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A System-Level Approach to Li Metal/Iron Fluoride Batteries Enabled by Optimal Electrolyte Choice

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SAND# Here

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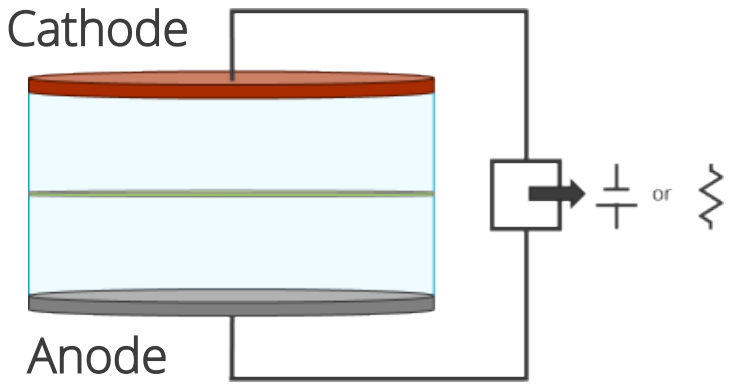
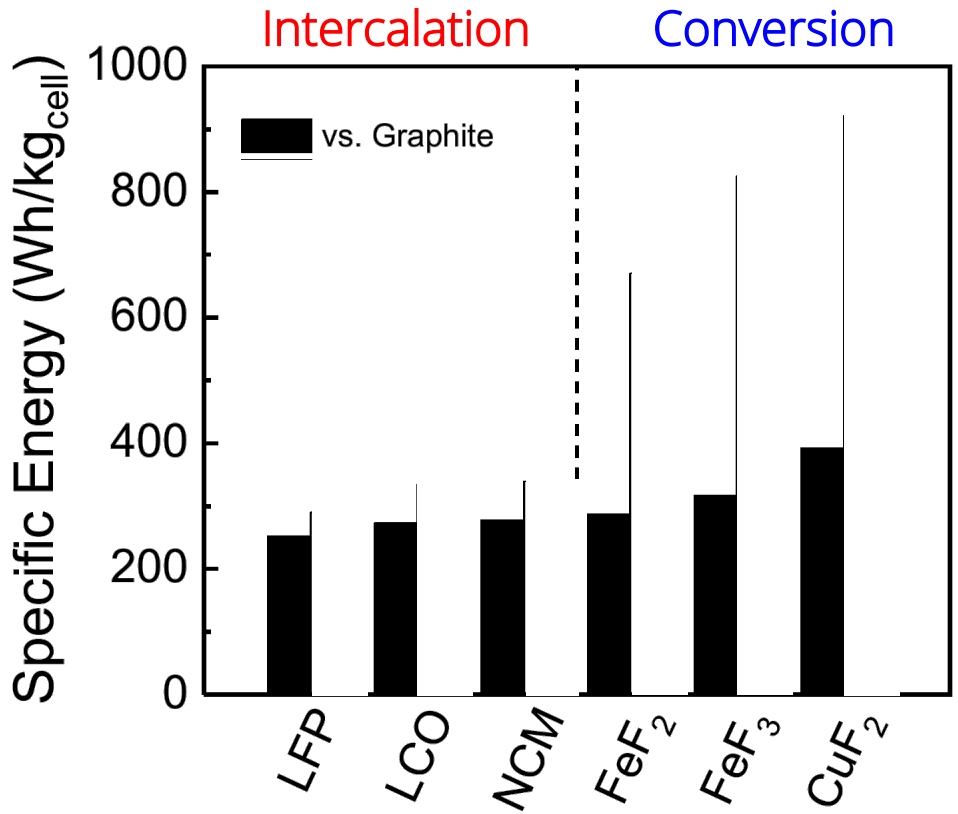
Pairing of high-capacity conversion cathodes with common anodes

- Choices of cathode **and** anode matter when building/testing a full cell battery
  - Conversion cathodes have higher capacities than intercalation cathodes
  - Need to balance energy density and system compatibility



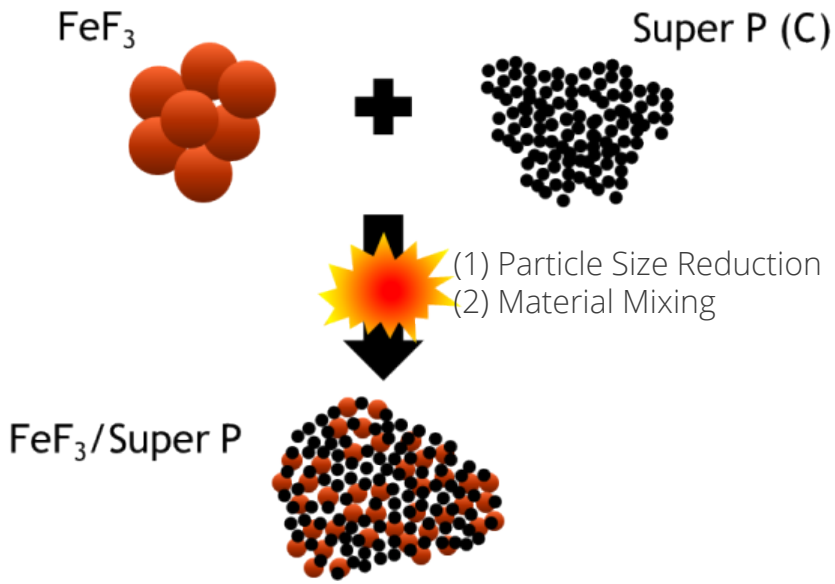


- Cathodes and Anodes are typically treated and optimized separately in studies
  - Is what's good for one electrode good for the other?

Wu *et al. Energy Environ. Sci.*, **2017**, *10*, 435--459

Compatibility of FeF_3/Li full cell batteries with electrolyte systems

- What is the most compatible electrolyte for a FeF_3/Li full cell?
  - Using Li metal anodes and ball-milled FeF_3/C cathodes
- Testing 4 electrolytes with known half-cell compatibilities
  - $Pyr_{13}FSI$ compatible with FeF_2
  - TTE/DME and Bisalt compatible with Li
- Using electrochemical, chemical, and physical characterization to study each of the electrodes separately and together



$Pyr_{13}FSI$[1] : 1M LiFSI in *N*-propyl-*N*-methylpyrrolidinium FSI ionic liquid

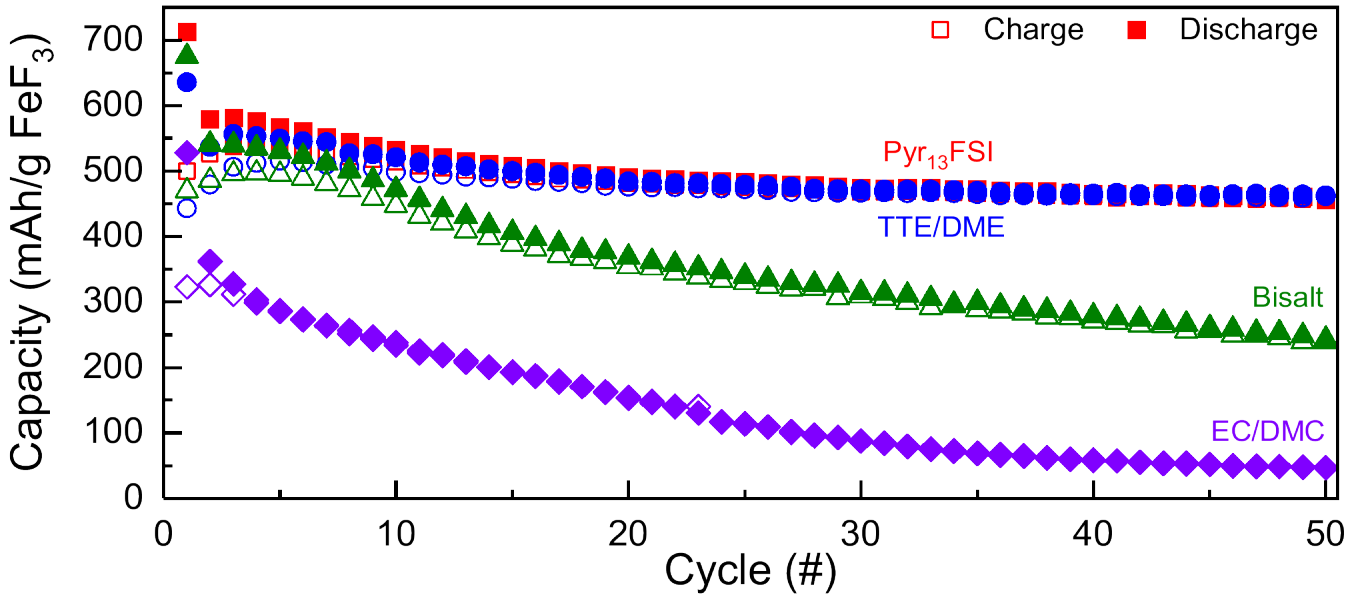
TTE/DME[2] : 1 mol eq. LiFSI in mixed perfluorinated/unfluorinated ethers (3:1.2 mol eq.)

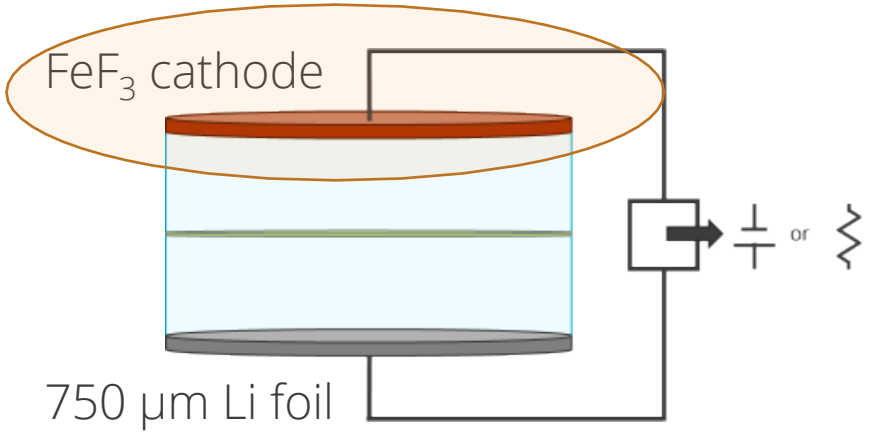
Bisalt[3] : 2M LiFSI + 1M LiTFSI in 1:1(vol) DOL/DME

EC/DMC : commercial 1M $LiPF_6$/carbonate electrolyte

[1]Xiao *et al.*, *Nature Mater.*, **2020**,
[2]Ren *et al. Joule.*, **2019**, *19*, 644-654
[3]Merrill *et al.*, *ACS Appl. Energy Mater.*, **2021**, *4*, 7589-7598

Compatibility of electrolytes with FeF_3



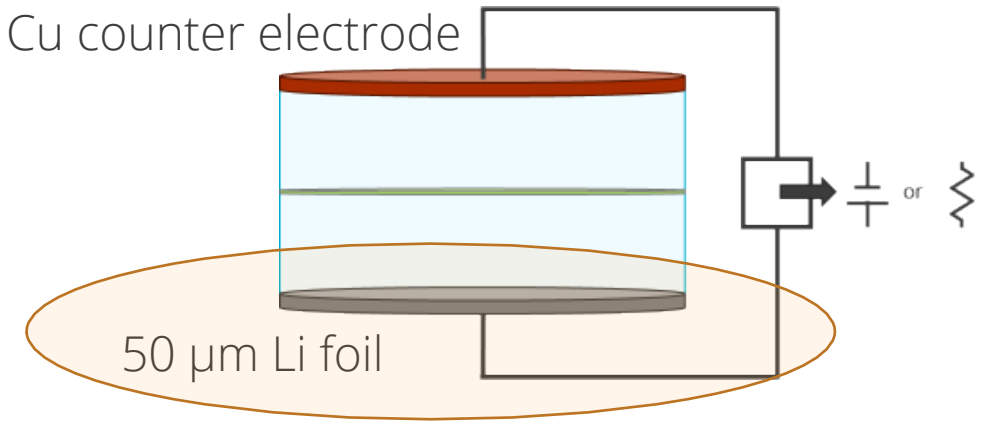


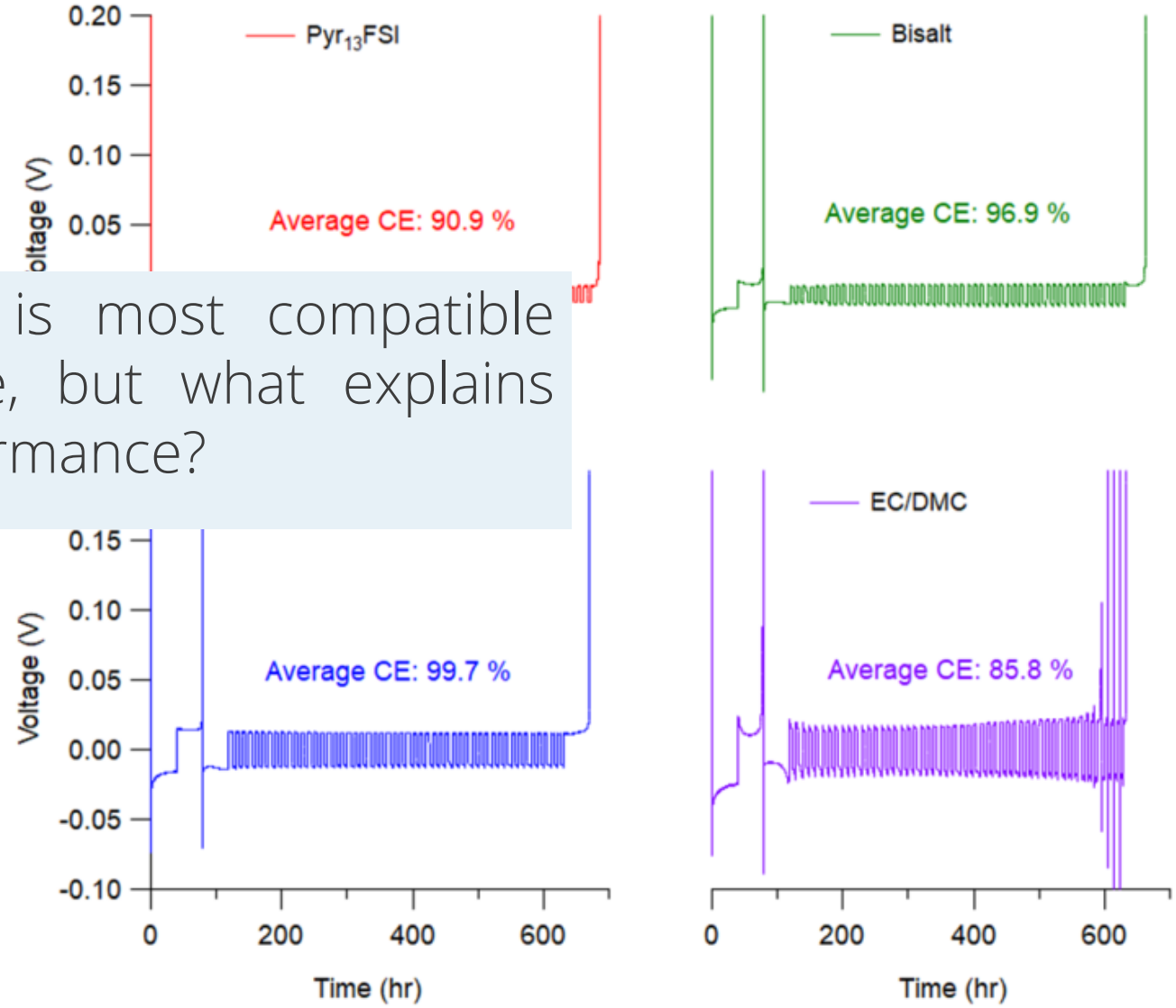
- FeF_3-limited cells made with excess Li, cycled at relatively slow rate (C/20)
- $Pyr_{13}FSI$ and TTE/DME show highest capacity retention
- Bisalt and EC/DMC show poor FeF_3 compatibility

Compatibility of electrolytes with Li metal

- Evaluated Li-compatibility of each electrolyte by measuring coulombic efficiency (CE) in a Cu/Li cell
  - CE = (#e^- out)/(#e^- in)
- TTE/DME and Bisalt sh
  CE and good behavior
- $Pyr_{13}FSI$ and EC/DMC a
  incompatible with Li metal

TTE/DME is most compatible electrolyte, but what explains this performance?

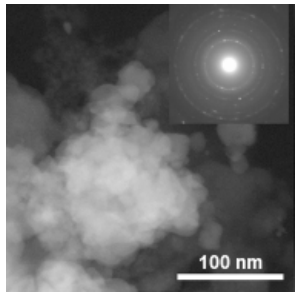




Micro/Nanoscopic changes to the electrodes

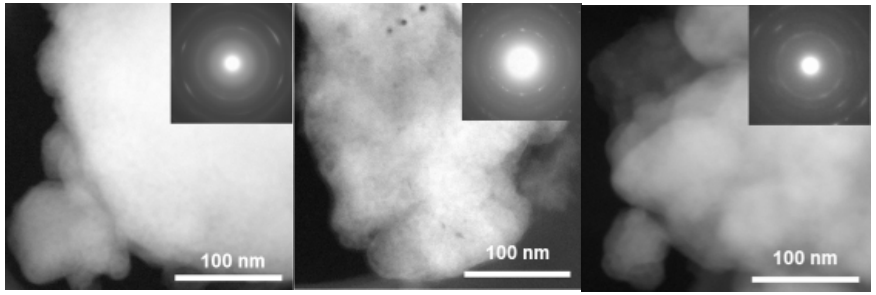
- Initial physical characterization by SEM and STEM showed important differences (and a lack of differences)

Minimal differences in final structure of FeF_3 cathodes



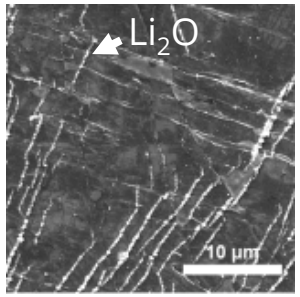
Uncycled

2 cycles



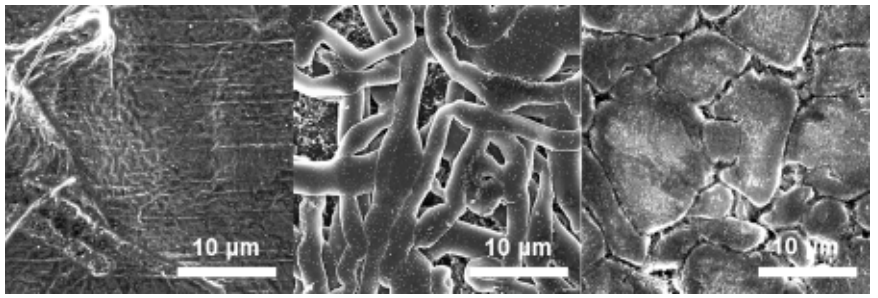
$Pyr_{13}FSI$ TTE/DME Bisalt

Notable differences in Li deposition morphology



Uncycled

2 cycles

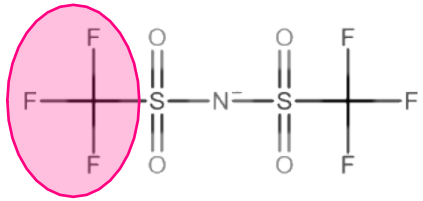


$Pyr_{13}FSI$ TTE/DME Bisalt

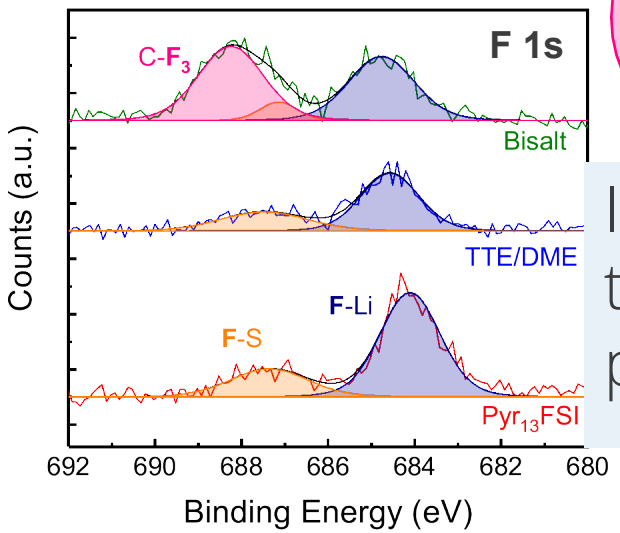
XPS shows important chemical differences in the CEI/SEI

- X-ray photoelectron spectroscopy (XPS) to probe differences in the chemistry of the electrode surfaces

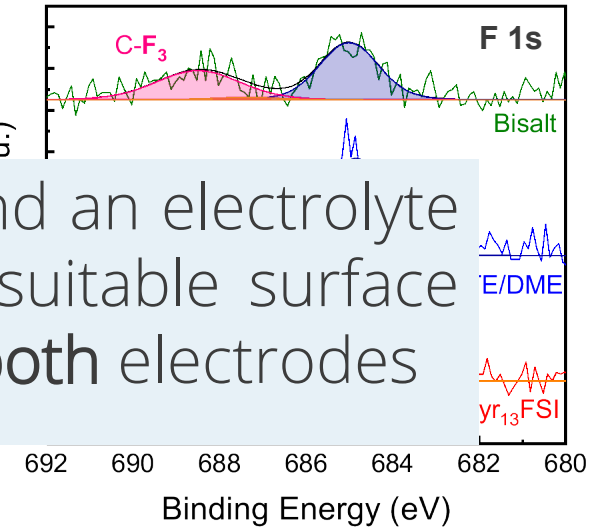
TFSI$^-$

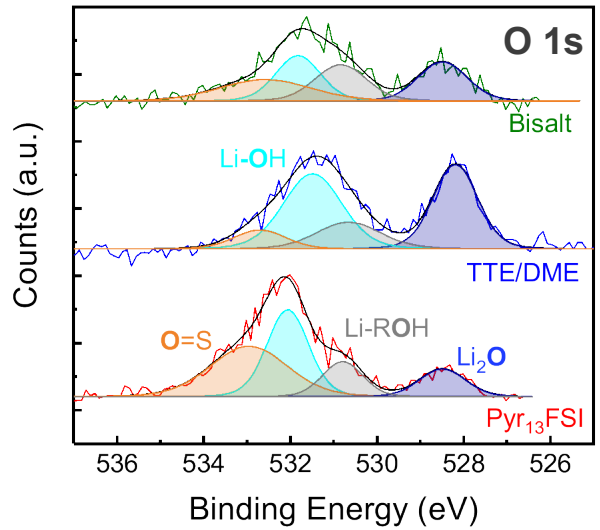


Cathode



Anode





Important to find an electrolyte that produces suitable surface protection for **both** electrodes

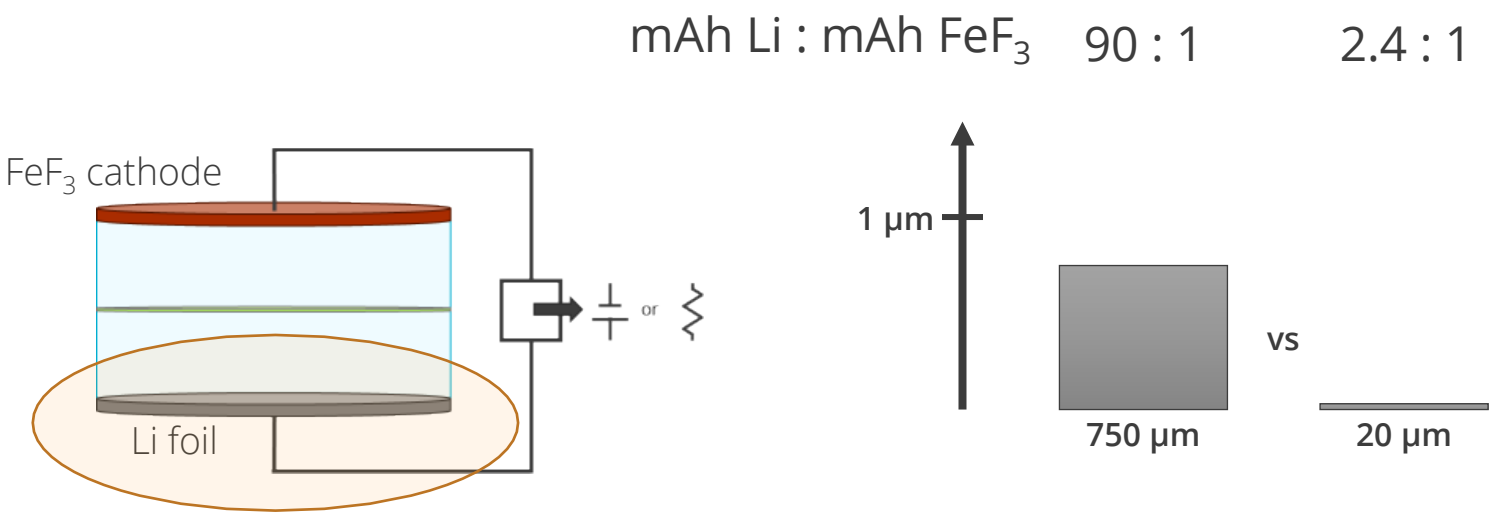
- Quantity of organic fluorine (C-**F_3**) in the cathode electrolyte interphase (CEI) appears correlated to worse cathode performance

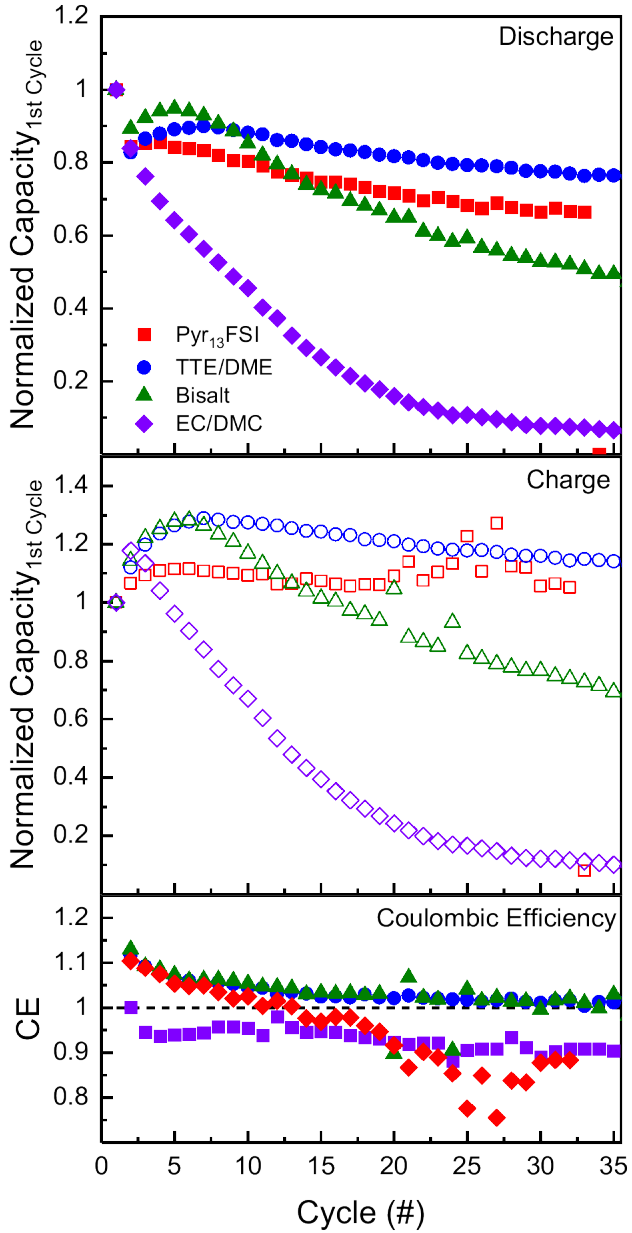
- Most fluorine in the solid electrolyte interphase (SEI) is from Li-F for all electrolytes
- Most significant difference is the relative Li_2O richness of the Li-optimized electrolytes relative to the $Pyr_{13}FSI$

	$Pyr_{13}FSI$	TTE/DME
Li_2O:LiOH –	1.1:1	and 2.8:1
Li_2O:LiF –	0.63:1	and 1.3:1

Application to limited-Li full cells

- Tested each electrolyte in a full FeF_3/Li cell with limited Li supply





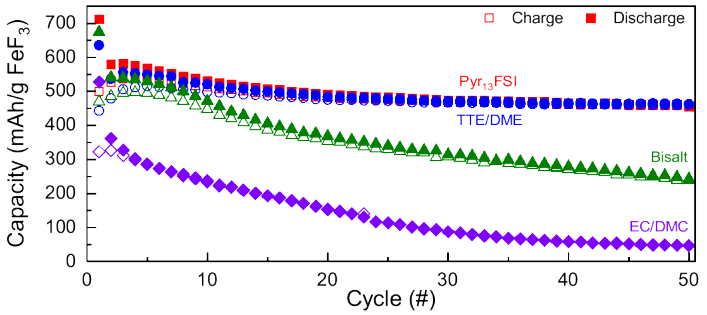
- Results agree with predictions
  - $Pyr_{13}FSI$ discharge appears stable, but begin to observe issues on charge and low coulombic efficiency due to Li

Summary

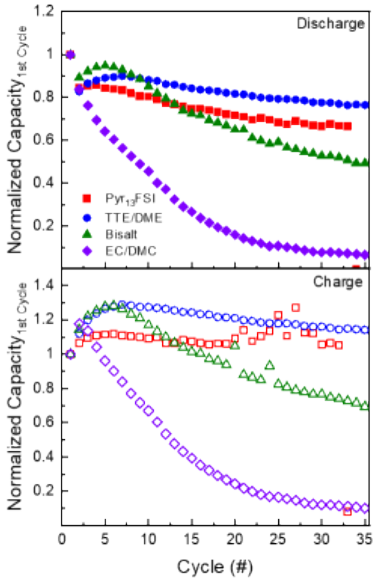
- Full cell compatibility should be taken into account when testing conversion cathode half cells

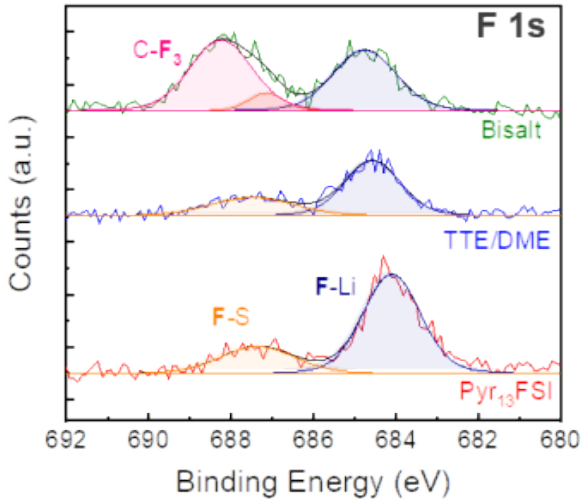
- Of the electrolytes tested, TTE/DME appears to be the best choice for a full cell FeF_3/Li secondary battery

- Chemical composition of CEI and SEI are corelated to electrode performance



Vs.





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