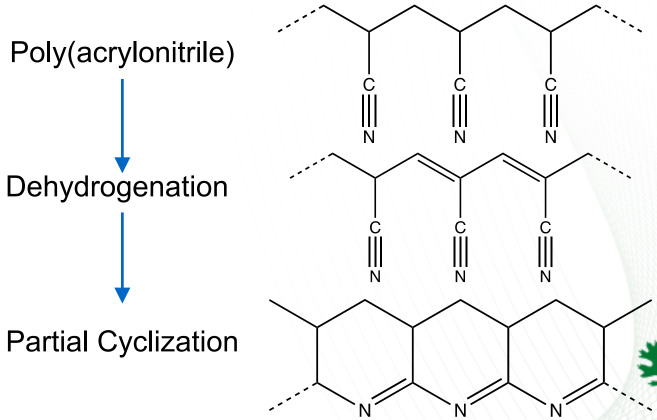
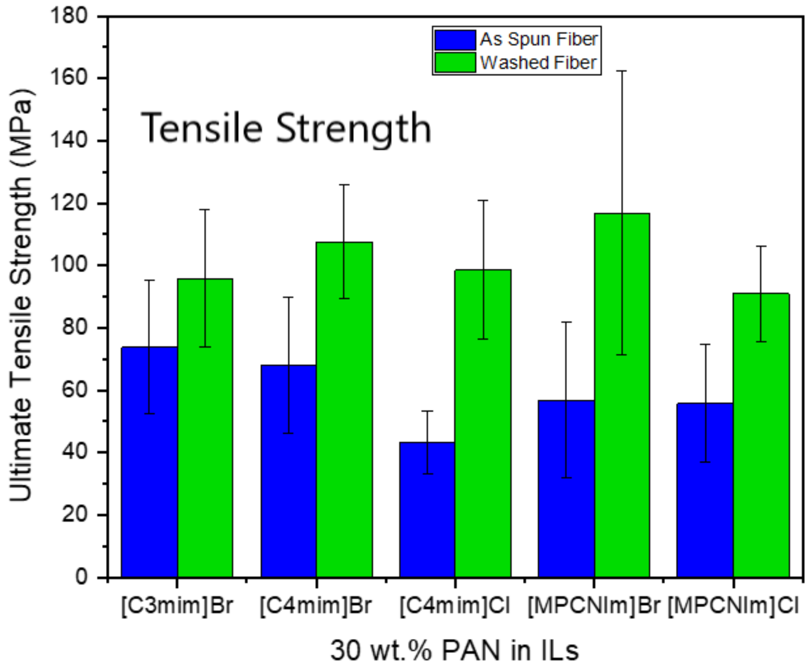
Accomplishment: Functional Group Characterization of Fibers

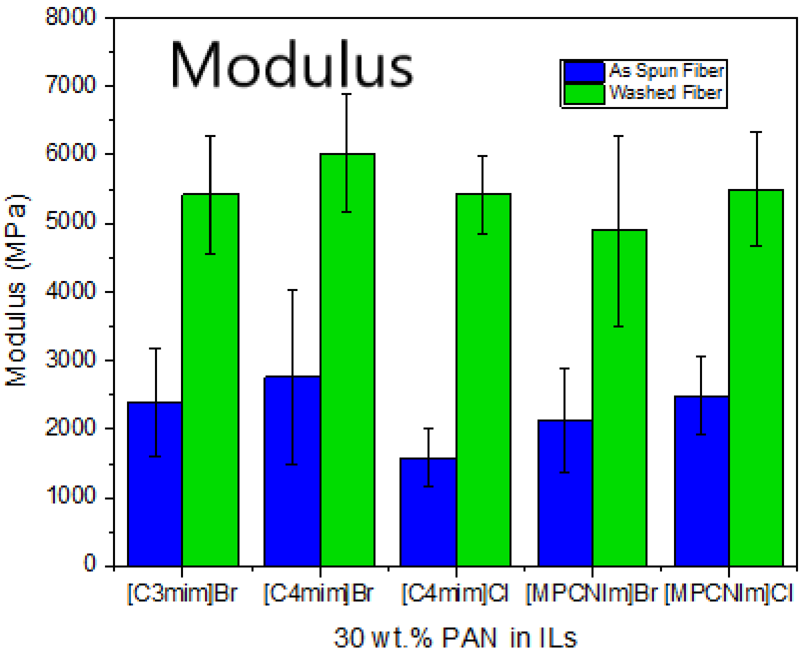
- FTIR was used to analyze the functional groups of PAN through out the fiber processing.
- PAN has a dominate IR band at 2240 cm^{-1} → C≡N stretching modes.
  - Intensifies throughout the fiber spinning process.
  - C≡N neighbor distance decreases
- As-spun fibers and washed fibers have formation of 2 new IR bands.
  - 1610 cm^{-1} → C=C and C=N vibrations, N-H stretching
  - 1680 cm^{-1} → C=O bending (oxygen uptake)
- ***PAN fibers are partially cyclized!***





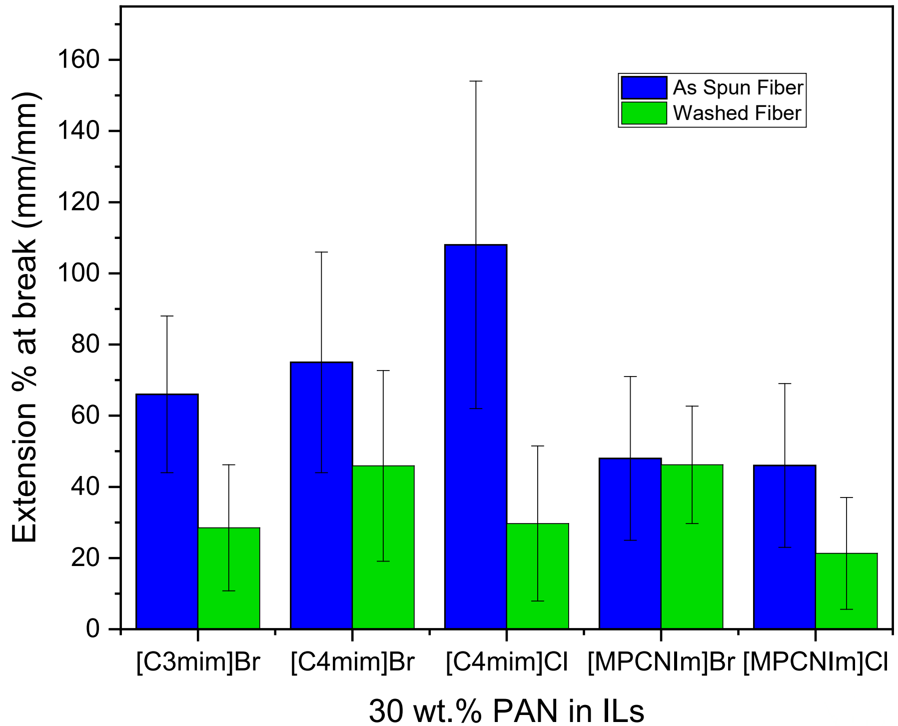
Comparison in Mechanical Performance of As-Spun Fiber and Washed Fiber





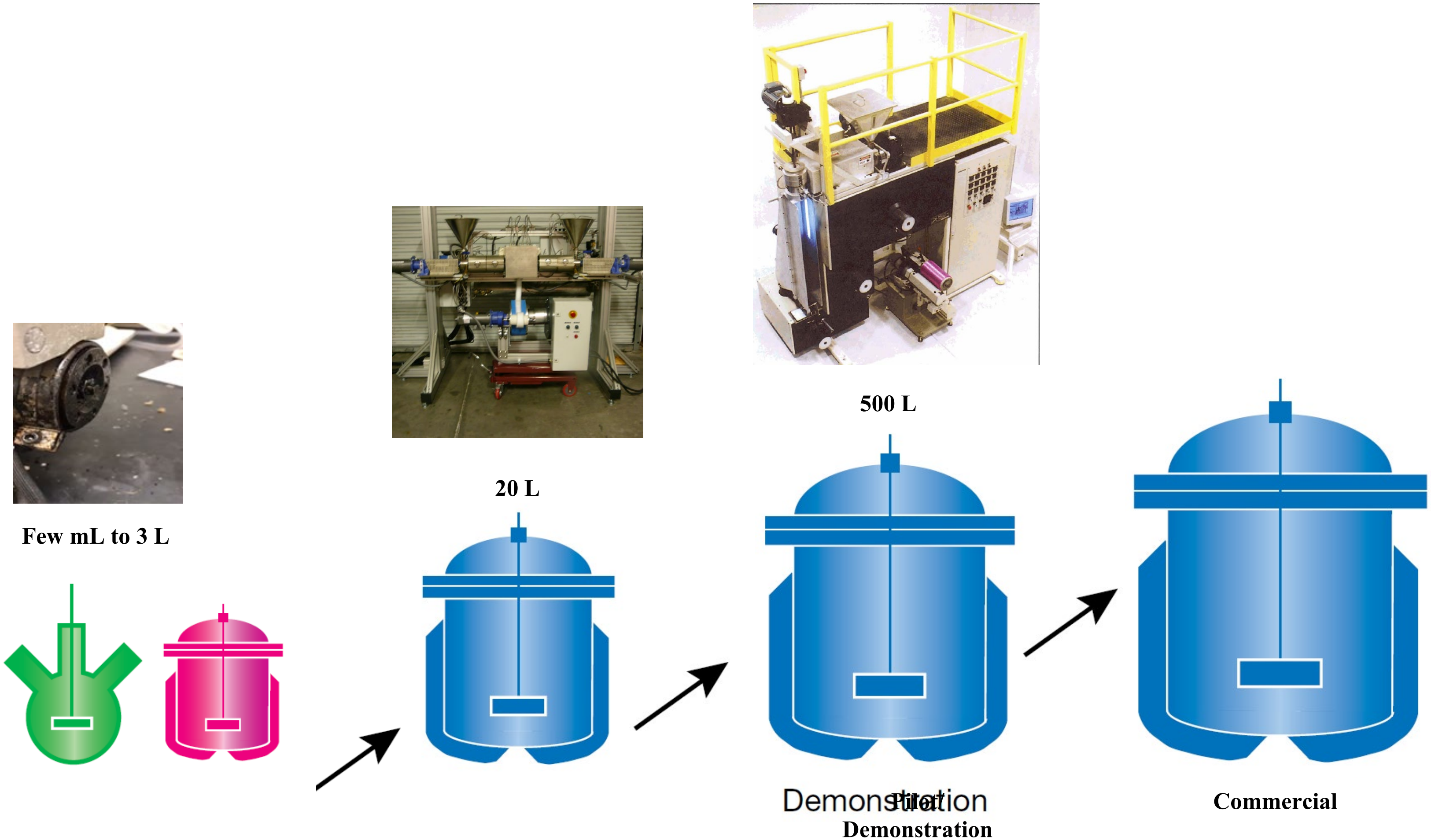
- Tensile strength is the stress needed to break a sample.
  - Tensile strength increases with the removal of ILs from fibers.
  - Amorphous regions dominate structure in as-spun fibers
- The modulus shows the rigidity/stiffness of fibers.
  - The modulus increases with the removal of the ILs form the fibers.
  - Comparative to literature values for PAN precursors

Mechanical Performance of PAN Fiber Precursors-Elongation



- The as spun fibers are able to be stretched or elongated upwards of 100% of its original length.
  - Ionic liquids are acting as a lubricant stretching the amorphous region of the polymer chains.
- Removal of ILs result in a decrease in fiber extension.
- *Fibers are in favor of stretching or drawing while in the presence of ILs.*

Technology scale-up stages



(adapted from *AIChE*, March 2015, 58)

Preliminary Scale-up Cost Analysis

	Year 1		Year 2		Year 3		Year 4	
Production Runs Per Day		*4*		*2*		*2*		*2*
Operating Days Per Year		*280*		*280*		*280*		*280*
Reactor Per Run, L		**20**		**500**		**500**		**500**
Ionic Liquid Per Run, kg		14.00		350.00		350.00		350.00
PLA Per Run, kg		6.00		150.00		150.00		150.00
Ionic Liquid Loss, kg/run		0.05		1.16		1.16		1.16
Daily Energy Used, kWh		100.00		2,500.00		2,500.00		2,500.00
PLA Cost, $/kg	$	5.00	$	3.00	$	3.00	$	3.00
Ionic Liquid Cost, $/kg		$10.00		$7.00		$7.00		$7.00
Energy Cost, $/kWh	$	0.14	$	0.14	$	0.14	$	0.14
Ionic Liquid Replinishment Cost, $/run	$	0.46	$	8.09	$	8.09	$	8.09
PLA Cost, $/run	$	30.00	$	450.00	$	450.00	$	450.00
Daily Energy Cost, $	$	14.00	$	350.00	$	350.00	$	350.00
Production Per Run, kg		**5.0**		**125.0**		**125.0**		**125.0**
Annual PLA Cost	$	33,600.00	$	252,000.00	$	252,000.00	$	252,000.00
Annual Ionic Liquid Cost	$	517.44	$	4,527.60	$	4,527.60	$	4,527.60
Annual Energy Cost	$	15,680.00	$	196,000.00	$	196,000.00	$	196,000.00
Annual Production, kg		**5,600.0**		**70,000.0**		**70,000.0**		**70,000.0**
Annual Production Cost, $	$	38,037.44	$	354,527.60	$	354,527.60	$	354,527.60
Production Cost, $/kg	**$**	**6.79**	**$**	**5.06**	**$**	**5.06**	**$**	**5.06**

525 SOLUTIONS

Assumptions

- IL and PAN costs are @ ton scale
- The IL used for the preliminary cost analysis is [C_4mim][Br] (the best performing IL to date)
- The operating schedule is 280 days/year
- The production cost include only the direct costs associated with PAN/IL dope preparation and IL recycle (process inputs, IL, water, PAN and energy cost)
- Optimization of all parameter at a smaller scale (20 L) is needed to get a more accurate sensitivity analysis to build a 500 L continuous fiber extrusion plant
- Operating expenses, equipment, and depreciation will be included in a final proforma

Responses to Previous Year Reviewers' Comments

- "It is not clear how any residual IL in carbon fiber might affect its mechanical properties."
  - The related information has been provided in slides 16 and 17.
- "Recommendations include that the project team (1) needs a comprehensive cost model, and of particular concern is the time required to wash the fiber"
  - 525 Solutions performed a comprehensive cost model in slides 18, 19, and 20. Based on 525 Solutions' experience with fiber spinning from IL solutions, while the fiber wash step is critical to the overall process, the contact time at larger scale can be significantly decreased by increasing the washing bath temperature, or adding a counter current flow column that would allow the ILs to be washed off the fiber fast without compromising fiber's morphology and strength.
- "The approach of the technoeconomic analysis needs to change to focus on the cost of the PAN fibers or the carbonized fiber, using traditional PAN as a baseline. Determining the cost of the IL alone does no good in determining whether using ILs results in cost savings."
  - 525 Solutions performed a comprehensive cost model in slides 18, 19, and 20. The model include costs associated with PAN fiber production. The final proforma will include the estimated OPEX associated with the final carbon fiber production.
- "The project team should delete the TechPAN work and concentrate on melt spinning of commercial PAN."
  - While we did not focus on TechPAN this year following the reviewer's opinion, we still think that TechPAN work is important and would like to collaborate with Dr. Metthew Weisenberger at University of Kentucky.

Collaboration and Coordination

Project Team

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Ionic liquids, carbon materials, and their energy-related applications

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Oak Ridge National Laboratory
Ionic liquids and their energy-related applications

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University of Tennessee-Knoxville
Postdoctoral Research Associate responsible for polymer characterization

Dr. Richard T. Mayes
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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.
Ionic liquids and their scale-up synthesis






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 by 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

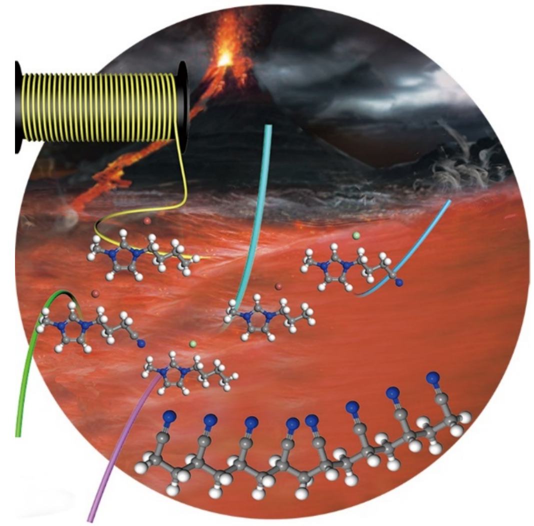
Proposed Future Work

- Remainder of FY20
  - Investigate properties of recycled ionic liquids (ORNL)
  - Investigate if IL can be used with a small amount of water or not
  - Technoeconomic analysis of IL production identifying synthetic inefficiencies and cost drivers (525 Solutions)
- Into FY21
  - Demonstrate melt spinning with recycled ionic liquids (ORNL)
  - Demonstration of filament diameter of ~20 micrometer after carbonization (ORNL)
  - Scale-up IL to >1 kg production for IL to realize anticipated decreased cost (525 Solutions and ORNL)
  - Technoeconomic analysis of scale-up (525 Solutions)
- 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

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.
  - Lower production temperatures decreases cost of carbon fiber production.
- 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 %.



A novel plasticized melt-spinning process to replace the current solution spinning process based on nonvolatile task-specific ionic liquids

Martin, H. J.; Luo, H. M.; Chen, H.; Do-Thanh, C. L.; Kearney, L. T.; Mayes, R.; Naskar, A. K.; Dai, S. Effect of the Ionic Liquid Structure on the Melt Processability of Polyacrylonitrile Fibers, *ACS Appl. Mater. Interfaces*, **2020**, *12 (7)* 8663, DOI: 10.1021/acsami.9b19704.

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Acknowledgements

U.S. DOE Office of Energy Efficiency and Renewable Energy (EERE) Hydrogen Fuel R&D, Fuel Cell Technologies Office (Program Manager: Ned T. Stetson and Bahman Habibzadeh)