

***Molecular Ionic Composites:
A New Class of Polymer Electrolytes to Enable
All Solid-State and High Voltage Li Batteries***

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Virginia Polytechnic Institute and State University
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Project ID: bat485



VIRGINIA TECH.

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Overview

Timeline

- Project start date: 10/01/2019
- Project end date: 12/31/2022
- Percent complete: 50%

Budget

- Total project funding \$1.25M
 - DOE Share \$1.0M
 - Contractor share \$250k
- Funding for FY 2019: **\$329,572(DOE)**
+ \$104,771(VT)
- Funding for FY 2020: **\$343,183 (DOE)**
+ 81,000 (VT)

Barriers

- Barriers addressed
 - Cost
 - Performance
 - Life

Partners

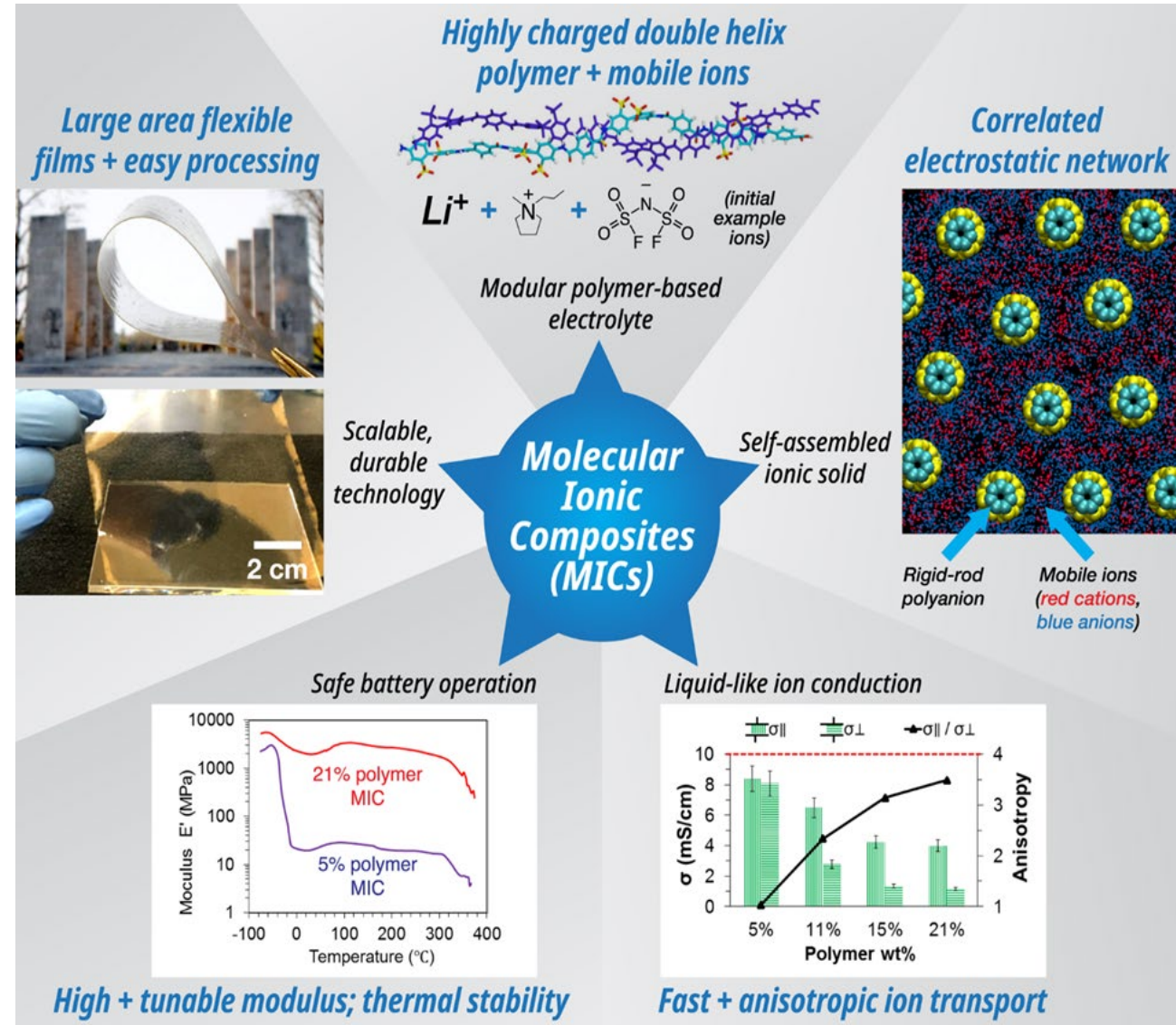
- Collaborations:
 - Penn. State Univ.
 - UNC-Chapel Hill
 - SSRL



Relevance

Objectives and projected outcomes:

- **Practical solid electrolytes:** Develop and optimize uniform and robust solid electrolyte films ($\geq 20 \mu\text{m}$ thickness) that possess $\sim 1 \text{ mS/cm}$ conductivity, high Li^+ transference number, excellent thermal stability ($>200^\circ\text{C}$), and stiff/strong mechanical properties.
- **Electrochemical measurements:** Quantify and feedback on electrochemical characteristics of solid MIC electrolytes.
- **Fundamental transport and interfacial studies:** Investigate ion transport mechanisms and electrode-electrolyte interfacial phenomena for this new class of electrolytes under practical operating conditions using NMR spectroscopy and diffusometry combined with synchrotron scattering and spectroscopy techniques.



Milestones

Milestone (through Q3, 2021)	Status	Description
Synthetic conditions determined	Completed	Determine synthetic conditions for 100 μm thick electrolyte, using both tape casting and ultrasonic spray methods
Optimal Li ion loading and chemical composition of the MIC electrolyte Determined	Completed (still optimizing)	Li ion conductivity: $\sim 1\text{mS/cm}$ at RT, transference number (TN): ~ 0.45 at room temperature
Testing protocols developed	Completed	Whether or not the testing protocols provide reproducible results
Film fabrication method down-selected	Completed	Direct comparison between tape casting and spray, the better method will be selected
Determine the optimal synthetic conditions, Li ion loading, and chemical compositions	Completed (still optimizing)	Targets: Conductivity $\sim 1\text{ mS/cm}$, TN ~ 0.45 at RT; upper voltage limit $> 4.5\text{ V}$; thermal stability up to $150\text{ }^\circ\text{C}$; Elastic modulus $> 1\text{ GPa}$
Determine the parameter spaces for film formation. Design Capable of Meeting performance requirements for film casting process	Go/Completed	Thickness measurement, morphology and porosity check by SEM. Analysis indicates technical approach capable of achieving performance targets.
Optimize oxidative stability by using NMC/MIC/NMC and Li/MIC/NMC cell platforms to determine the upper limit of cycling voltage.	In progress	The upper limits will be 4.4 V , 4.45 V , 4.5 V , 4.6V , 4.7V . Depending on the electrochemical results, down select these limits to one.

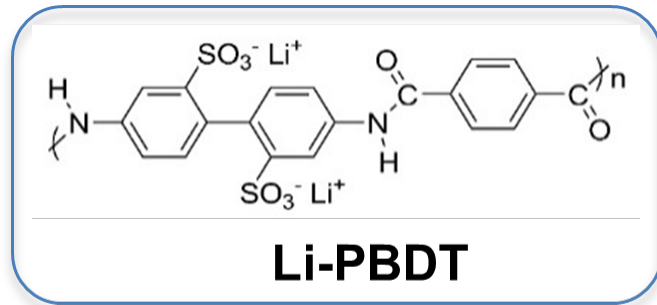


Approach/Strategy

- **Development and optimization of uniform and robust MIC electrolyte films with tailored Li ion loading and chemical composition**
 - Development of the baseline Li ion loading and chemical composition
 - Establishing the basic electrochemical, thermal, and mechanical testing protocols
 - Selection of the project chemical composition and Li ion loading
- **Detailed electrochemical quantification of key performance metrics (electrolyte stability, interfacial reactions, and compatibility with electrode materials)**
 - Optimization of oxidative stability of the solid electrolyte
 - Establishing the parameters for minimal interfacial impedance
- **Comprehensive investigation of ion transport mechanisms, electrode-electrolyte interfacial phenomena, and electrolyte/interface optimization**
 - Origination and refinement of a predictive model for diffusion and mobility of all ions and mobile species in MIC electrolytes
 - Identification of methods to mitigate interfacial degradation

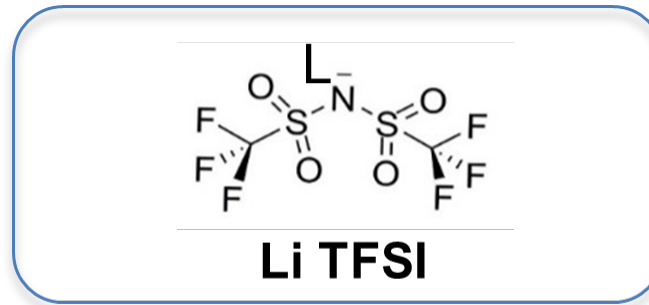


Approach



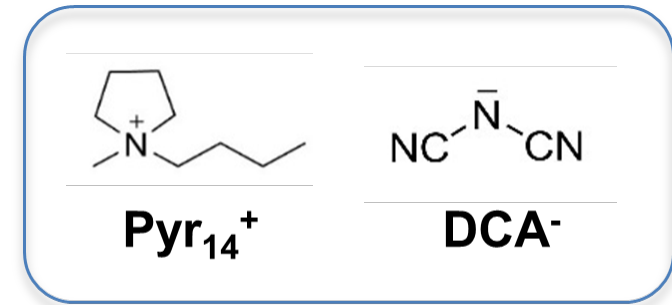
Li-PBDT

10 wt%



Li TFSI

10 wt%

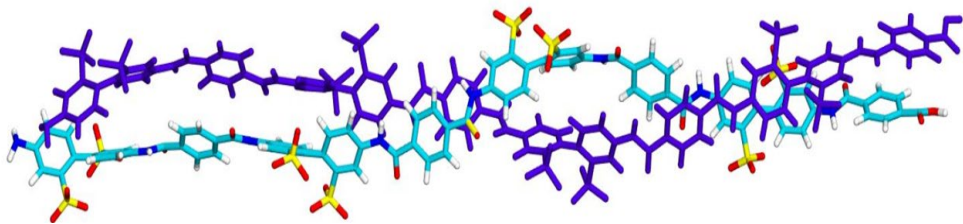


Pyr₁₄⁺

DCA⁻

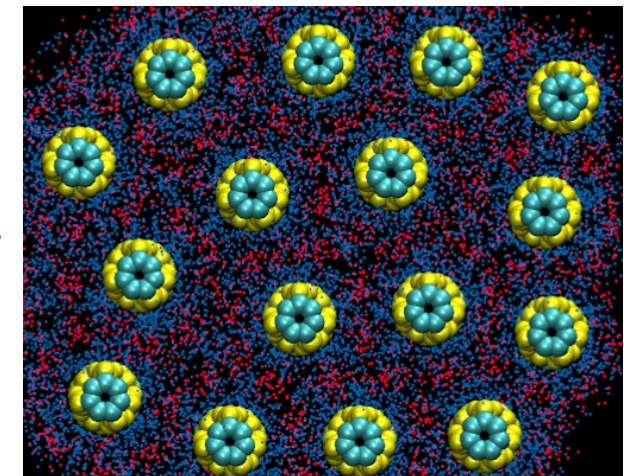
80 wt%

**Molecular ionic composite (MIC)
electrolytes**

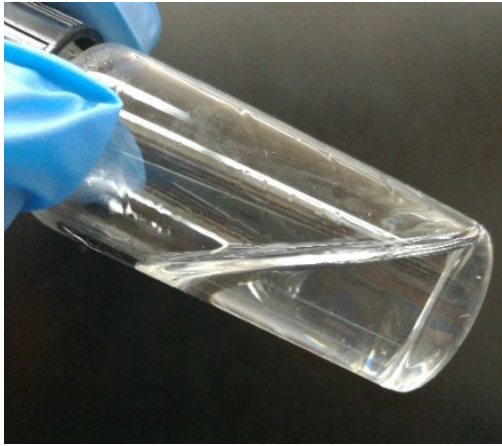


*PBDT: highly rigid and
charged double helical
polymer*

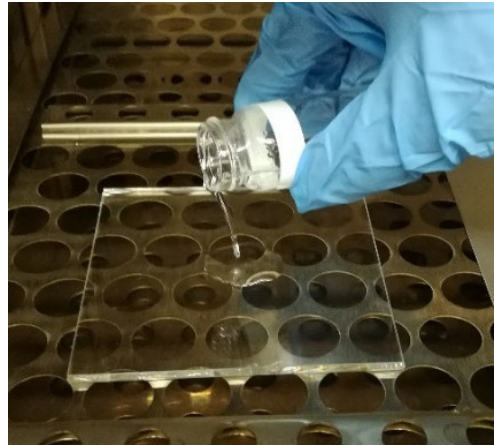
*Collective
electrostatic
network*



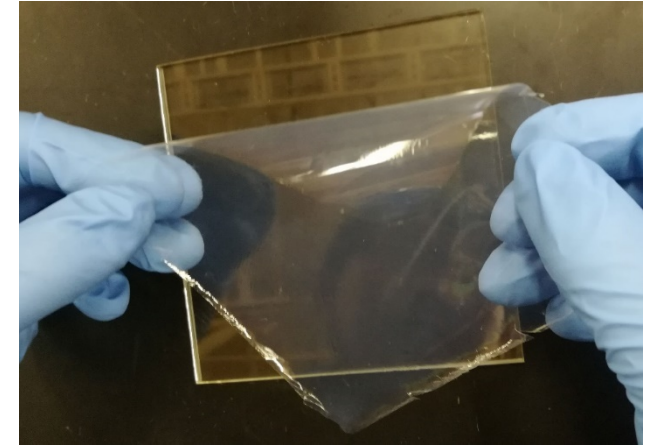
Technical Accomplishments and Progress



85°C
→



Dry
→

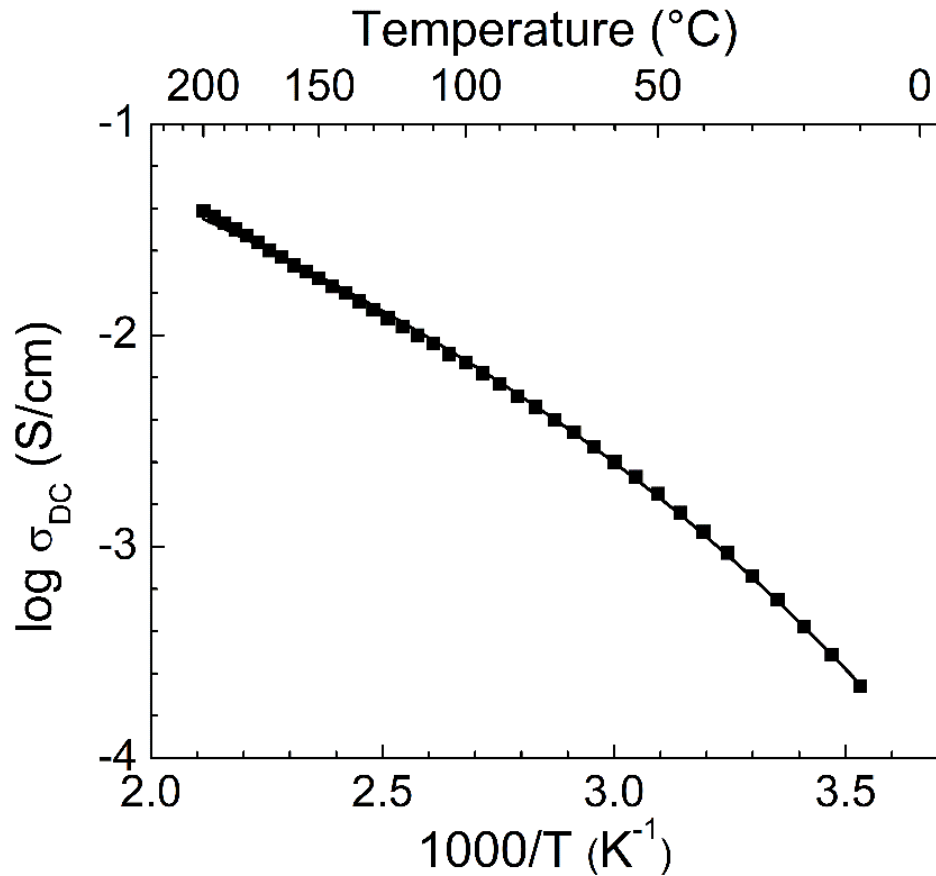


Low-cost processing of molecular ionic composite (MIC) films

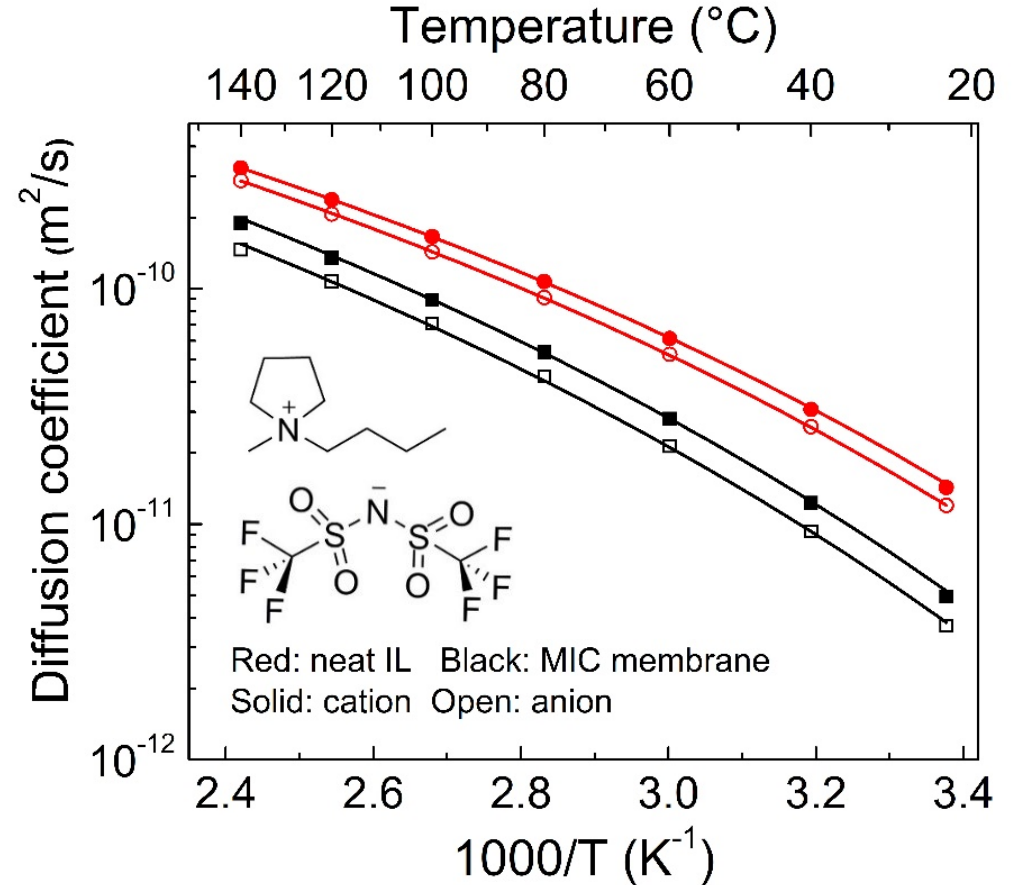
*ACS Applied Mater Interf. 2019
Adv. Energy Materials 2021
1 more submitted*



Technical Accomplishments and Progress

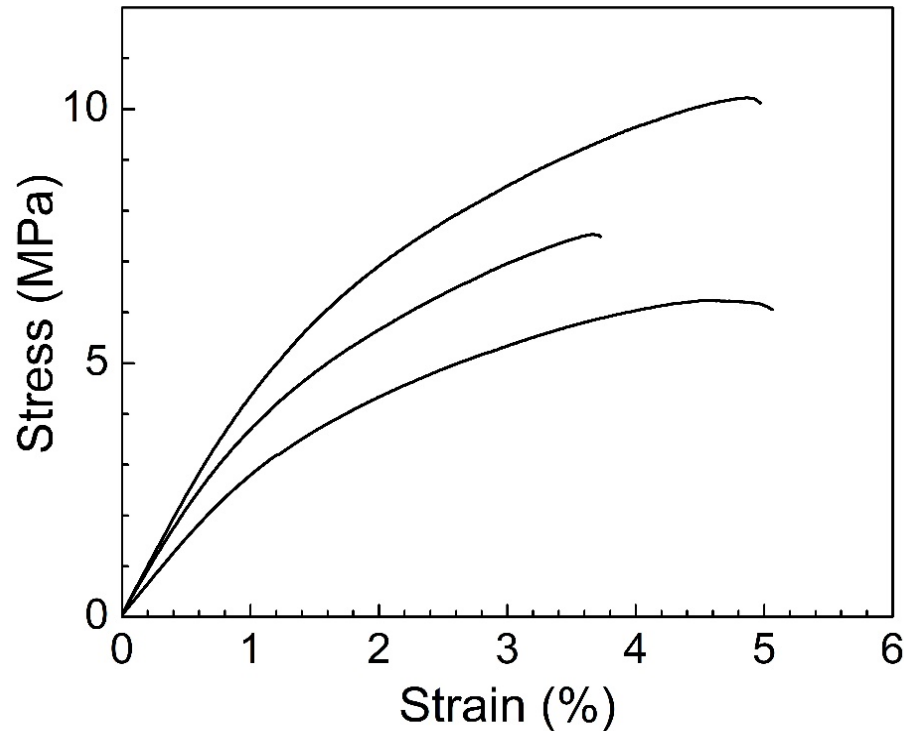


0.56 mS/cm at 25 °C
39 mS/cm at 200 °C



Diffusion coefficient of (ionic liquid) IL in MIC is only 3× smaller compared to neat IL

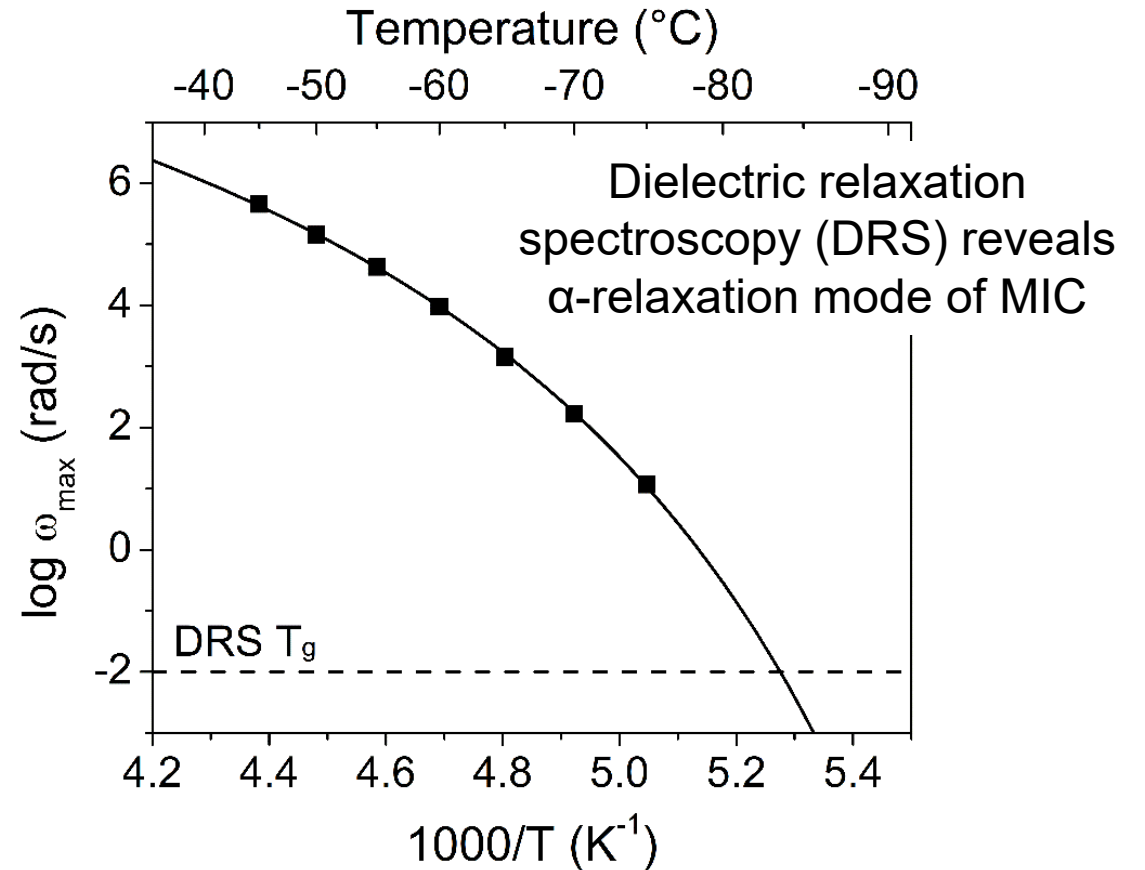
Technical Accomplishments and Progress



Young's modulus: 410 MPa

Tensile strength: 8.0 MPa

Strain at break: 4.6 %



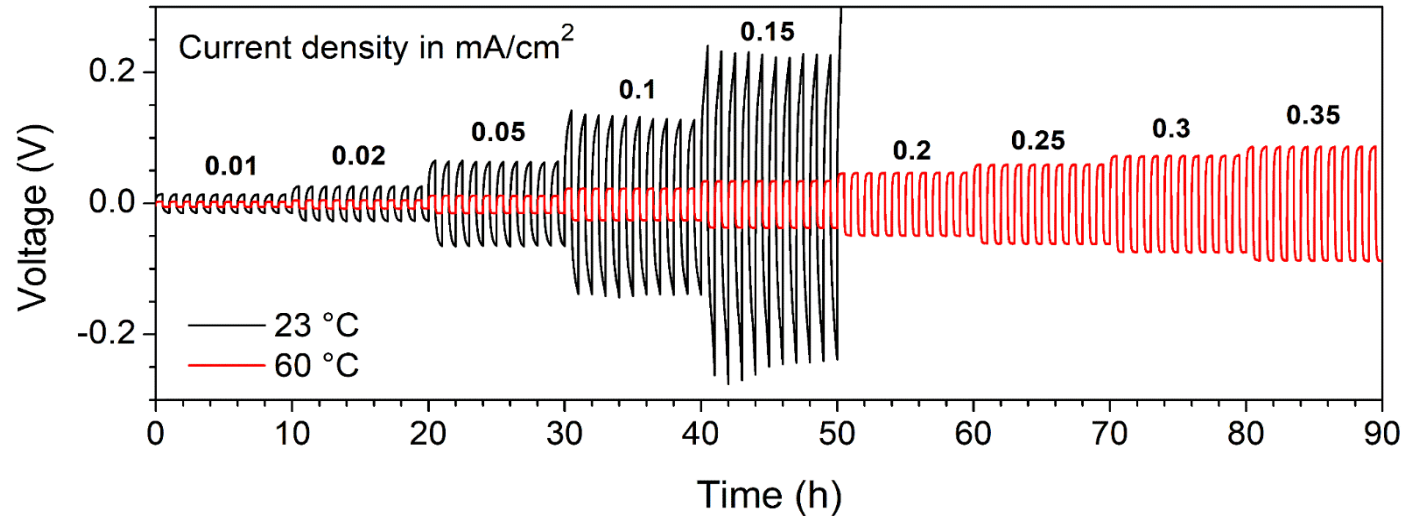
T_g of neat IL: -87 °C

Ion transport decoupled from polymer T_g

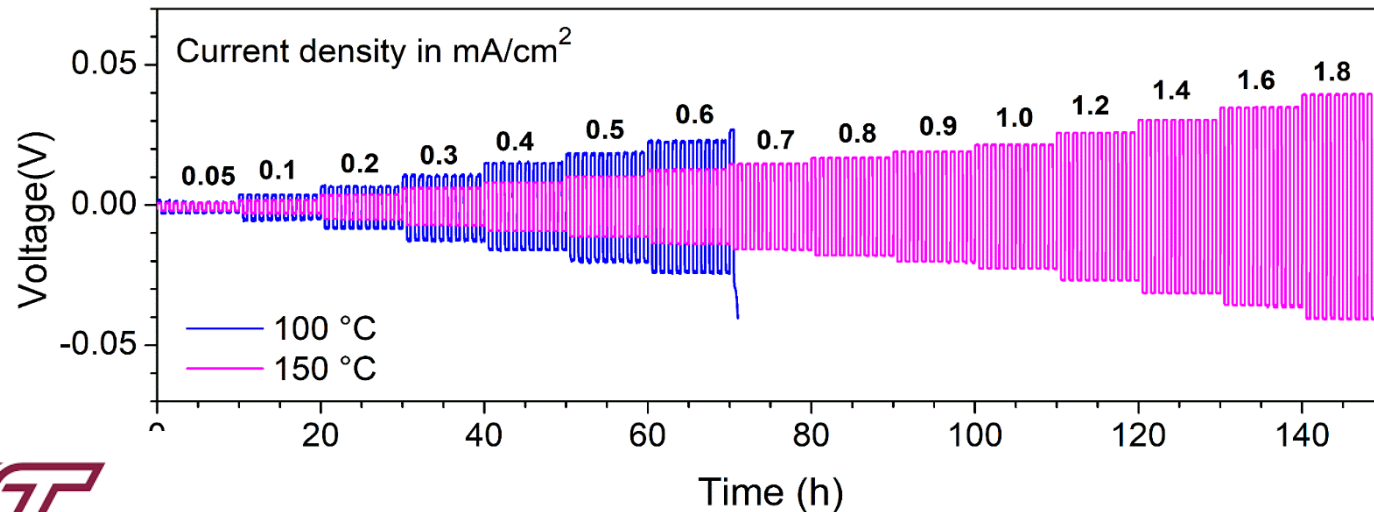


Technical Accomplishments and Progress

23 °C to 150 °C lithium symmetric cell polarization measurements

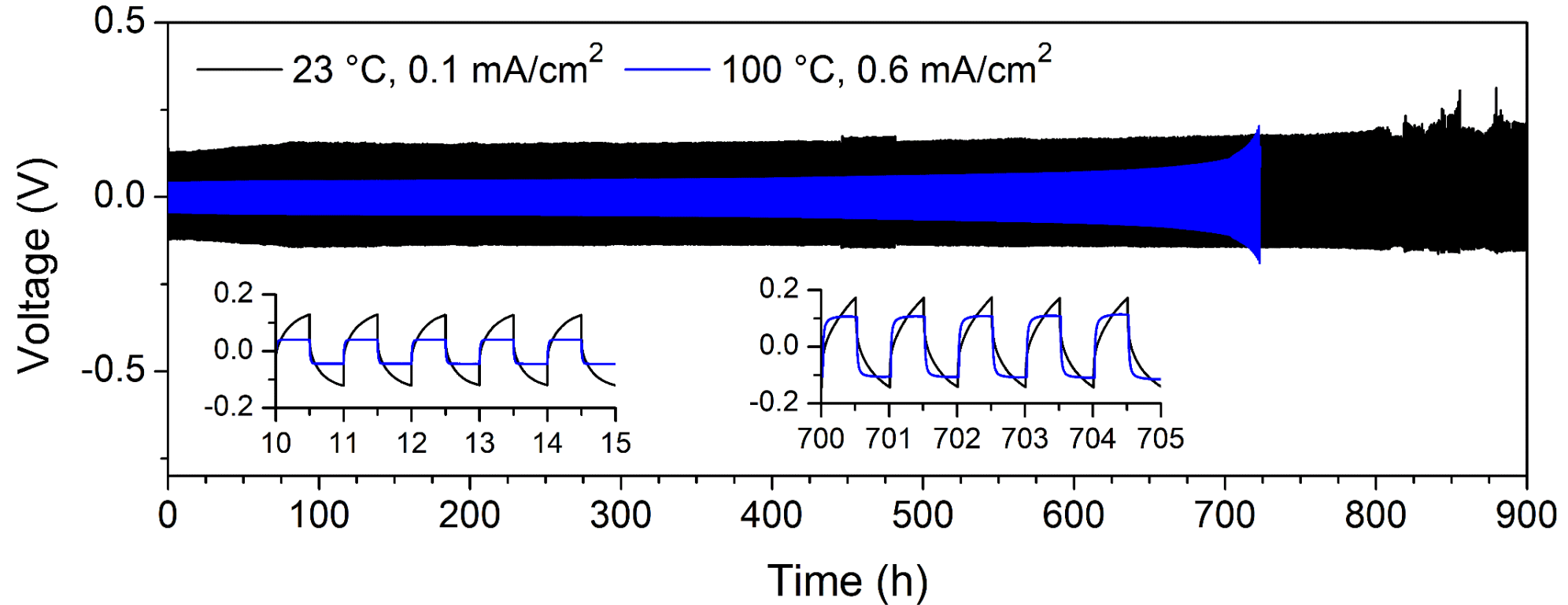


Li/MIC/Li cycled at varying current density from **23 °C to 150 °C**.



Stable cycling against Li at 150 °C.

Technical Accomplishments and Progress

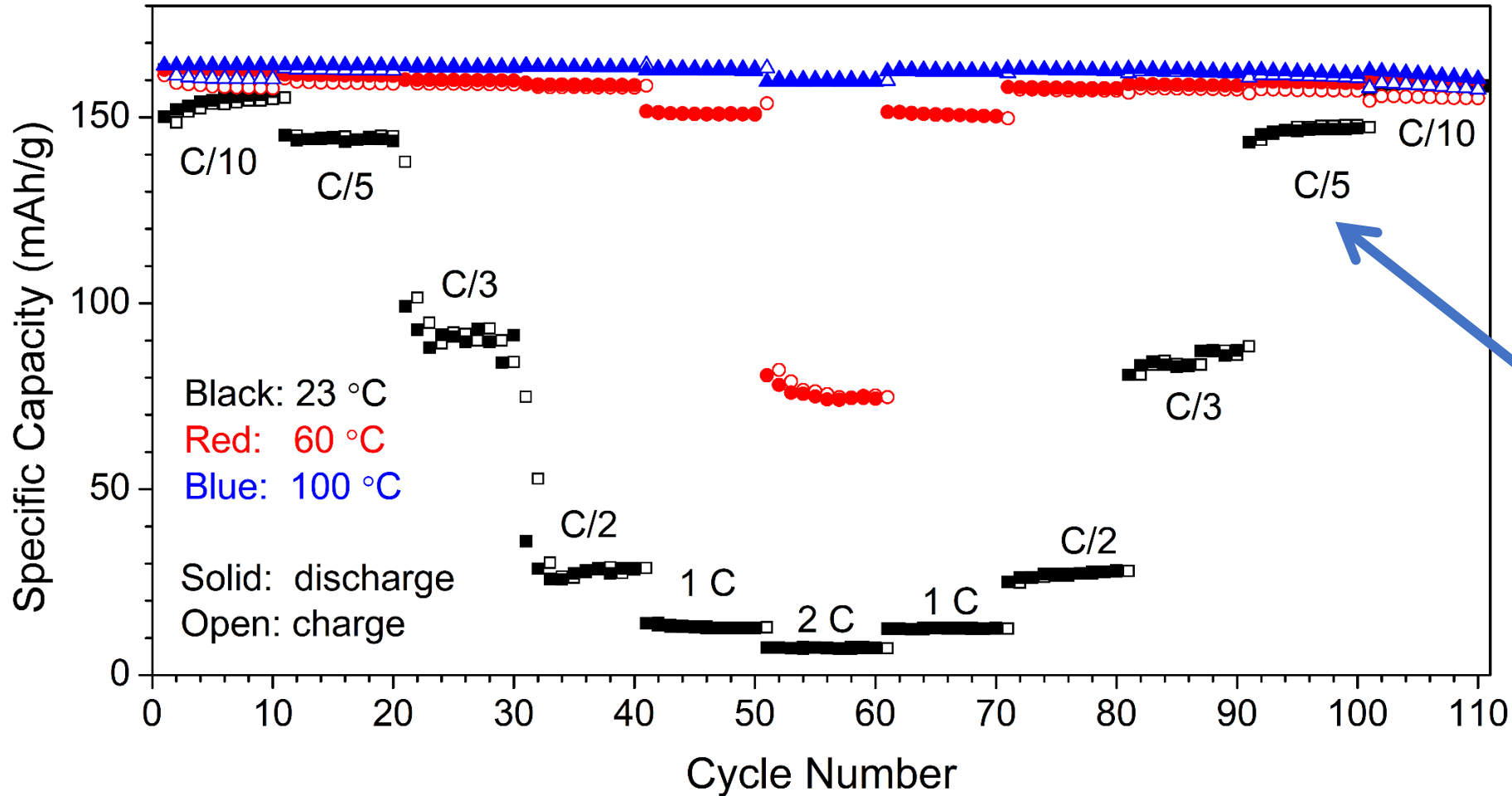


Li/MIC/Li shows stable long-term cycling over wide temperature range.



Technical Accomplishments and Progress

Li/MIC/LiFePO₄ cell rate capability



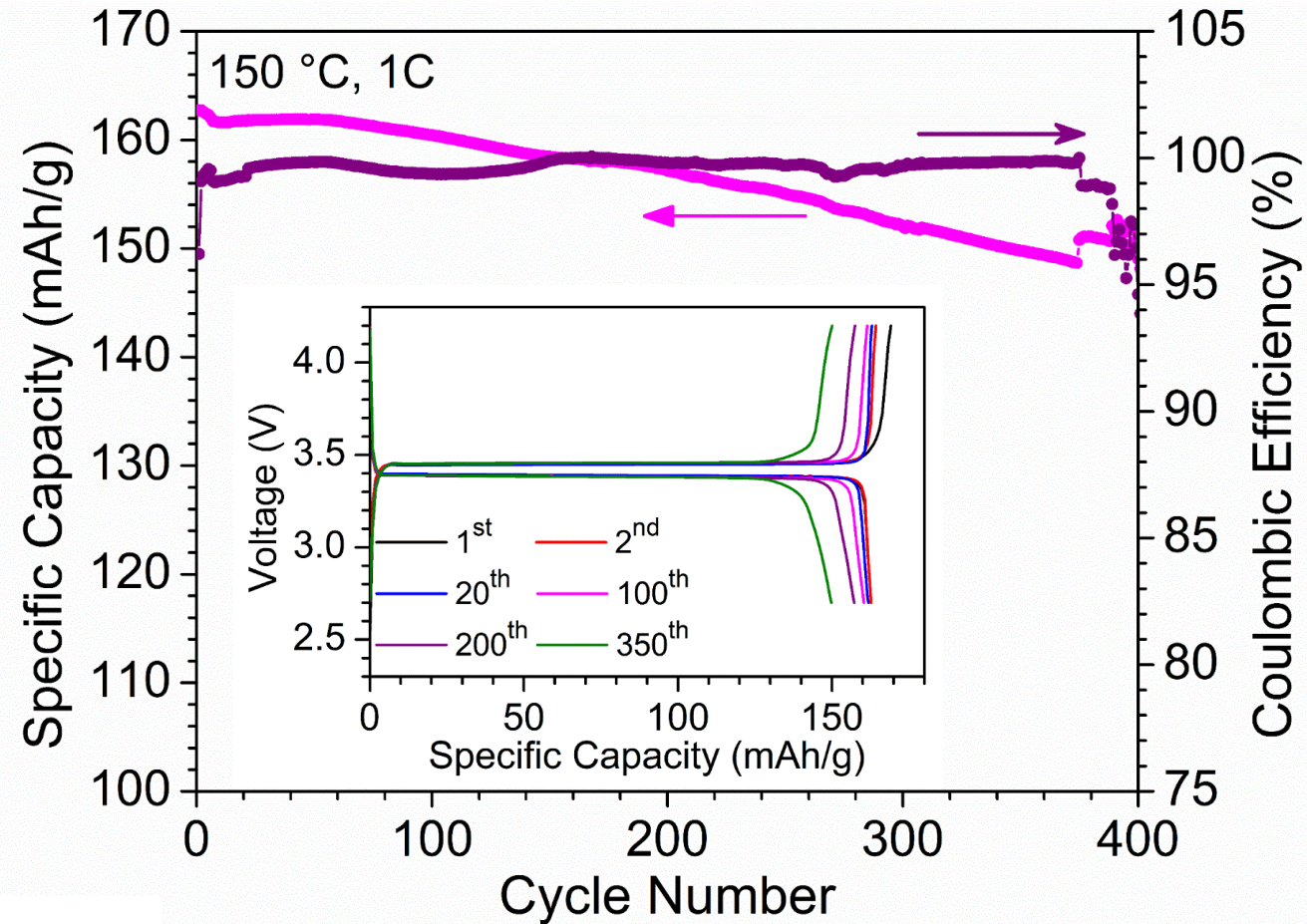
Challenge: Low t_{Li^+} (0.12) causes low performance at high C rate at 23 °C

Full capacity recovery with decreased C rate

No sign of cell shorting at high C

Technical Accomplishments and Progress

Li/MIC/LiFePO₄ cell cycling stability at 150 °C



**Stable cycling @ 150 °C
achieved using
electrolyte w/only 10 wt%
polymer**



Technical Accomplishments and Progress

Using *PBDT* as conductive binder for LiFePO_4/C cathodes

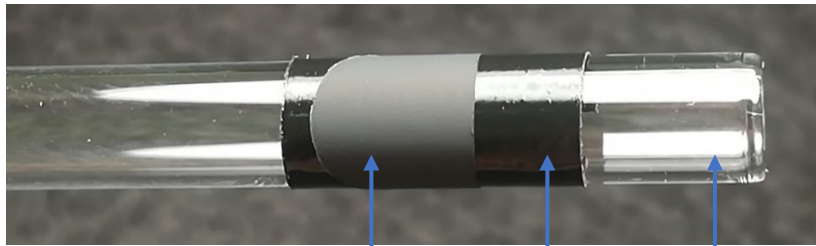
3% **PBDT-LFP** (competitor for PVDF)

3 wt% **Li-PBDT**

10 wt% Acetylene back

87 wt% LiFePO_4

Solvent: H_2O (NMP needed w/PVDF)



Electrode Tape Tube (5 mm OD)



LiFePO_4/C electrode with

PBDT as binder

Using *MIC* as binder for cathode (“catholyte” system)

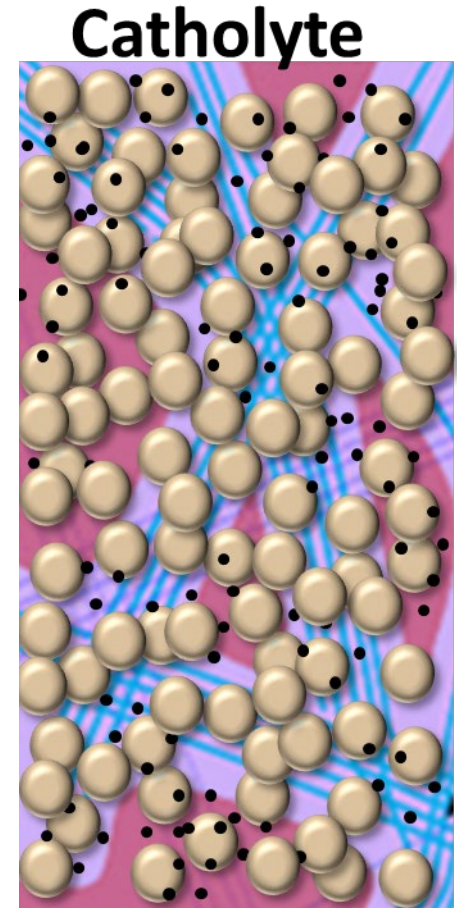
Polymer solution

+

Carbon Black

+

NMC 811



● NMC particle

• Carbon black

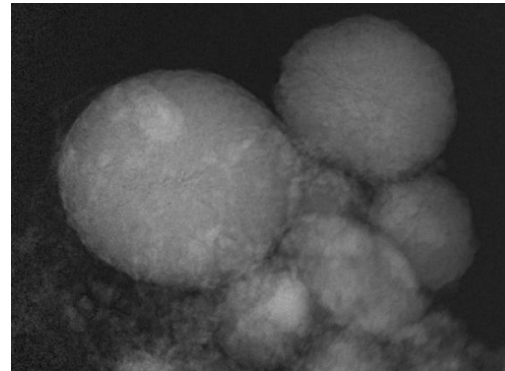
NMC 811:CB:MIC = 8:1:1

Technical Accomplishments and Progress

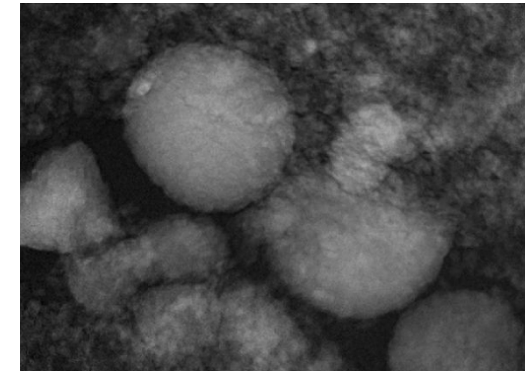
How does MIC govern redox reactions in NMC particles?

2D Ni valence state distribution of charged NMC particles
4.4 V, after 10 cycles

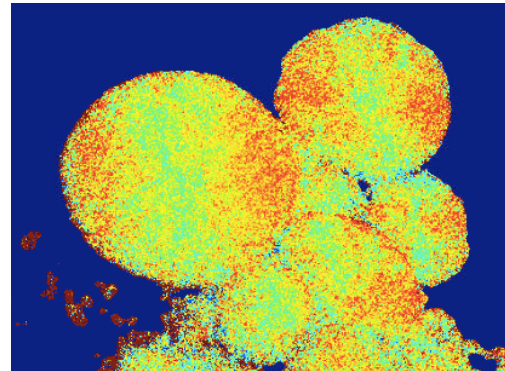
Cathode/MIC



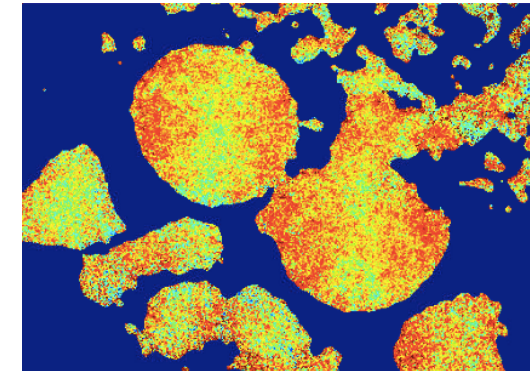
Catholyte/MIC



Particles in inner cathode matrix may be affected by introducing ionically conducting MIC into cathode system



8342.5 eV



8344.5 eV

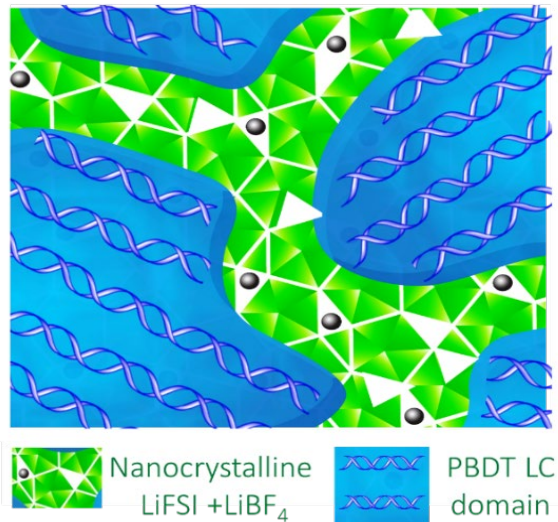


Technical Accomplishments and Progress

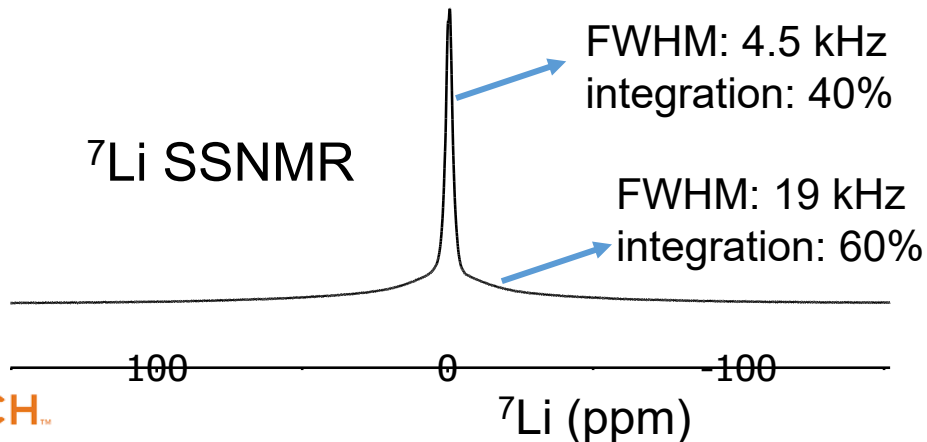
Emerging MIC electrolytes with nanocrystalline conductive phase

New MIC membrane internal structure

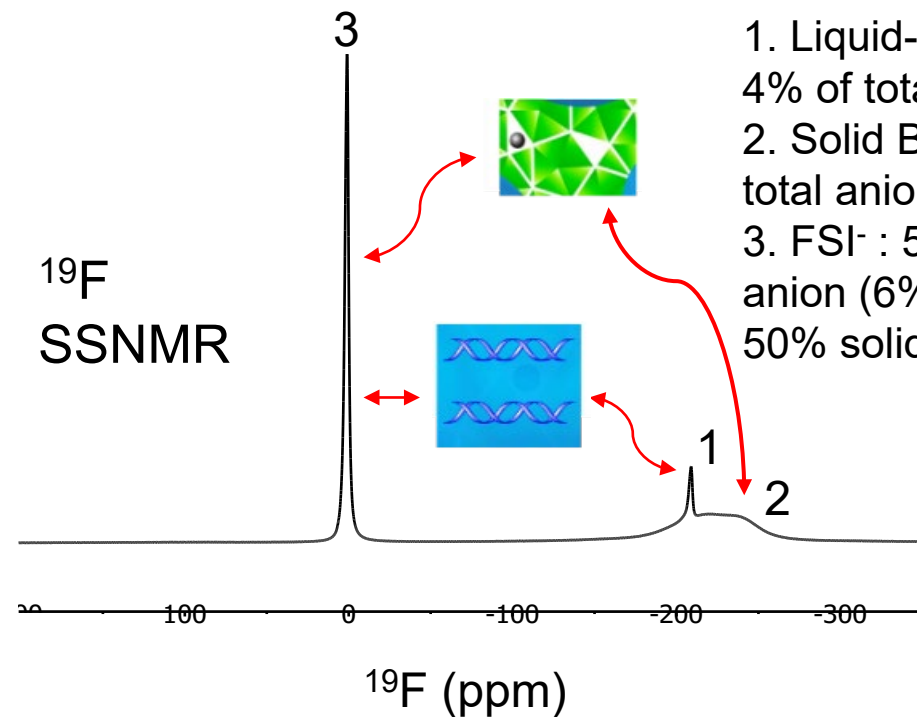
$\sigma = 1.5 \text{ mS/cm}$
@ 25°C



^7Li SSNMR



^{19}F
SSNMR



^{19}F NMR analysis:

1. Liquid-like BF_4^- : 4% of total anion
2. Solid BF_4^- : 33% of total anion
3. FSI^- : 56% total anion (6% liquid-like, 50% solid)

^7Li SSNMR integration shows all lithium is found in a single, locally anisotropic environment



Responses to Previous Year Reviewers' Comments

There have been no reviewers' comments on this project.
(This is a new project.)



Collaborators

Collaborators	Institution	Nature of Collaboration
Ralph H. Colby	Penn. State Univ.	Rheology and broadband dielectric spectroscopy
Yijin Liu	SSRL/SLAC	X-ray diagnostics
Dennis Nordlund	SSRL/SLAC	X-ray diagnostics
Theo J. Dingemans	UNC Chapel Hill	Polymer synthesis



Remaining Challenges and Barriers

- Fabrication of robust films with $\approx 20 \mu\text{m}$ thickness (currently $> 40 \mu\text{m}$).
- Quantifying electrochemical characteristics of solid MIC electrolytes using various cell geometries and with various high voltage electrode materials.
- Elucidating detailed ion transport mechanisms and electrode-electrolyte interfacial phenomena for this new class of electrolytes under practical operating conditions.
- Achieving conductivity and Li^+ transference number sufficient to enable high rate batteries operating at sub-ambient and room temperature.



Proposed Future Research

- Establish fabrication protocols for ~ 20 μm thick electrolyte
- Optimize high energy density Li/NMC full cell configurations
- Optimize oxidative stability of the solid electrolyte
- Establish parameters for minimal interfacial impedance
- Study surface chemistry of MIC electrolyte before and after cycling
- Develop and optimize convenient film fabrication process for MIC electrolytes with nanocrystalline phase and higher σ and t_{Li^+} .
- Continue to investigate/develop PBDT polymer or MIC as cathode binder, and MIC as catholyte.

Summary

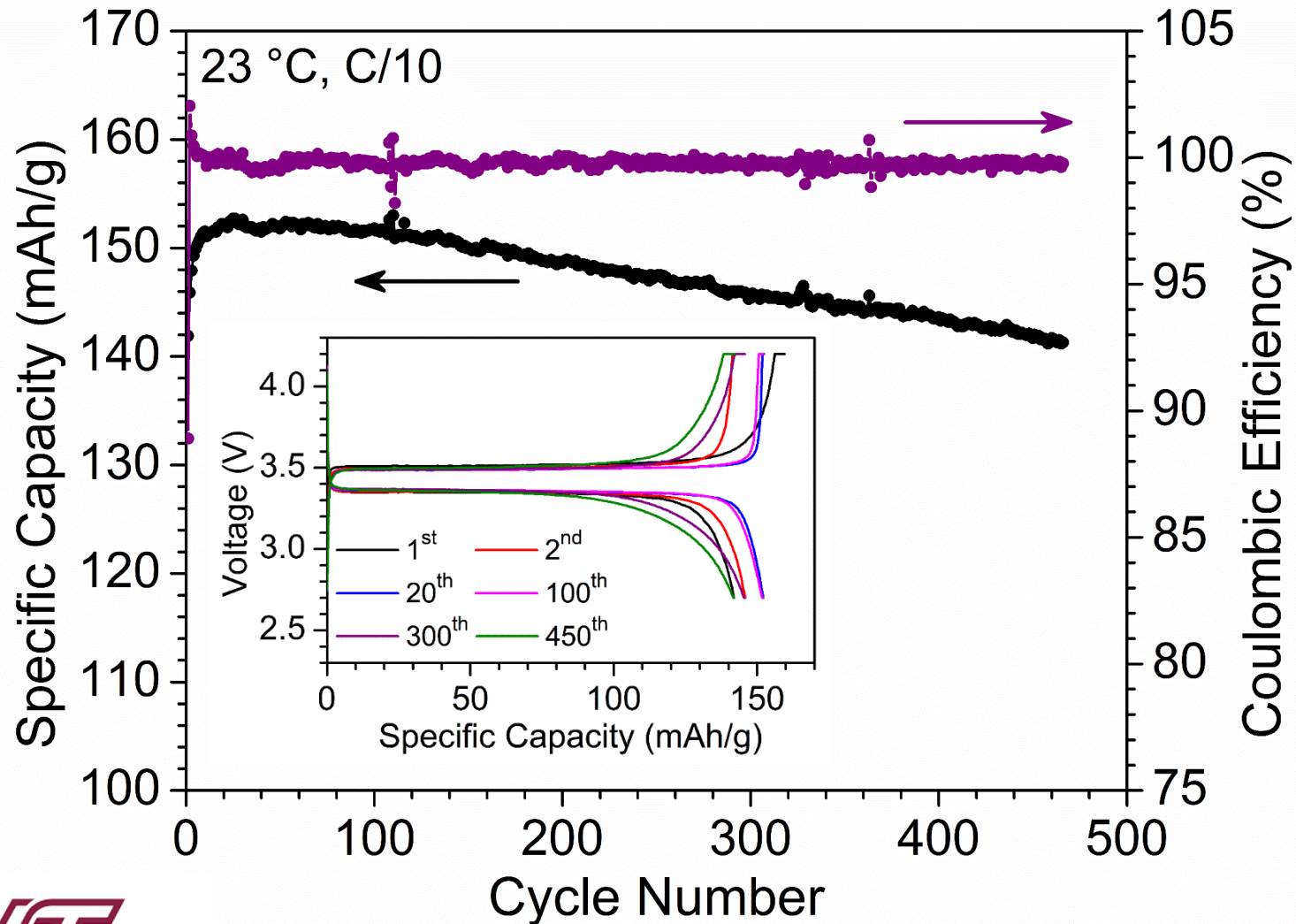
- Solid-state cell testing platform established (electrochemical protocol, temperature, etc).
- Wide temperature cyclability of MIC-based batteries with $\text{LiFePO}_4|\text{Li}$ cells.
- Homogeneous solid-state electrodes with MIC catholyte demonstrated. NMP-free formulation process. MIC can replace PVDF, enabling better full cell performance.
- Promising high-voltage cycling demonstrated in full cells. Cathode particles, surrounded by an ionic conductive matrix, can be charged sufficiently.
- Cell automatically shuts down at extreme high C rates and can return to normal cycling afterwards.
- Fundamental studies initiated to better understand MICs and their conducting mechanism.
- New MIC variants with nanocrystalline conducting phase show higher σ and t_{Li^+} .



Technical Backup Slides



Li/MIC/LiFePO₄ cell cycling stability at 23 °C



**Capacity retention
after 400 cycles: 94%**

Using PBDT as binder for LiFePO_4/C cathodes – additional details

**3% PBDT-LFP (competitor for PVDF)
LFP**

3 wt% **Li-PBDT**

10 wt% Acetylene back

87 wt% LiFePO_4

Solvent: **H_2O**

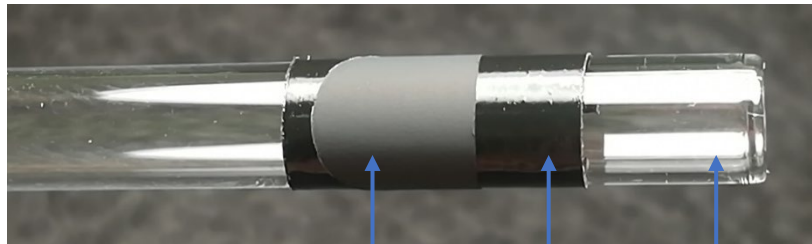
3% PVDF-

3 wt% **PVDF**

10 wt% Acetylene back

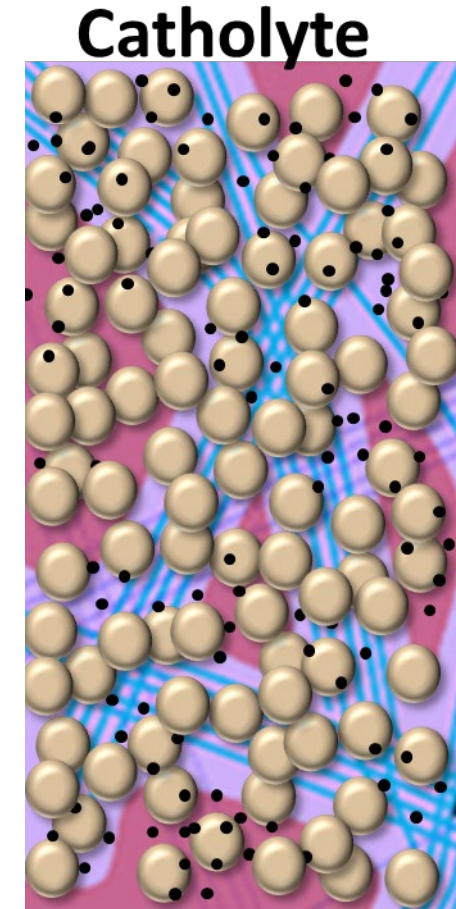
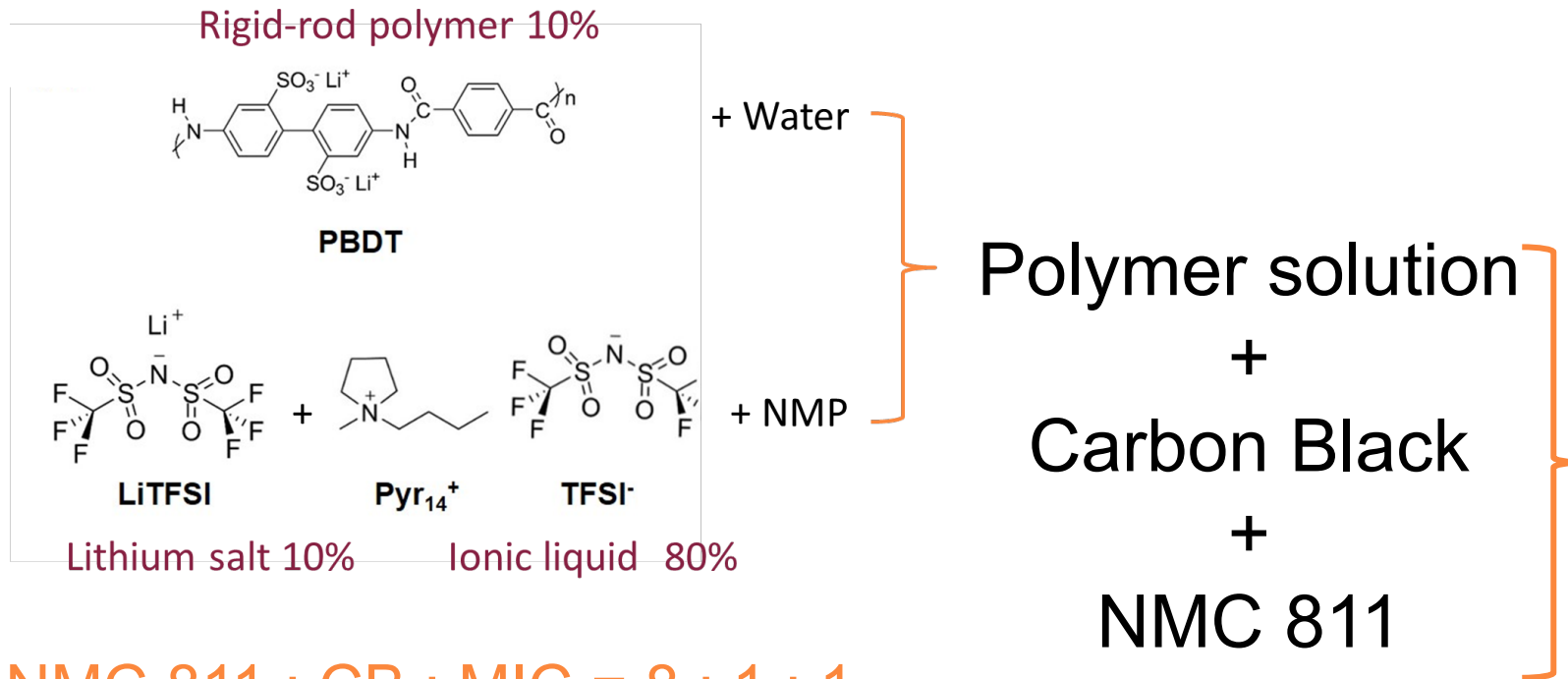
87 wt% LiFePO_4

Solvent: **NMP**



Electrode Tape Tube (5 mm OD)

Using MIC as binder for cathode (“catholyte” system) – additional detail



- NMC particle
- Carbon black

NMC 811 : CB : MIC = 8 : 1 : 1

Catholyte NMC 811 : CB : PBDT : LiTFSI : IL = 8 : 1 : 0.1 : 0.1 : 0.8

Cathode NMC 811 : CB : PVDF = 8 : 1 : 1