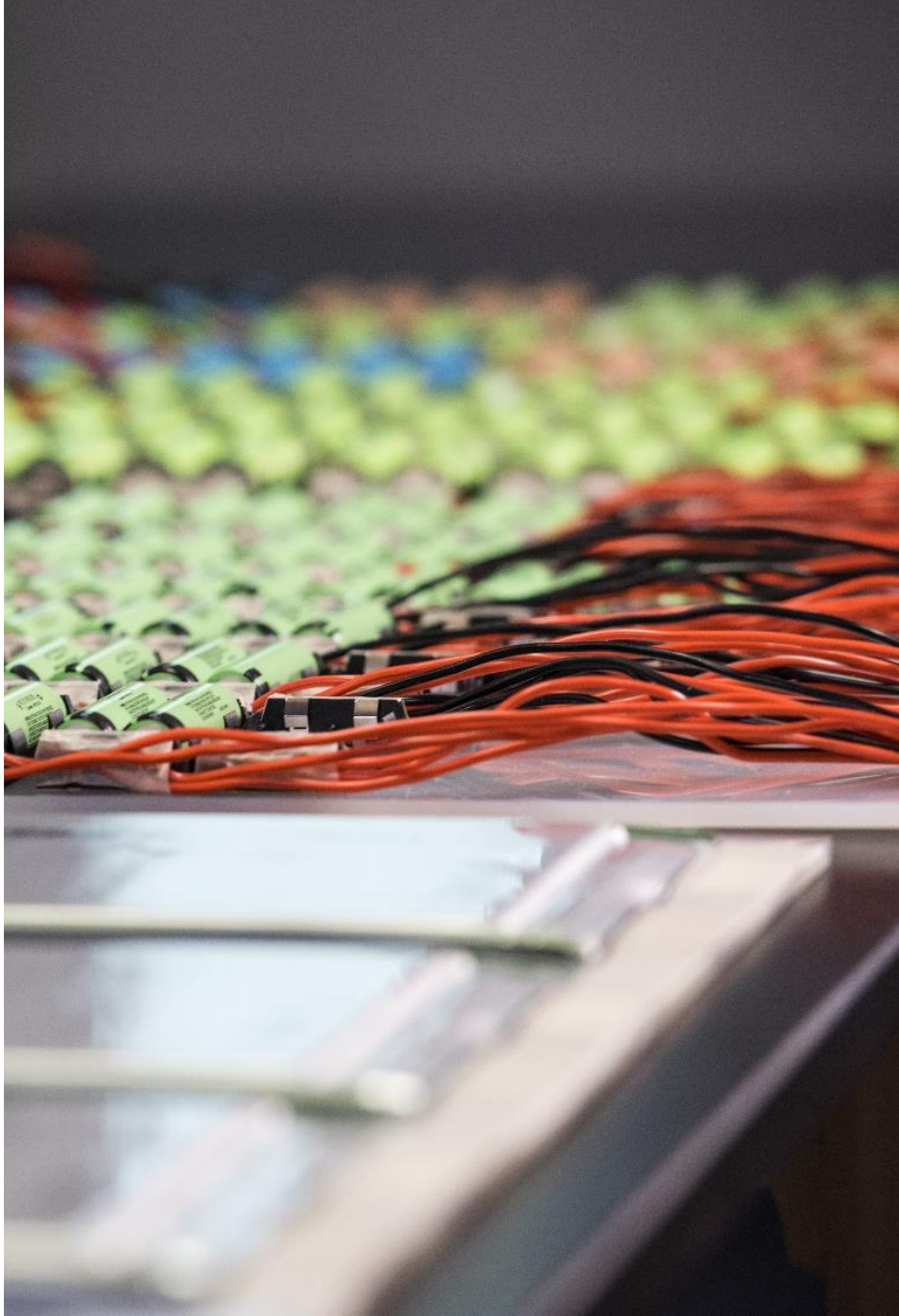
Lithium Dendrite Prevention for Lithium Batteries

Wu Xu (PI)
Ji-Guang Zhang

2019 DOE VTO Annual Merit Review

June 12th, 2019

Project ID #bat275



Overview

Timeline

- Start date: Oct. 2017
- End date: Sept. 2019
- Percent complete: 85%

Barriers

- Growth of lithium dendrites
- Low Coulombic efficiency
- Low charge current density

Budget

- Project funding
  - DOE share 100%
- Funding received in FY18: $400k
- Funding received in FY19: $400k

Partners

- Argonne National Laboratory
- U.S. Army Research Laboratory

Relevance/Objectives

- Enable lithium (Li) metal to be used as an effective anode in rechargeable Li-metal batteries for long cycle life.
- Explore various factors that affect the ionic conductivity, Li Coulombic efficiency (CE), Li anode morphology, and battery performances.
- Develop hybrid polymeric composite electrolytes to protect Li metal anode.
- Investigate compatibility of such electrolytes with 4-V high-Ni NMC cathode.

Milestones

Date	Milestones	Status
June 2018	Develop an inorganic/polymeric hybrid composite electrolyte with ionic conductivity over 1 mS cm^{-1} and Li CE over 99%	Completed
Sept. 2018	Achieve over 300 cycles for 4-V Li||NMC batteries with ~ 2 mAh cm^{-2} cathode loading	Completed
Dec. 2018	Investigate effects of high-concentration electrolytes on Li CE and deposited Li morphology.	Completed
March 2019	Investigate effects of polymers on Li CE and deposited Li morphology.	Completed
June 2019	Develop an HPICE with Li CE >98% and oxidation potential up to 4.4V.	On track
Sept. 2019	Achieve over 100 cycles for Li||NMC532 batteries with medium loading.	On track

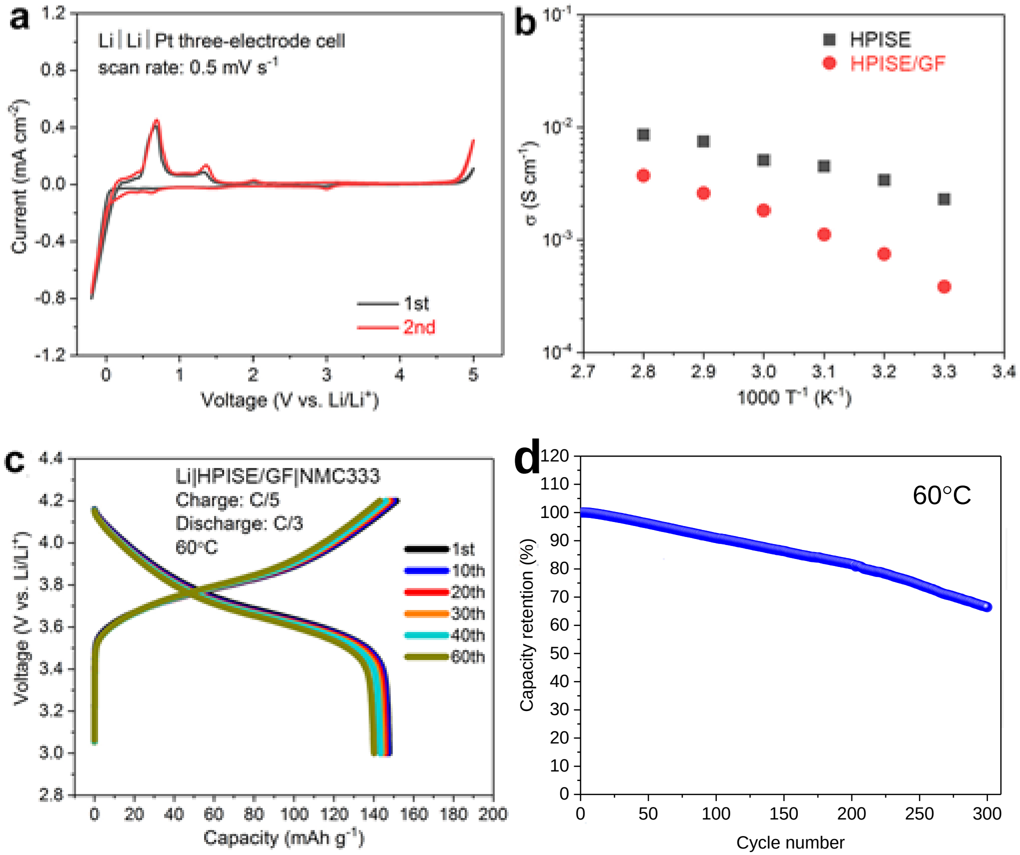
Approach

- Develop appropriate liquid high-concentration electrolytes (HCEs) to achieve high Li CE and stable with high voltage cathode.
  - Develop carbonate based HCEs.
  - Develop alkyl phosphate based HCEs.
  - Develop ether based HCEs.

- Develop new hybrid polymeric composite electrolytes to protect Li metal anode and enhance cycling performance of Li metal batteries.
  - Develop polymer in ‘quasi-ionic liquid’ electrolytes with high oxidation stability and high conductivity.
  - Develop solid-state polymer-in-salt electrolytes to enable Li metal battery cycled at high voltage.

Technical Accomplishments

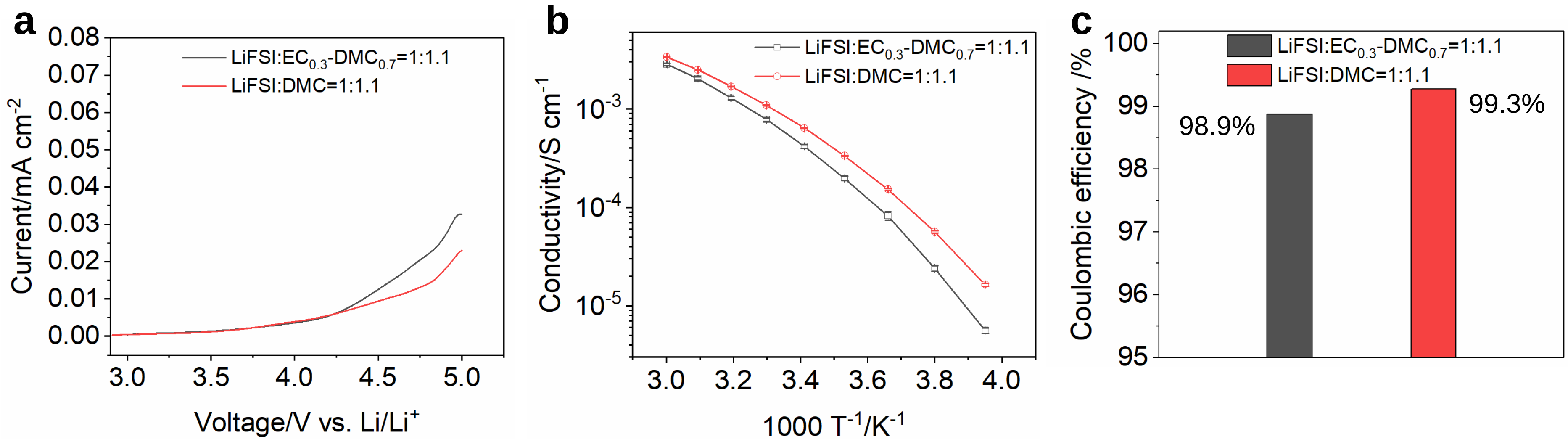
Performance of hybrid polymer-in-salt electrolyte (HPISE)



- The HPISE is stable up to 4.8 V on Pt, has a good ionic conductivity of 2.3 mS cm^{-1} at 30°C, and exhibits a reasonably stable cycling stability for 300 cycles in Li||NMC333 cells at 60°C.

Technical Accomplishments

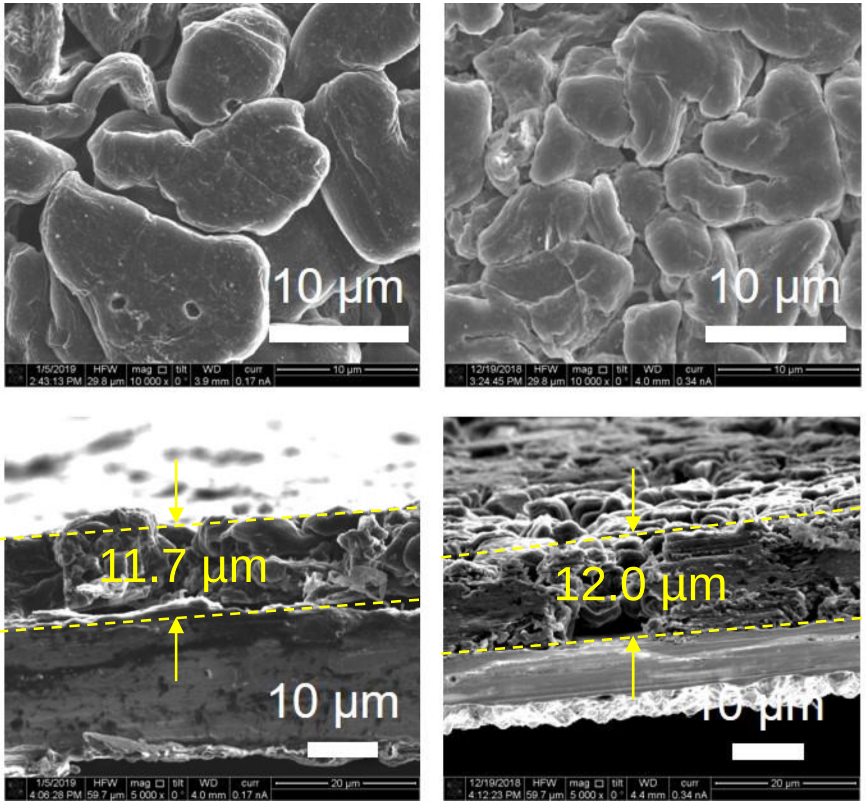
Carbonate high-concentration electrolytes (HCEs)



- DMC-based HCE has slightly higher oxidation potential, ionic conductivity and Li CE than EC-DMC based HCE.
- DMC-based HCE has electrochemical oxidation voltage around 4.55 V.
- DMC-based HCE has high ionic conductivity >1 mS cm^{-1} at 30°C and high Li CE of 99.3%.

Technical Accomplishments

Morphology of Li deposition in carbonate based HCEs

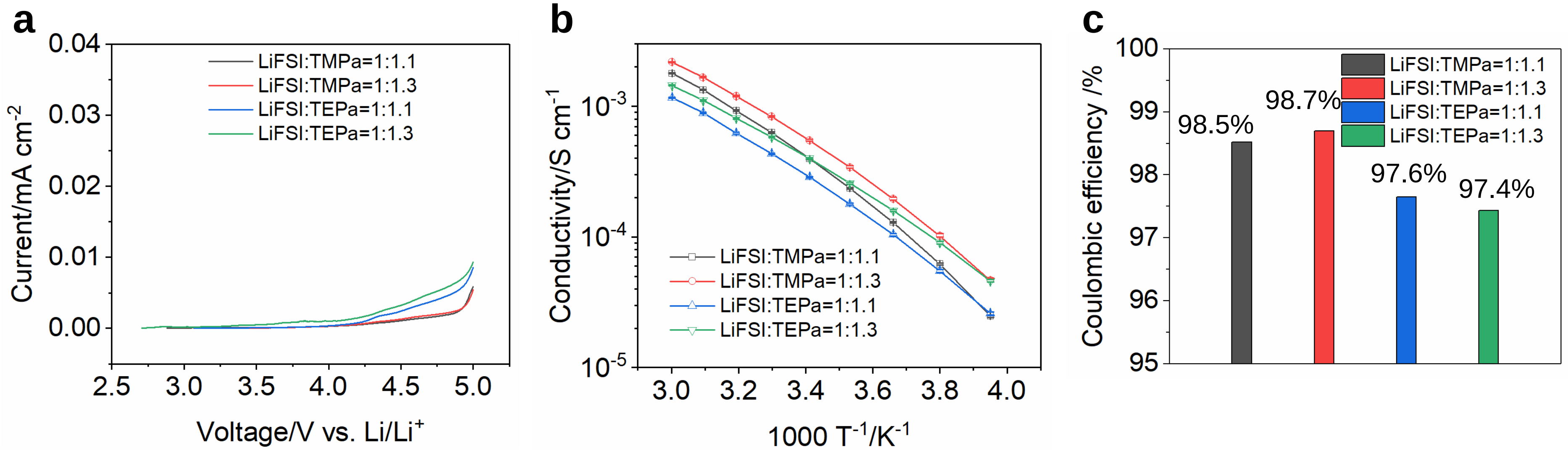

LiFSI:DMC=1:1.1

LiFSI: $EC_{0.3}$-$DMC_{0.7}$=1:1.1

- Both carbonate based HCEs lead to large granular and compact Li particles.

Technical Accomplishments

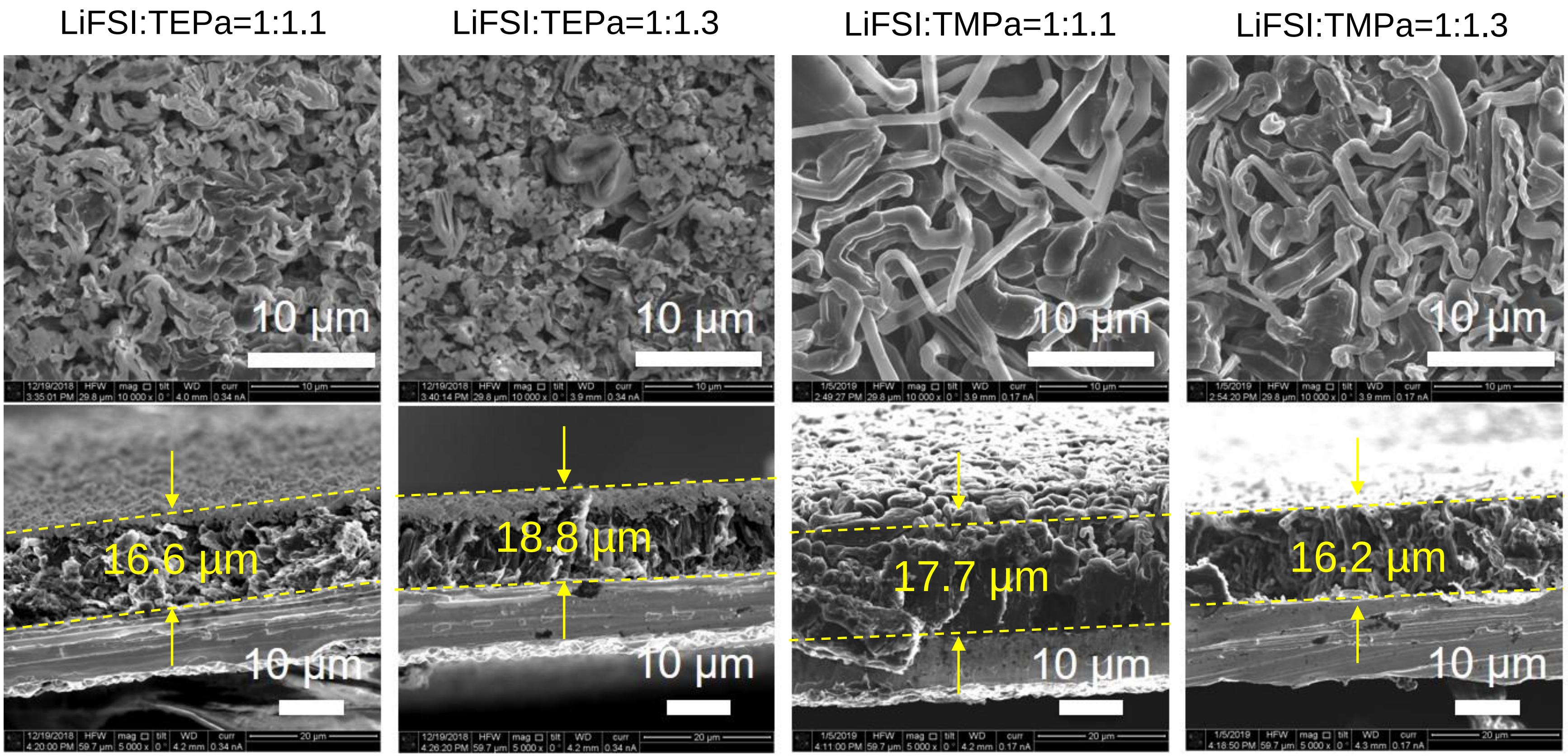
Alkyl phosphate based HCEs



- TMPa-based HCEs have slightly higher oxidation potential, ionic conductivity and Li CE than TEPa-based HCEs.
- TMPa-based HCEs exhibit about 5 V stability.
- TMPa-based HCEs have Li CE larger than 98%.

Technical Accomplishments

Morphology of Li deposition in phosphate based HCEs



LiFSI:TEPa=1:1.1

LiFSI:TEPa=1:1.3

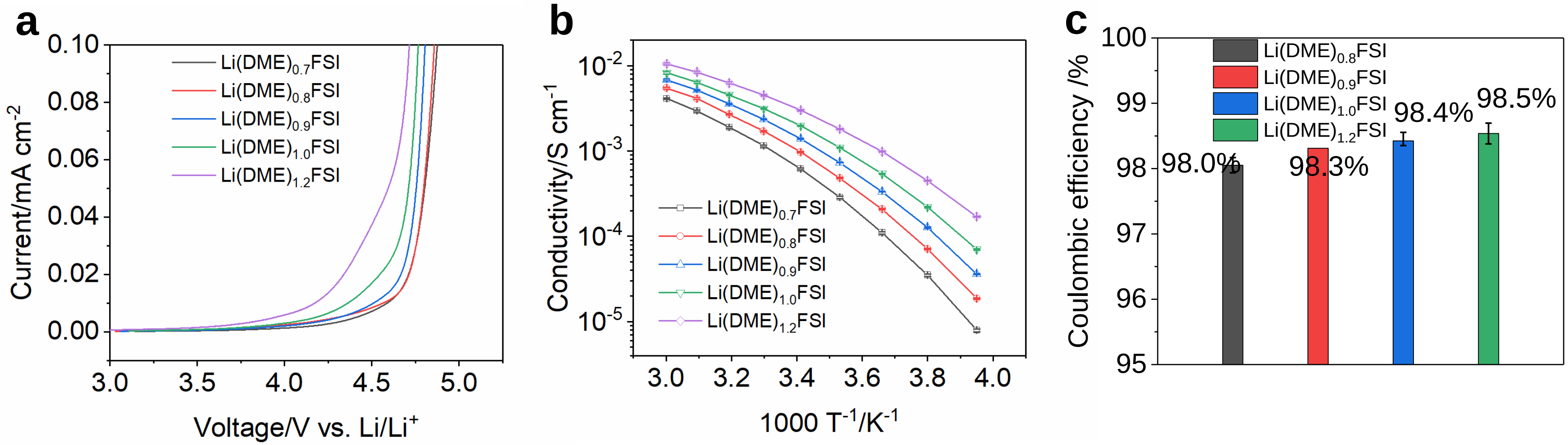
LiFSI:TMPa=1:1.1

LiFSI:TMPa=1:1.3

- TEPa electrolytes lead to irregular Li deposition.
- TMPa electrolytes lead to fibrous Li deposition.

Technical Accomplishments

Ether based HCEs — 'Quasi-ionic liquid' electrolytes

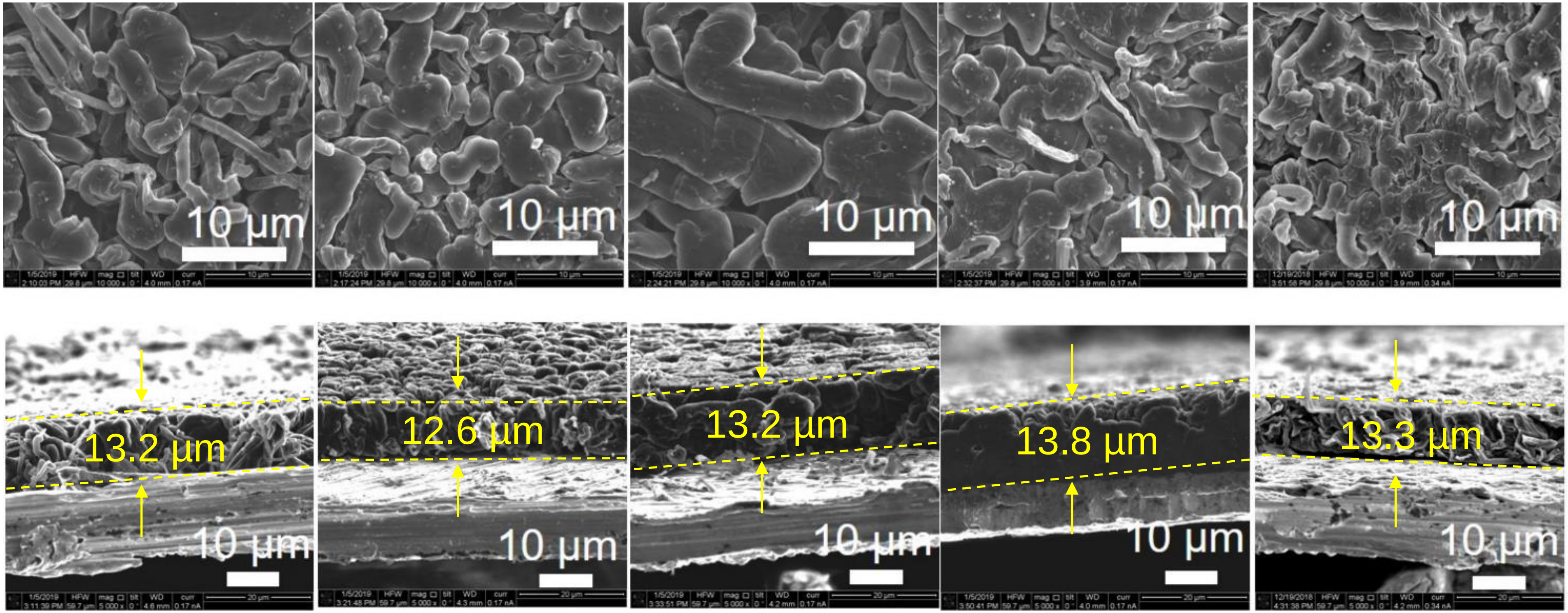


- With increasing the solvent content in HCEs, the ionic conductivity increases, the Li CE slightly increases, but the oxidation voltage decreases.
- Li(DME)$_{0.7}$FSI has stable oxidation potential up to 4.53 V, ionic conductivity over 1 mS cm^{-1} at 30°C, although its average Li CE could not be measured at RT.

Technical Accomplishments

Morphology of deposited Li metal in ether based HCEs

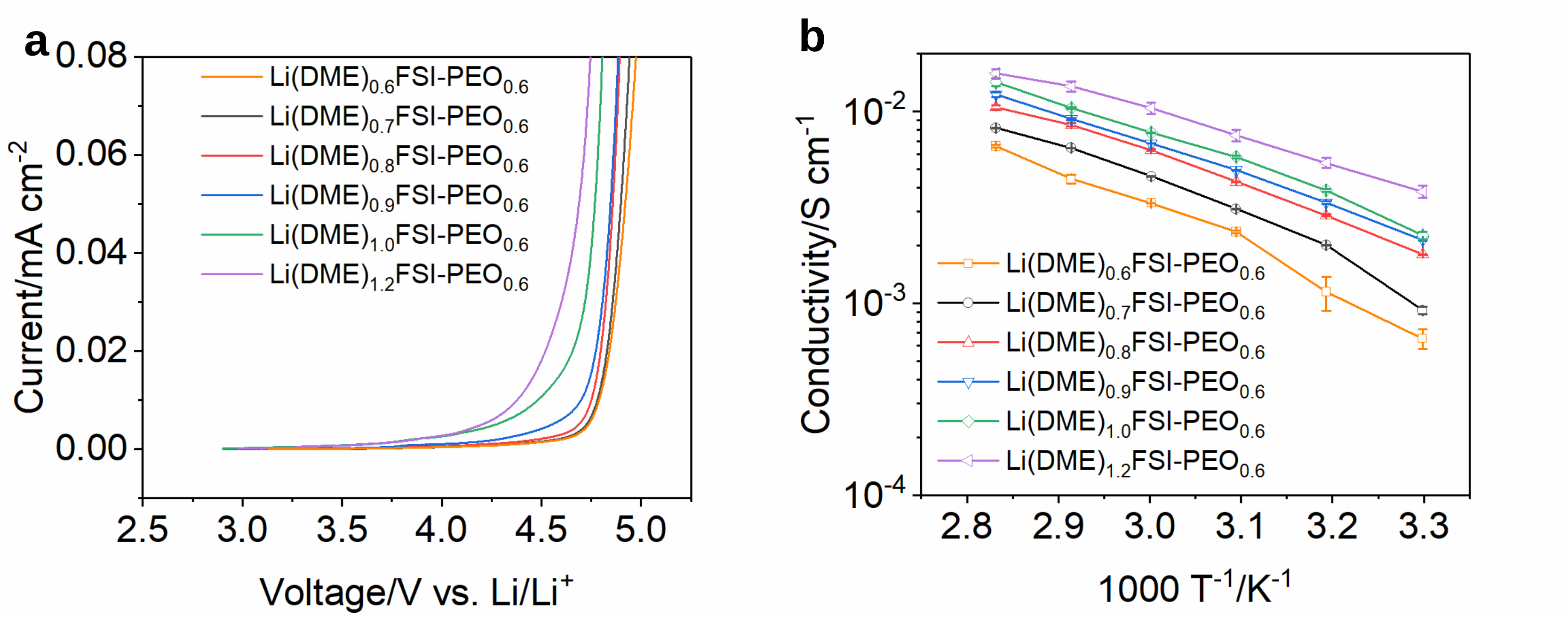
Li(DME)$_{0.7}$FSI Li(DME)$_{0.8}$FSI Li(DME)$_{0.9}$FSI Li(DME)$_{1.0}$FSI Li(DME)$_{1.2}$FSI



- All investigated electrolytes lead to large granular Li particles with similar thickness of Li deposition.

Technical Accomplishments

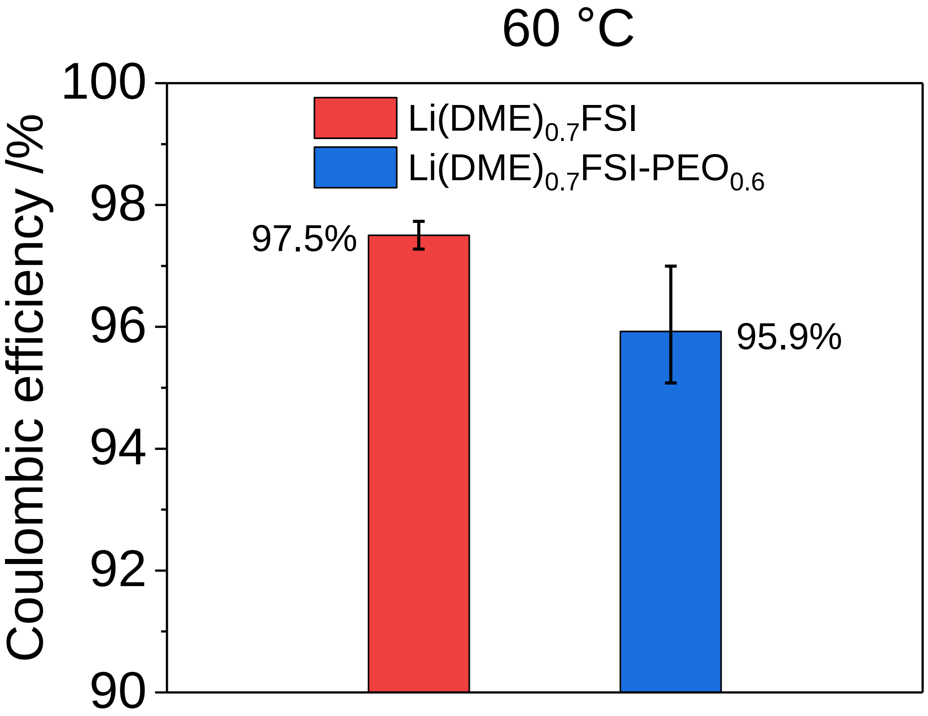
Polymer in ‘quasi-ionic liquid’ electrolytes (PQILEs)

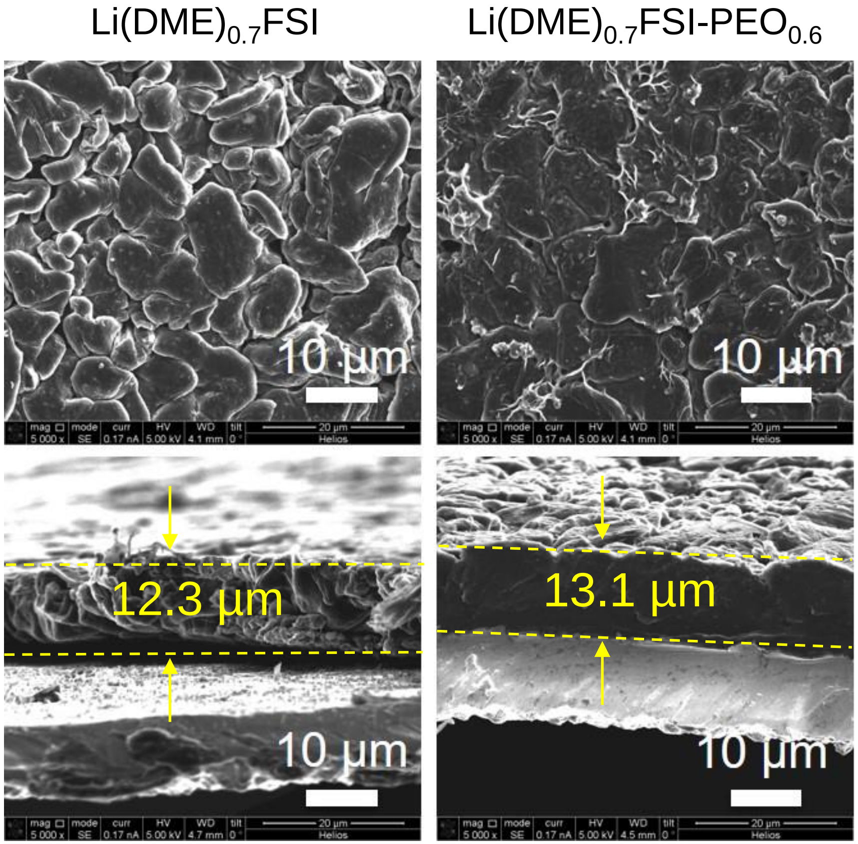


- PEO in ether-based ‘quasi-ionic liquid’ electrolytes.
- With increasing the solvent content in PQILEs, the ionic conductivity increases, but the oxidation voltage decreases.
- PQILE of Li(DME)$_{0.7}$FSI-PEO$_{0.6}$ has a wide potential window about 4.55 V and a high ionic conductivity >1 mS cm^{-1} at 30°C.

Technical Accomplishments

Effects of PEO on Li CE and morphology of deposited Li

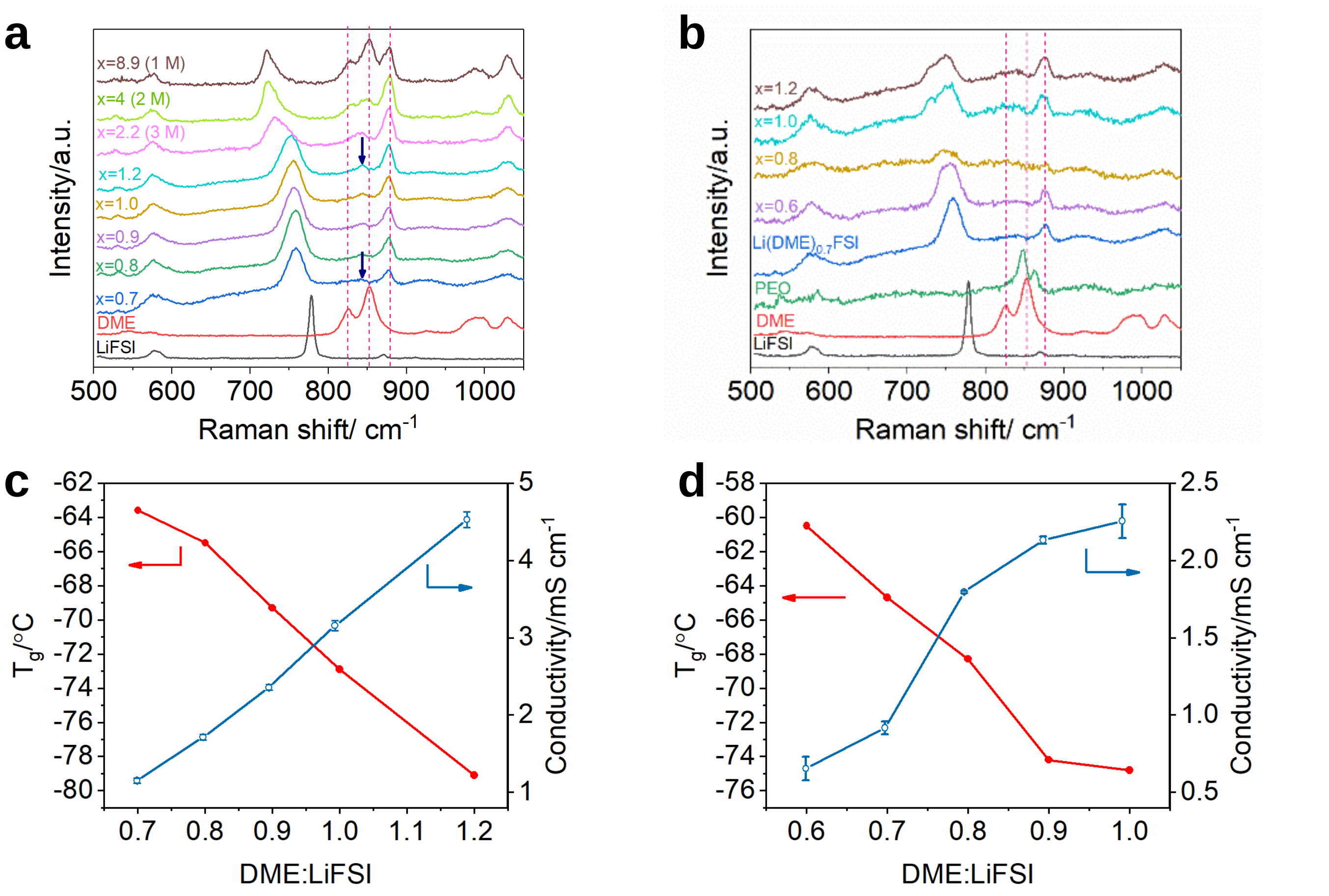




- PEO reduces the Li CE a little.
- PEO in PQILEs makes the deposited Li smoother.

Technical Accomplishments

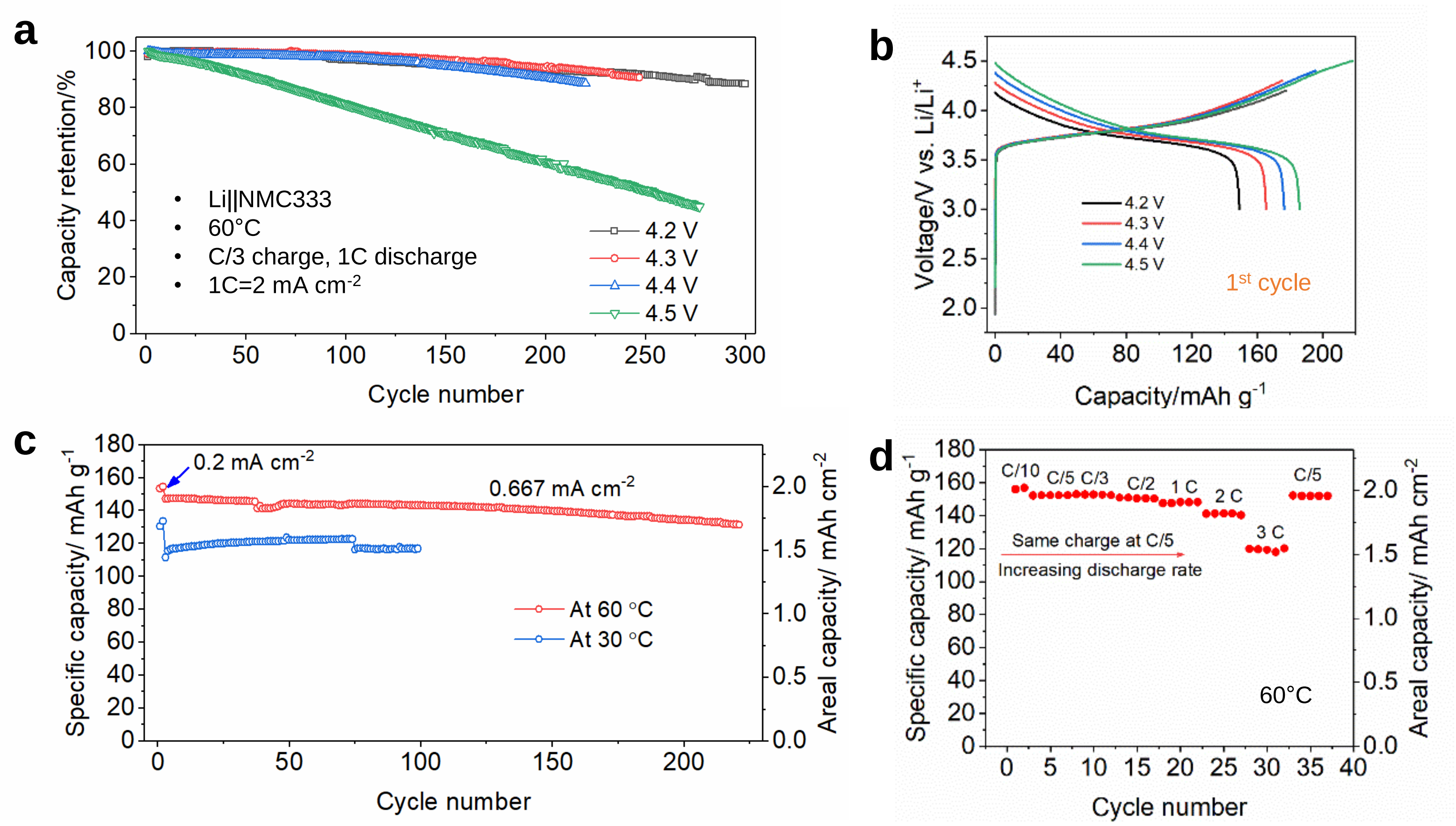
Solvation structure and glass transition temperature (T_g)



- Raman spectra demonstrate decrease of free DME and PEO with reducing the solvent (DME) content, due to the strong coordination with Li^+.
- T_g decreases with increasing DME, which can explain the increase of conductivity.

Technical Accomplishments

Li metal batteries test with PQILEs



- Stable Li||NMC333 cycling performance with a cut-off voltage up to 4.4 V.
- Good stability at both around room temperature and high temperature.
- Good rate capability.

Responses to Previous Year Reviewers' Comments

- This project was not reviewed last year.

Collaboration and Coordination with Other Institutions

- Argonne National Laboratory: Provided coated NMC cathode sheets for testing.

- U.S. Army Research Laboratory: Provided purified solvents and conducted DSC measurements.

Remaining Challenges and Barriers

- Low Coulombic efficiency of Li metal anode during cycling.
- Cycling stability of Li metal batteries with high loading cathodes.
- Cycling stability of Li metal batteries with limited electrolyte amount.
- Li metal dimension or volume change during charging and discharging cycles.

Proposed Future Work

- Continue the development of hybrid polymer-in-salt composite electrolytes and the evaluation in Li metal batteries.
- Study solid state polymer-in-salt electrolytes and Li metal batteries. Evaluate the effects of inorganic fillers or solid-state inorganic electrolyte.
- Increase CE of Li cycling to be ≥98% and achieve stable cycles for 4-V Li||NMC532 cells.

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

Summary

- Investigated high-concentration electrolytes for Li metal batteries.
  - Carbonate HCEs have oxidation voltage of 4.55 V and Li CE of 99.3%.
  - TMPa based HCEs exhibit 5 V stability and CE of 98.7%.
  - Ether HCEs have oxidation voltage above 4.5 V, Li CE around 98% and conductivity above 1 mS cm^{-1}.

- Developed hybrid polymer-in-salt electrolytes.
  - Polymer in "quasi-ionic liquid" electrolytes has a wide potential window around 4.5 V vs. Li/Li$^+$ and high conductivity above 1 mS cm^{-1}.
  - Li metal batteries have excellent stability with a cut-off voltage of 4.4 V.
  - More development and tests are currently under way.

Acknowledgements

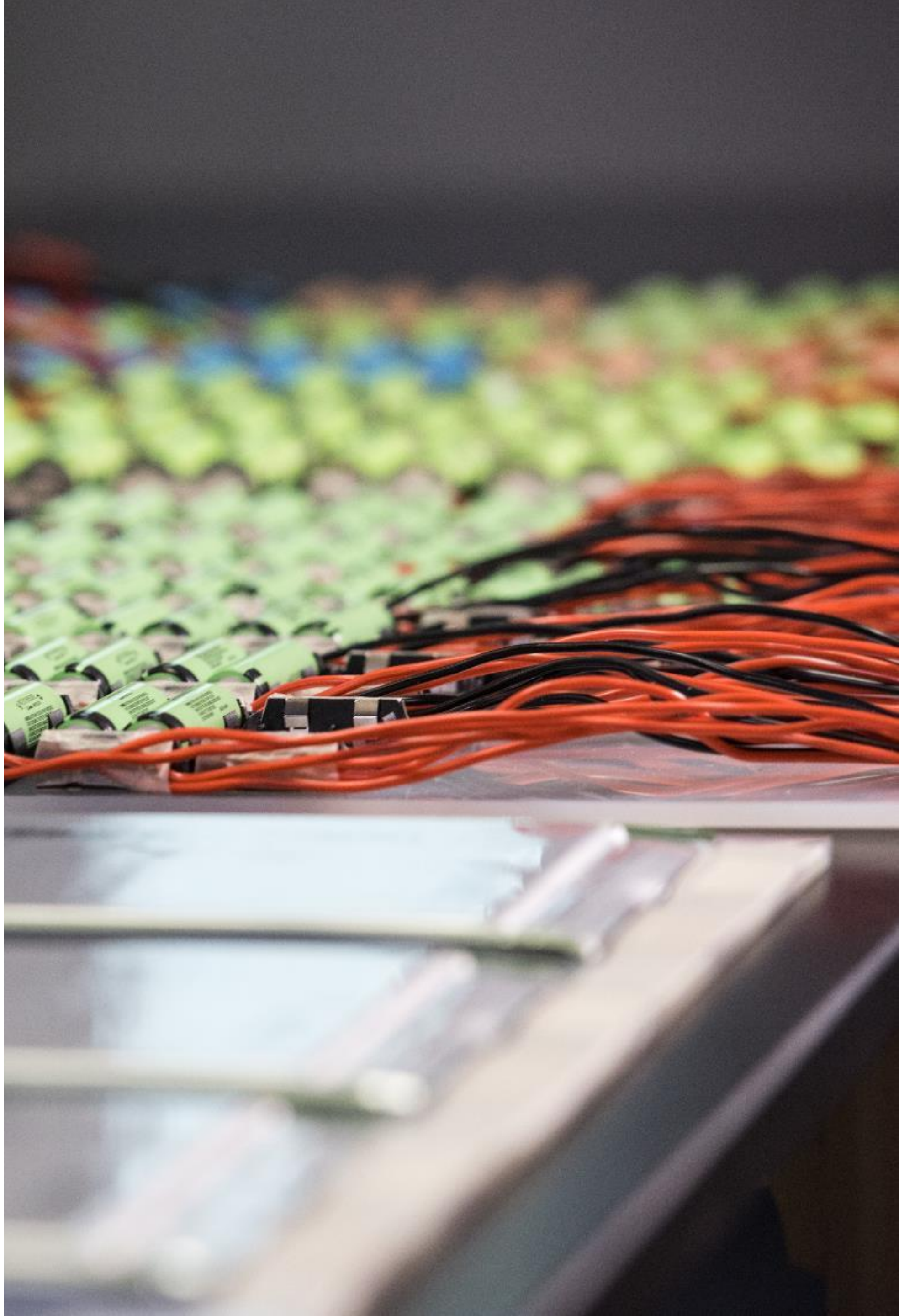
- Financial support from the DOE Vehicle Technologies Office Advanced Battery Materials Research program is greatly appreciated.

- DOE / BER / EMSL for microscopic and spectroscopic characterizations and computational calculations.

- Team Members:

  Haiping Wu, Bin Liu, Linchao Zhang, Mark H. Engelhard,
  Patrick El-Khoury, Qiuyan Li

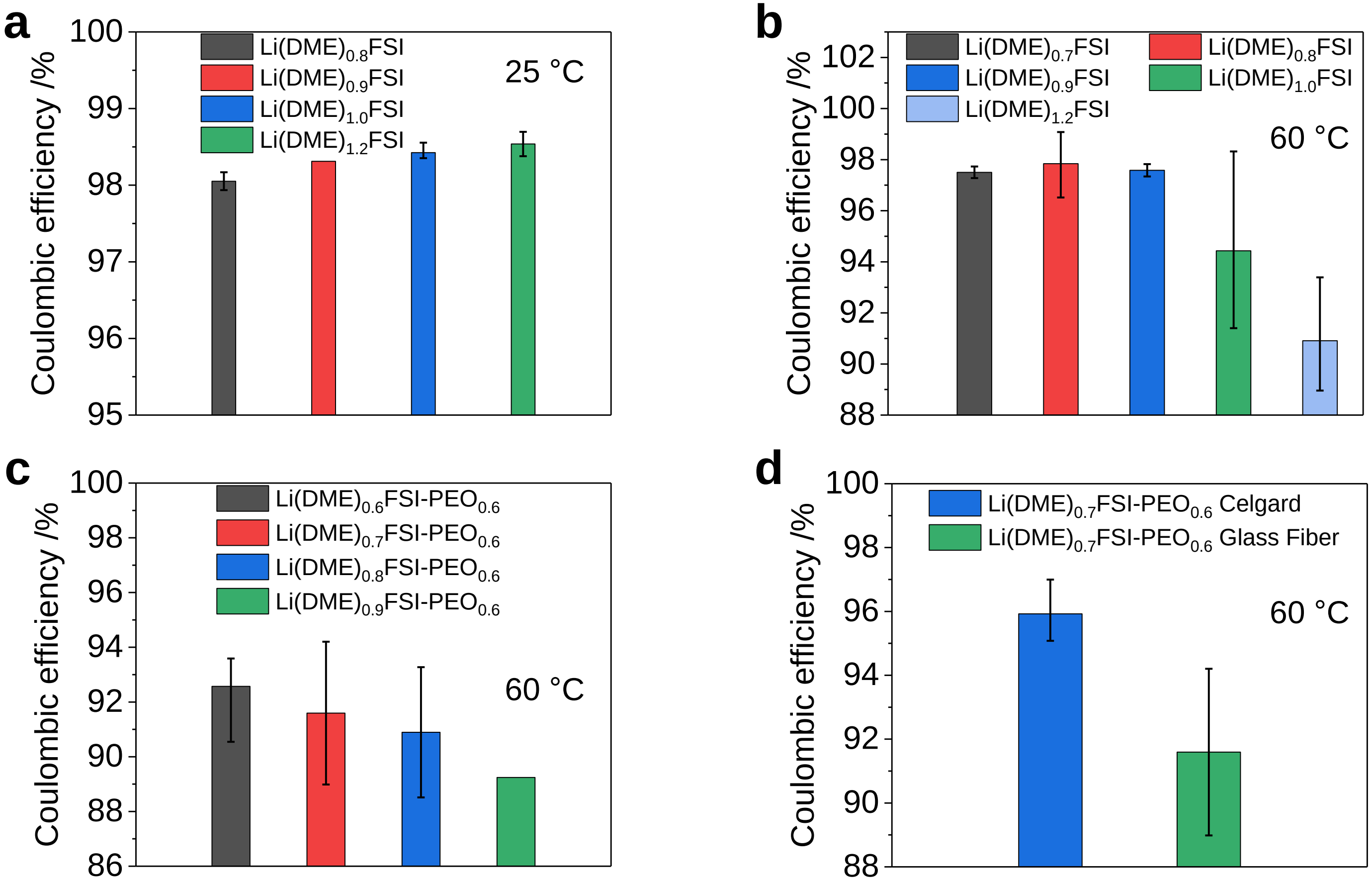
Technical Back-Up Slides



PNNL is operated by Battelle for the U.S. Department of Energy

Technical Accomplishments

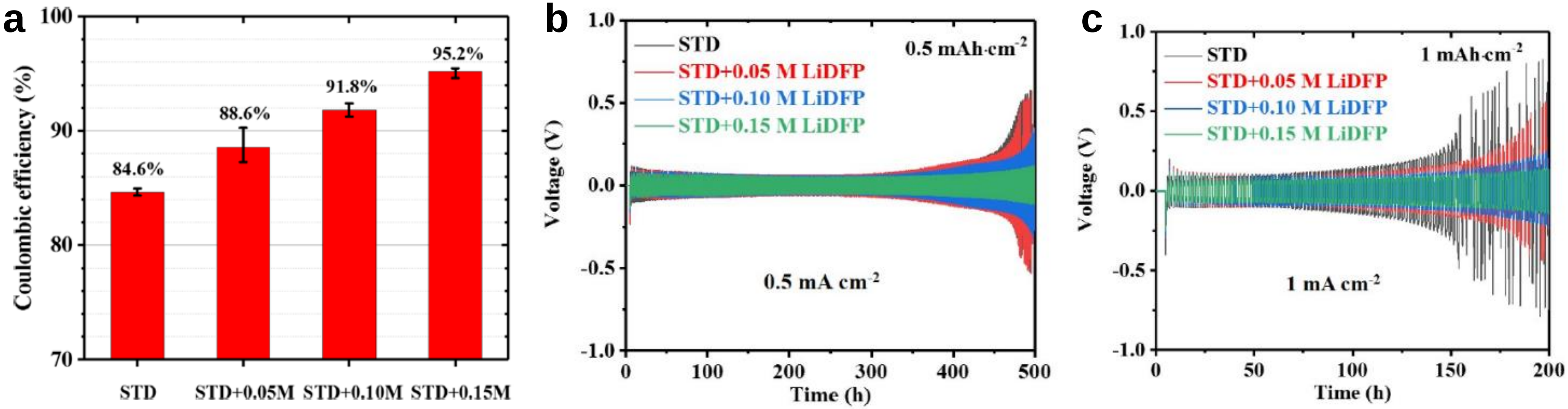
Effects of DME ratio, temperature, separator on Li||Cu CE



- At 25 °C, CE increase with increase of DME. At 60 °C, CE decrease with increase of DME.
- Polymer in “quasi-ionic liquid” electrolytes have lower CE than quasi-ionic liquids.
- CE decreases with the use of glass fiber as separator.

Technical Accomplishments

Effect of LiDFP additive in $LiPF_6$-carbonate electrolyte on Li CE and cycling stability



- Addition of LiDFP increases Li CE and cycling stability.
- The polarization could be reduced by introducing the LiDFP additive.

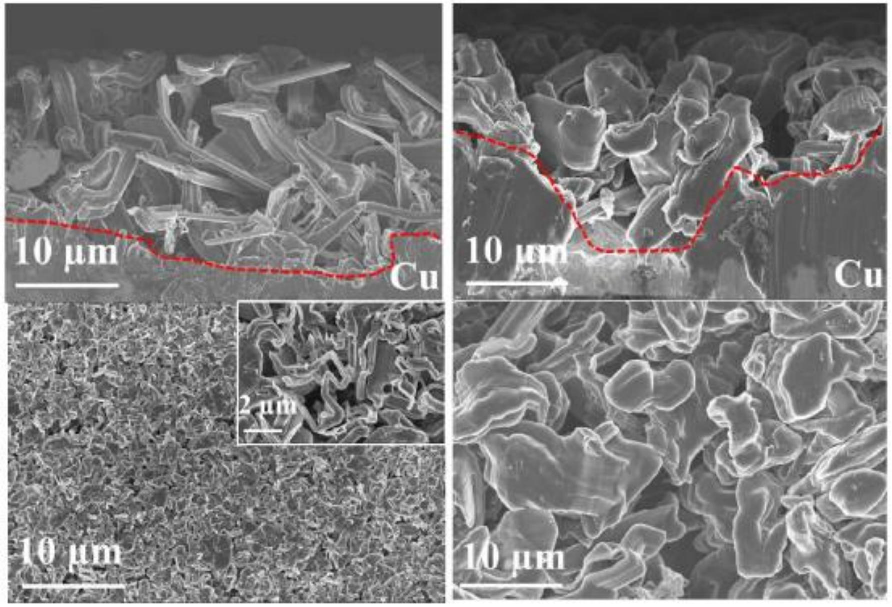
Technical Accomplishments

Effect of LiDFP additive in $LiPF_6$-carbonate electrolyte on Li morphology

After 1 deposition in Li||Cu cells

No LiDFP

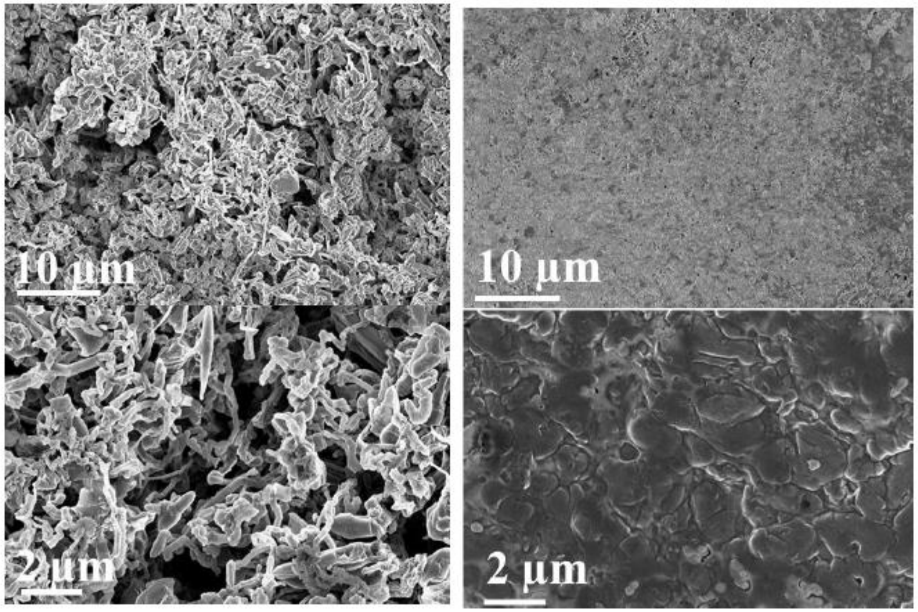
0.15 M LiDFP



After 100 cycles in Li||Li cells

No LiDFP

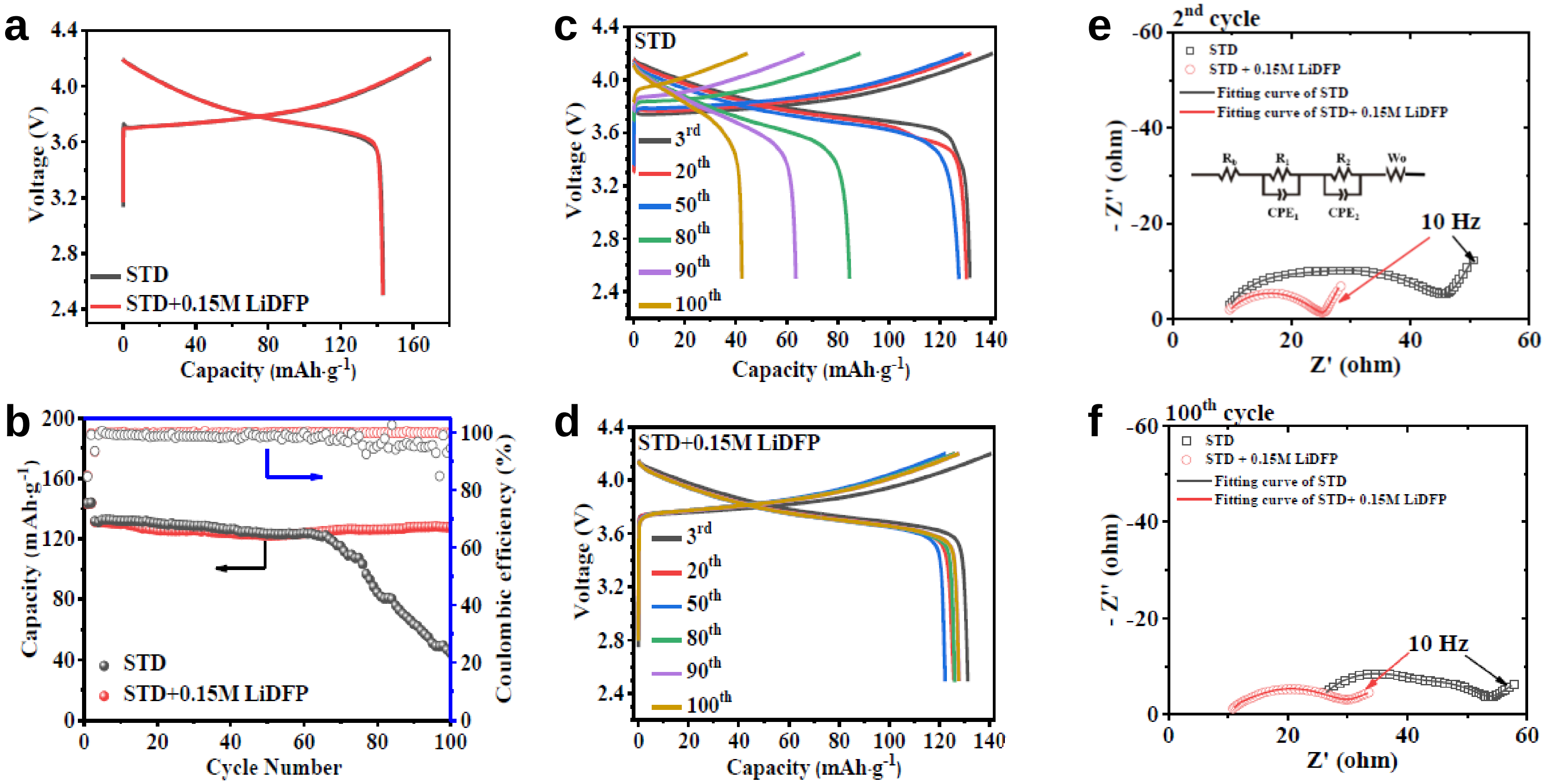
0.15 M LiDFP



- Rough, cracked surface and dendrites shown on Li in cells without LiDFP.
- Dense and uniform Li deposition without dendrite formation achieved in cells with LiDFP.

Technical Accomplishments

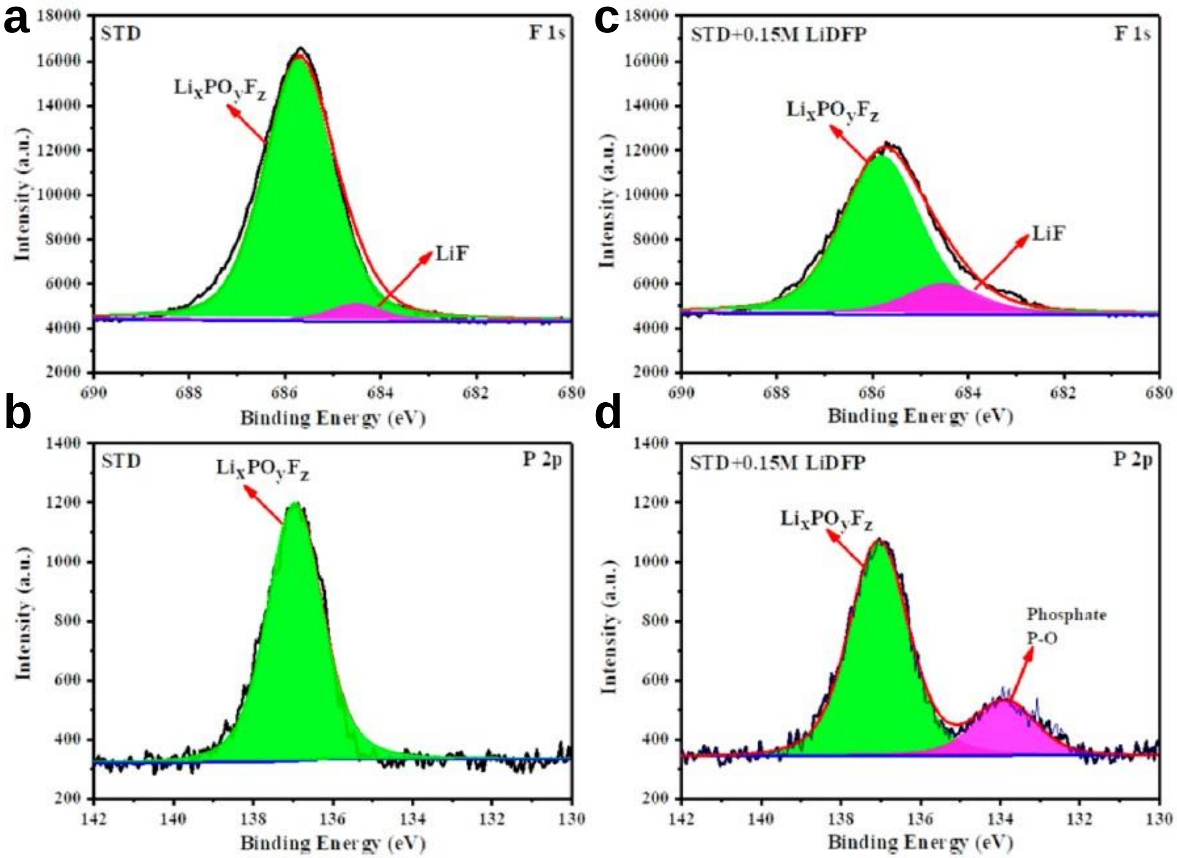
LiDFP additive in $LiPF_6$-carbonate electrolyte improves cycling stability of Li||NMC cells



- Stable Li||NMC333 cycling performance achieved with addition of LiDFP.
- Addition of LiDFP reduces electrolyte side reactions and cell resistance.

Technical Accomplishments

LiDFP additive induces different SEI components



- SEI layer rich in LiF and phosphate compounds, which prevents the continuous decomposition of electrolyte and facilitates Li^+ deposition with dendrite-free.