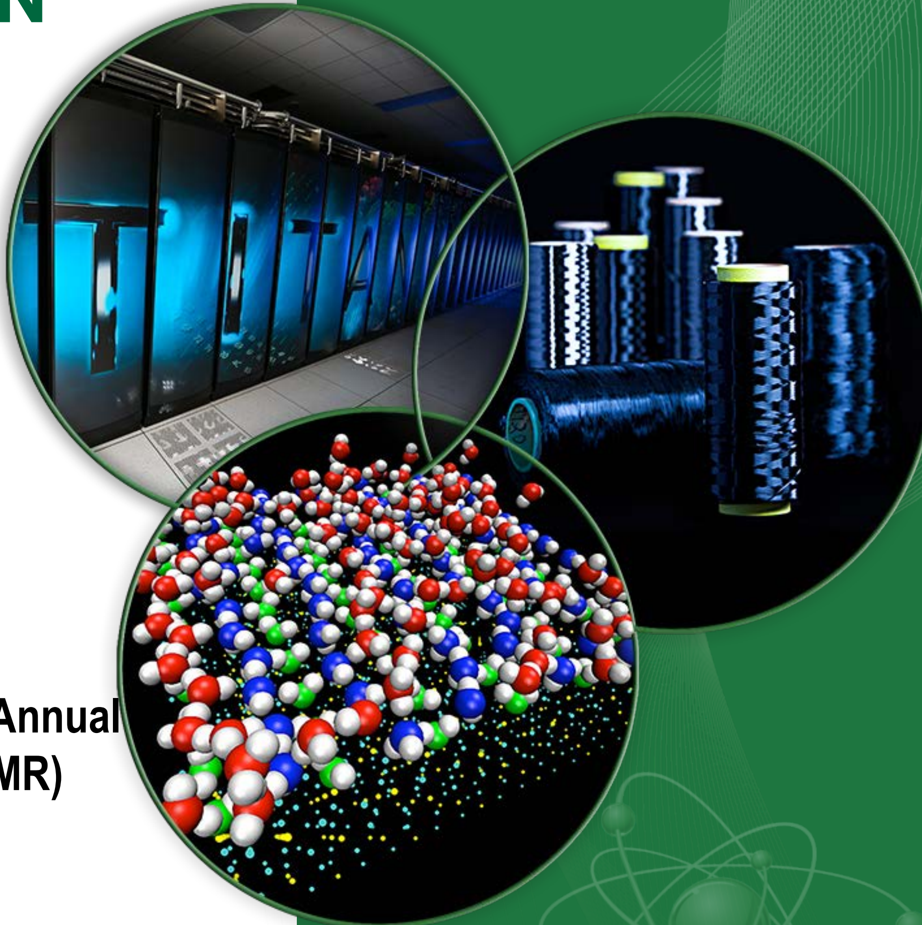
Novel Plasticized Melt Spinning Process of PAN Fibers Based on Task-Specific Ionic Liquids

Sheng Dai
Email: dais@ornl.gov
Phone: 865-576-7307

Oak Ridge National Laboratory



2018 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting (AMR)

June 14, 2018 **Project ID: ST148**

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Overview

Timeline

- Project Start Date: 10/01/17
- Project End Date : 9/30/20
- Percent Complete: 18%

Budget

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

Barriers

- Barriers Addressed
  - **The production of high strength carbon fibers is an energy intensive process, and thus costly**
  - **One significant cost that has yet to be mitigated involves the production of polyacrylonitrile (PAN) fibers prior to carbon fiber production.**
  - **The current technology for PAN fiber production involves wet-spinning**

Partners

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

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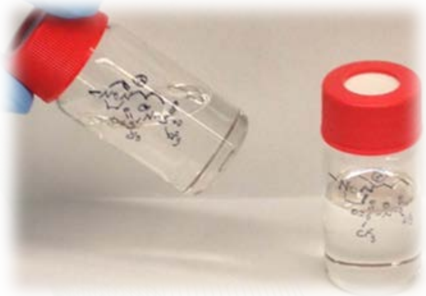
Relevance

- 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). The three 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, and
  - 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)



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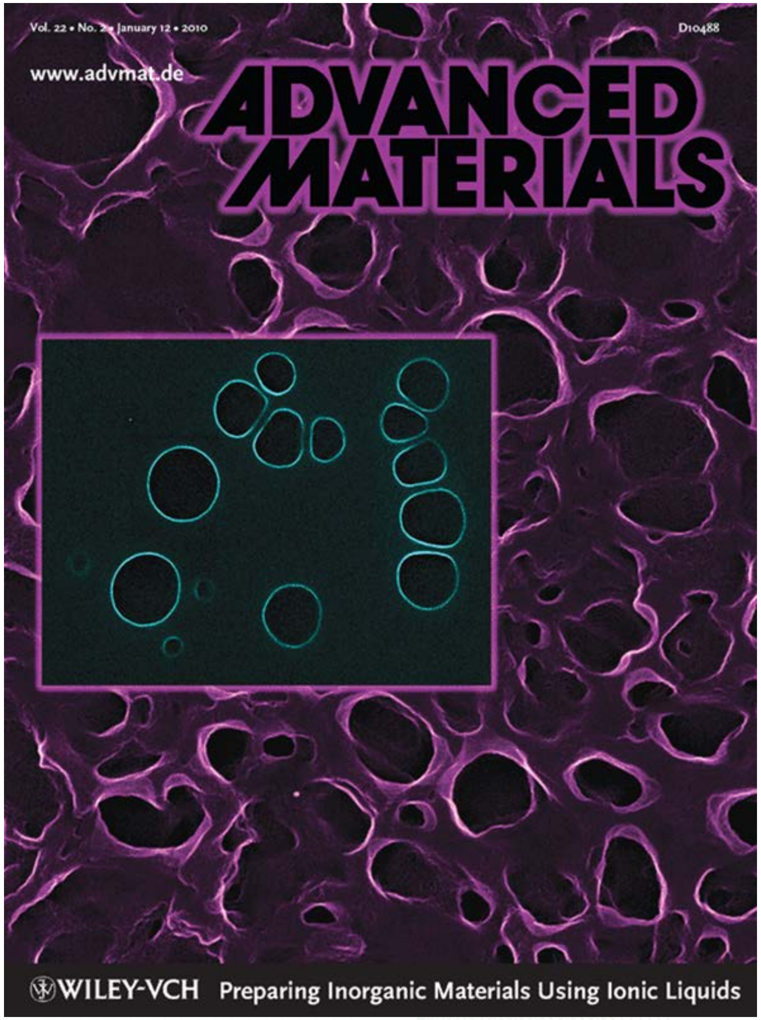
Approach

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* (-100^0C to around 300^0C)
- *Wide Electrochemical Window*
- *Tunable Lewis Acidity*

Ideal as plasticizers and designer solvents

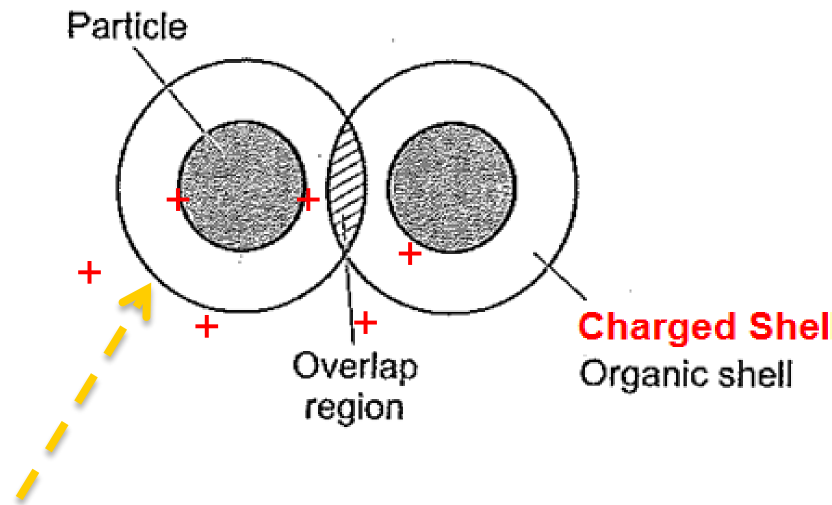


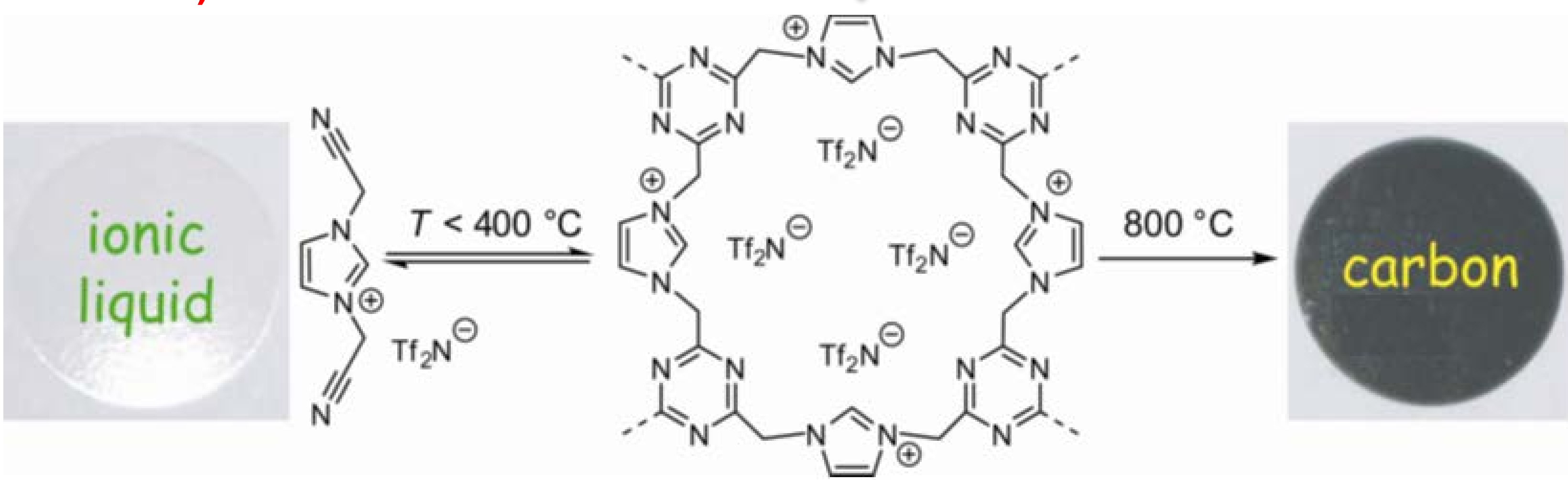
Ma, Yu, Dai, *Adv. Mater*. 2010, *22*, 261

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

Milestone Summary Table							
Recipient Name:	Oak Ridge National Laboratory						
Project Title:	Novel Plasticized Melt Spinning Process of PAN Fibers Based on Task-Specific Ionic Liquids						
Task Number	**Task or Subtask (if applicable) Title**	**Milestone Type (Milestone, Go/No-Go Decision Point, End of Project Goal)**	**Milestone Number* (Go/No-Go Decision Point Number)**	**Milestone Description (Go/No-Go Decision Criteria)**	**Milestone Verification Process (What, How, Who, Where)**	**Anticipated Date (Months from Start of the Project)**	**Anticipated Quarter (Quarters from Start of the Project)**
1.0	1.1	Quarterly Progress Measures	1.1 ✓	Demonstrate > 30 wt% IL solubility in PAN	PAN must have IL solubility > 10 wt %	6	2
1.0	1.2	Quarterly Progress Measures	1.2	PAN-IL synthesis with carbon yield > 50 %	PAN-IL must be synthesized with >50% carbon formation	9	3
1.0	1.3	Quarterly Progress Measures	1.3	Demonstrate > 10 °C decrease in PAN melt temperature	Decreased melt temperature observed	9	3
1.0	1.4	Quarterly Progress Measures	1.4	Development effort will continue if PAN melting point suppression is > 15°C in composite	Demonstrate PAN-IL melt properties with sufficiently low melting point and minimal PAN degradation	12	4

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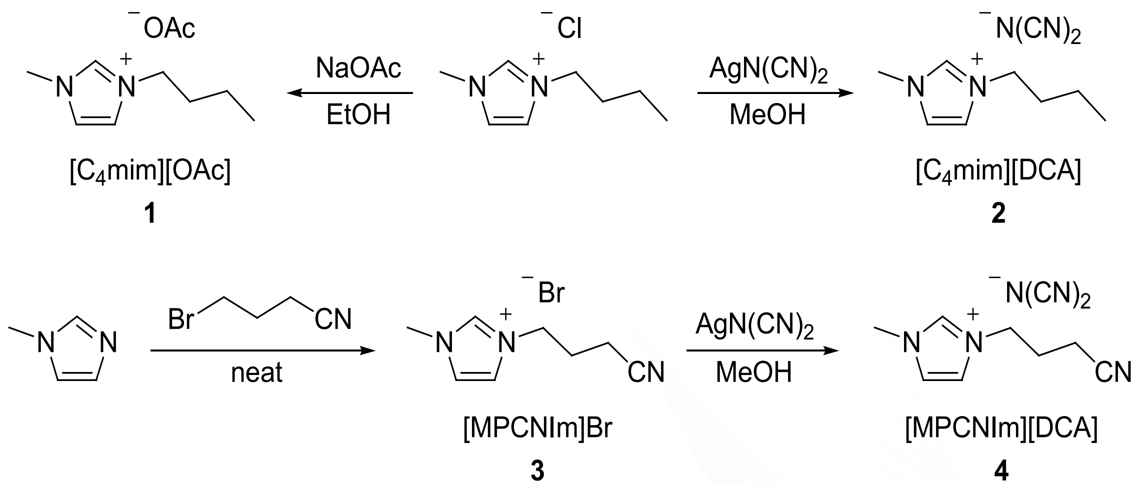
Accomplishments: Several new ionic liquids have been synthesized and characterized

Typical ionic liquids synthesis method: Equal mole ratio of 1-methylimidazole and bromo-alkane or chloro-alkane were mixed at room temperature and stirred over a period of time and the reaction was monitored with NMR until the disappearance of starting materials. The obtained $[C_n mim]Br$ or $[C_n mim]Cl$ can be used in the preparation of melts along with PAN. The bromide or chloride can also be further reacted with certain reagent through metathesis reaction to produce desired ionic liquids containing various different anion.



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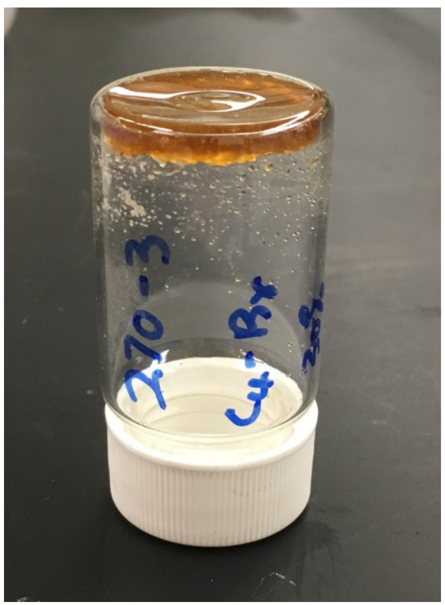
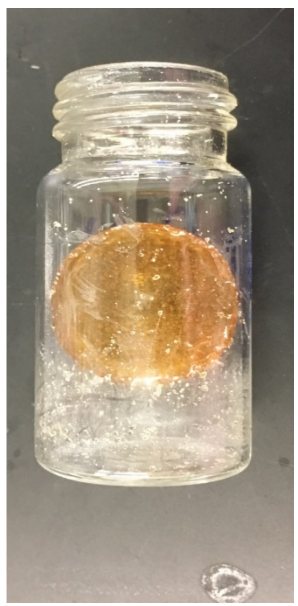
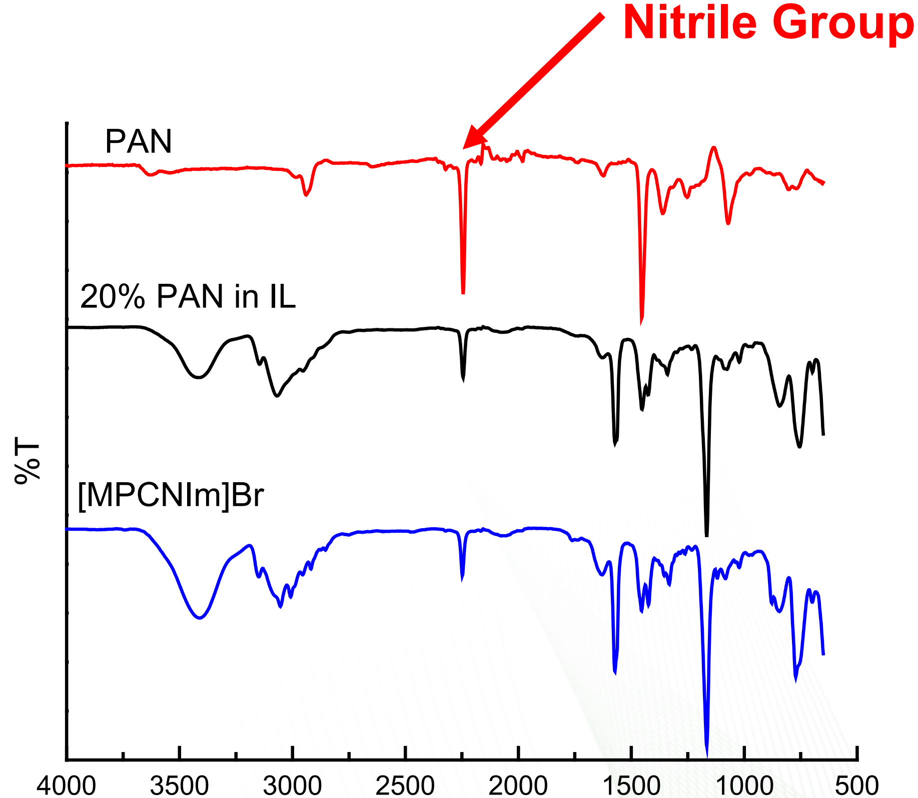
Accomplishments: Effect of PAN percentage and ILs on the formation of melts-1

This picture shows ~30% PAN in [C4mim]Br. A transparent gel can be formed after 30 min at 140℃.







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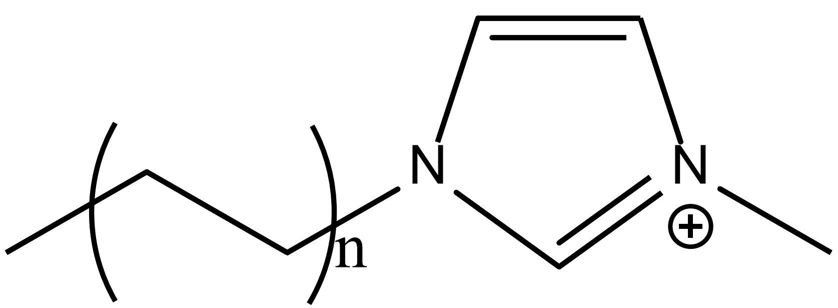
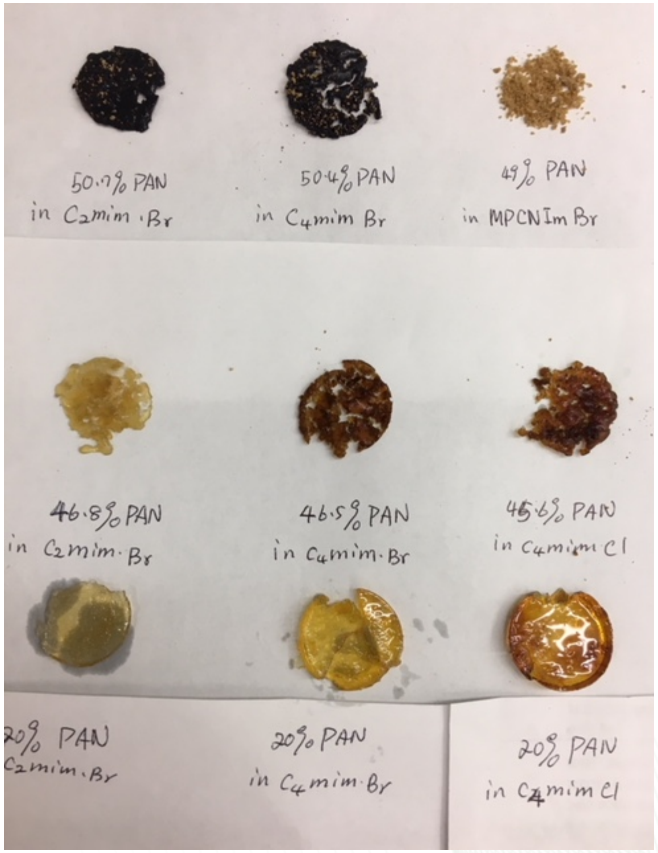
Accomplishments: Effect of PAN percentage and ILs on the formation of melts-2

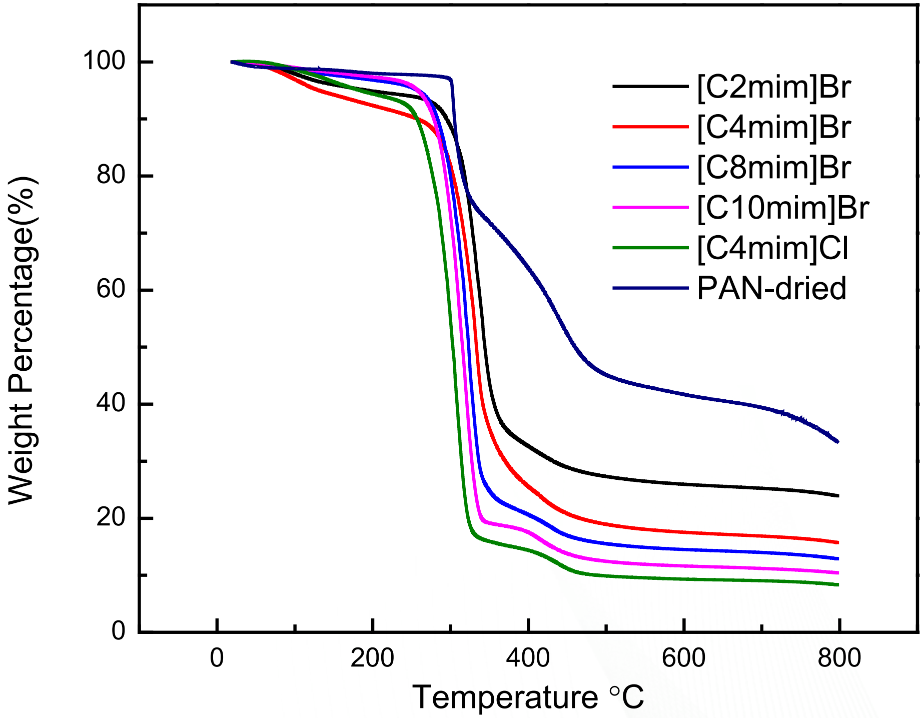
This picture shows that different gels or melts were formed from 20% to 50% PAN in ionic liquid. In general 20% PAN mixture produced light colored soft gel and higher percentage PAN gave dark colored hard melts or powder in some cases.

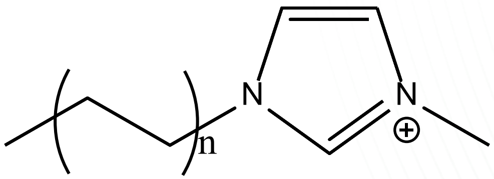




Accomplishments: Effect of carbon chain length of imidazolium-based ILs on formed melts

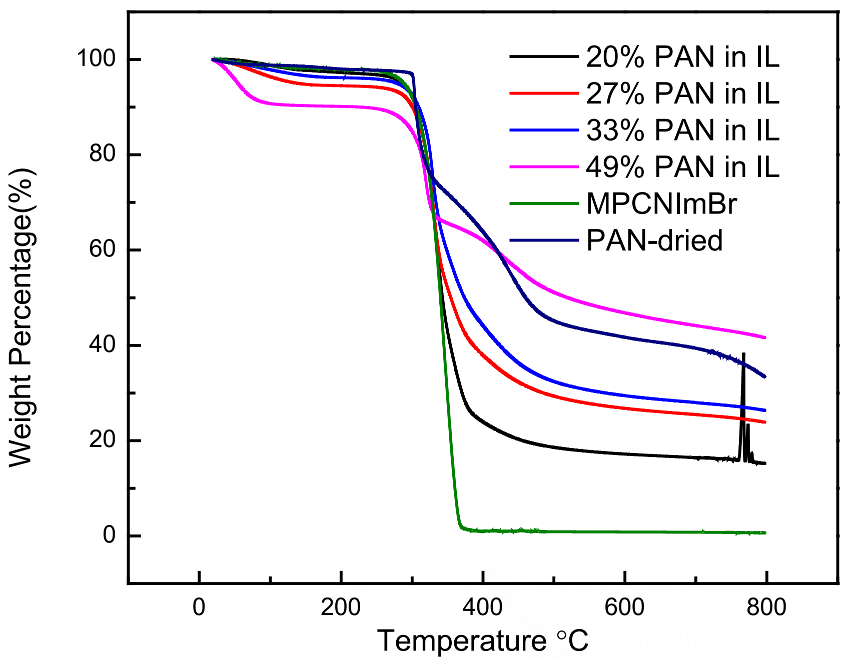
Preparation of gel or melt: ~20% PAN white powder was mixed with IL, purged with Argon for a minute and heated to ~120 to 170 ºC till it melted. As carbon chain increased from C_2 to C_{10} the mixture became difficult to melt. [C_4mim]Br is better than [C_4mim]Cl. The melts were evaluated by TGA to give the carbon yield. As shown in figure on the right, the shorter carbon chain gave higher carbon yield and bromide gave higher carbon yield when the cation is same.

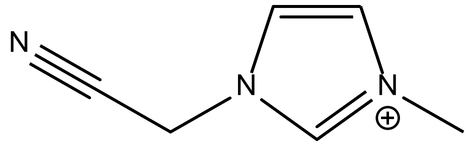




Accomplishments: Effect of percentage of PAN in [MPCNIm]Br on formed melts

Ionic liquids containing nitrile group were synthesized. The melts containing 20%, 27%, 33%, and 49% PAN were prepared and studied by TGA and FTIR. As expected, the carbon yield increased as the percentage of PAN increased. It is interesting to notice that 49% PAN melt gave higher carbon yield than PAN itself even though IL gave lower carbon yield.





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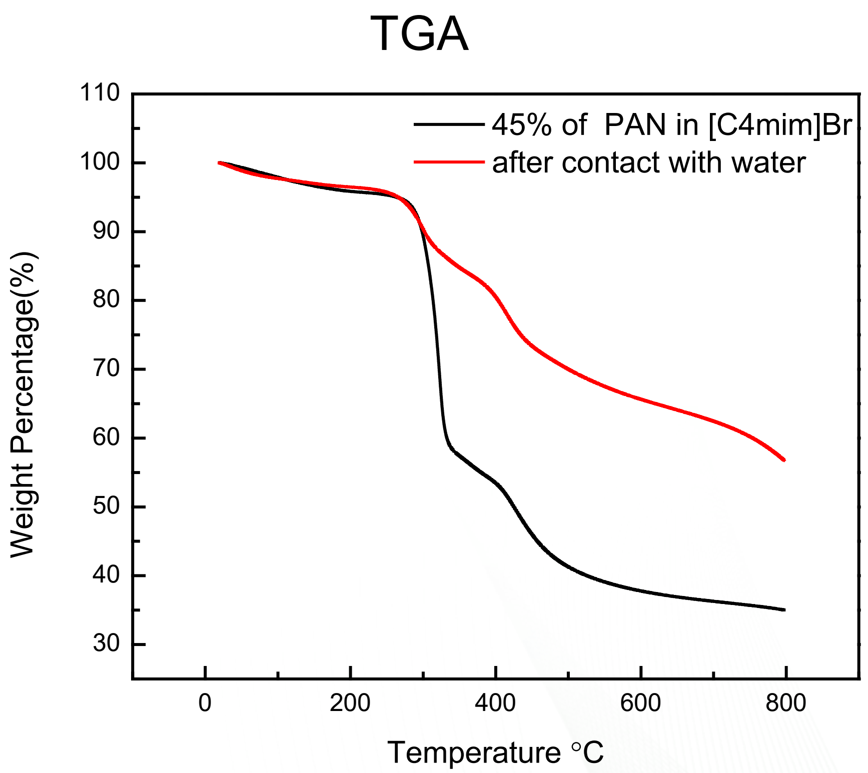
Accomplishments: Initial test of recycling of ionic liquids from melts

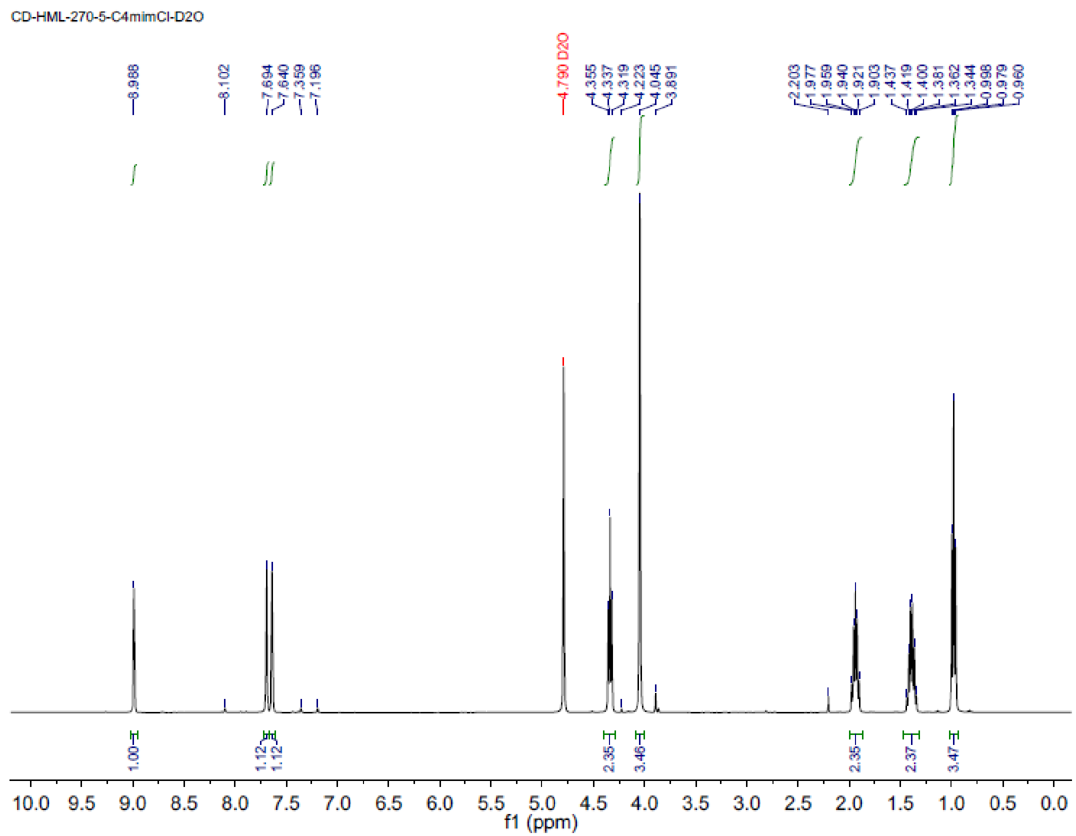
The melt formed from 45% PAN in [C_4mim]Br and ~5.0 mL of deuterium water was contacted overnight and the solid melt used for TGA measurement. The melt was dried under vaccum at ~100 ºC for ~3 hours. The melt was hardened and studied by TGA to give the carbon yield as higher as 57% (red line in the figure on the right), increased about 20% .



Accomplishments: Initial test of recycling of ionic liquids from melts

The melt formed from 45% PAN in $[C_4mim]Br$ and ~5.0 mL of deuterium water was contacted overnight and the aqueous solution sampled for NMR measurement. The NMR experiments indicated the presence of $[C_4mim]Br$ in the aqueous phase, highlighting the ease recovery of $[C_4mim]Br$.

NMR Spectrum



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Collaboration and Coordination

Project Team

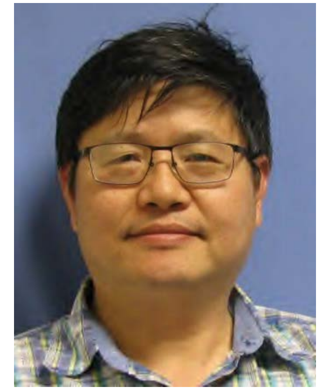
Dr. Sheng Dai
Oak Ridge National Laboratory
Ionic liquids, carbon materials, and their energy-related applications

Dr. Huimin Luo
Oak Ridge National Laboratory
Ionic liquids and their energy-related applications

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.
Ionic liquids and their scale-up synthesis





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Proposed Future Work

- Remainder of FY18
  - Design and synthesis of task-specific ionic liquids with enhanced PAN interactions (ORNL)
  - Investigate IL miscibility in PAN (ORNL)
  - Preliminary technoeconomic analysis of IL production identifying synthetic inefficiencies and cost drivers (525 Solutions)
- Into FY19
  - Thermophysical characterization of PAN-IL composites (ORNL)
  - Optimization of the PAN-IL interaction (ORNL)
  - Target IL synthetic optimization and scale-up (525 Solutions)
  - Technoeconomic analysis of IL production (525 Solution)

- 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

- Two types of ionic liquids containing either nitrile group or without nitrile group have been synthesized, purified and evaluated.
- Gels or melts formed from different percentage PAN have been studied with TGA and FTIR. Some interesting trends have been observed. Ionic liquids containing bromide as anion gave a higher carbon yield than chloride as anion did.
- New ionic liquids with different anions such as acetate (OAc^-) and dicyanamide ($N(CN)_2^-$) have been synthesized and characterized.
- Preliminary tests indicated that ionic liquid can be recycled by simply contacting with water.

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

Acknowledgements

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