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Identifying Limitations of the Lithium Metal Anode through Laser Plasma Focused Ion Beam Cross-Sectional Imaging

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Identifying Limitations of the Lithium Metal Anode through Laser Plasma Focused Ion Beam Cross-Sectional Imaging

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Lithium Metal – “The Holy Grail Anode Material”

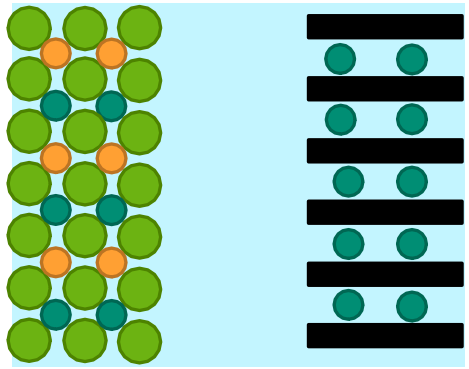
Ideal for High Energy Density Applications

- Large volumetric/gravimetric capacity
  - 2045 mAh/cm^3
  - 3830 mAh/g
- Negative reduction potential
  - -3.04 V vs. SHE

Limitations relating to:

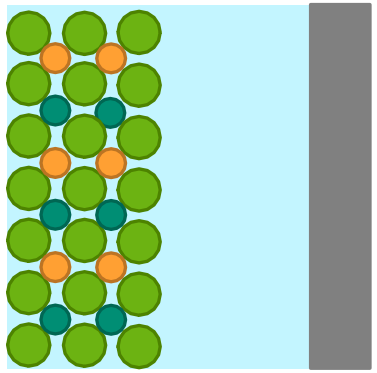
- Reversibility (Coulombic efficiency, CE)
- “Non-ideal” morphologies

Graphite Anode



~558 mAh/cm^3

Lithium Anode



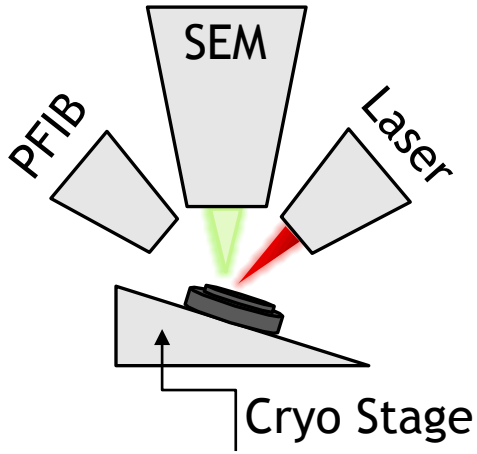
~2045 mAh/cm^3

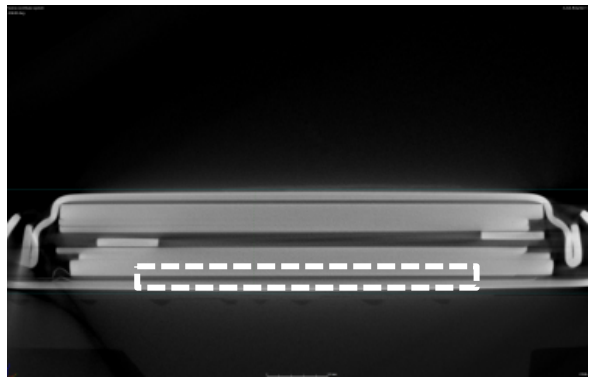
Laser Plasma Focused Ion Beam (Laser PFIB)

Cross-sections coin cell without destroying interfaces

CT scans cannot get level of detail
- Chemical information
- Scale

Previously used tool to show:
- *Separator shredding
- +Short circuiting





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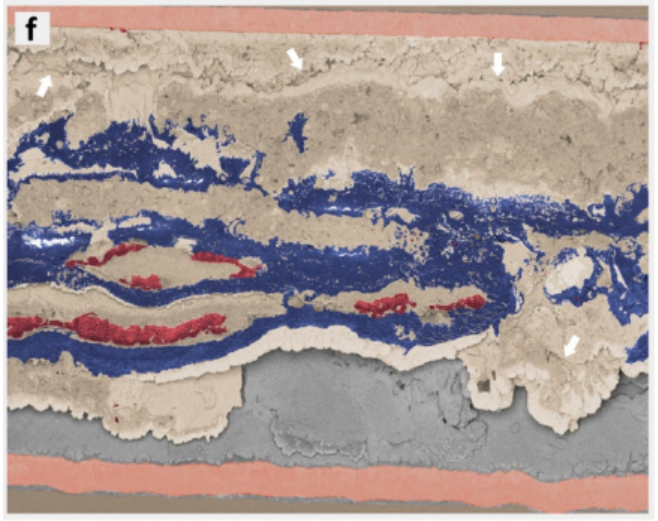
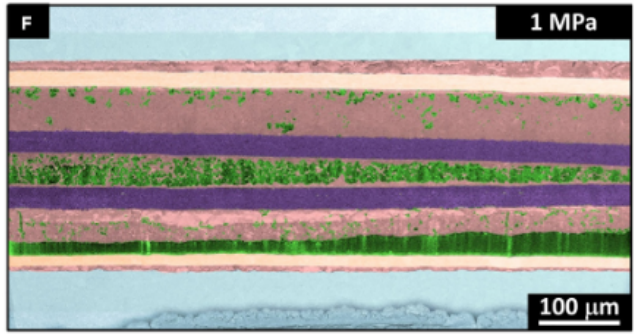


+



*Jungjohann *et al.*, *ACS Energy Lett.*, 2021, 6(6), 2138-2144

+Harrison, Merrill, *et al.*, *iScience*, 2021, 24(12), 103394

Electrolytes Under Investigation

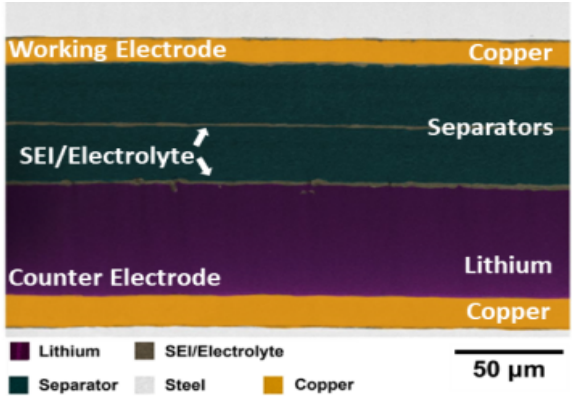
1 M $LiPF_6$ in EC:DEC ("Commercial Carbonate")
- Ionic Conductivity: 8.4 mS/cm
- Average CE*: 90.4 %

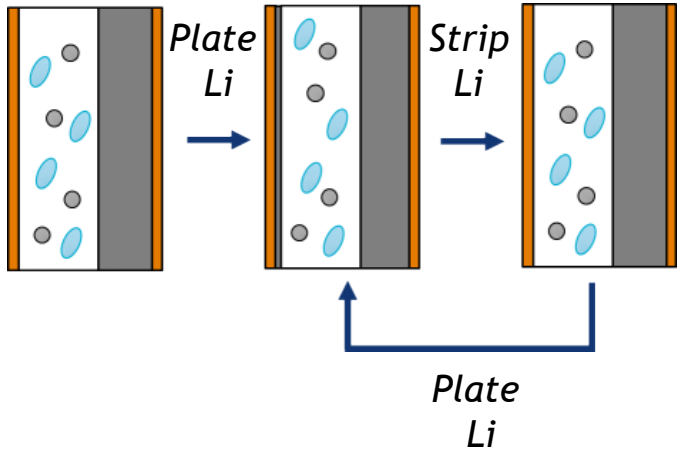
4 M LiFSI in DME
- Ionic Conductivity: 5.2 mS/cm
- Average CE: 99.0 %

2 M LiFSI – 1 M LiTFSI in DOL/DME ("Concentrated Bisalt")
- Ionic Conductivity: 8.6 mS/cm
- Average CE: 99.1 %

*average of first 20 cycles before cell failure began
**Li cycling performed at 0.47 mA/cm^2 for 1.88 mAh/cm^2

Pristine Cell





$$CE(\%) = \frac{charge\ stripped}{charge\ plated} * 100$$

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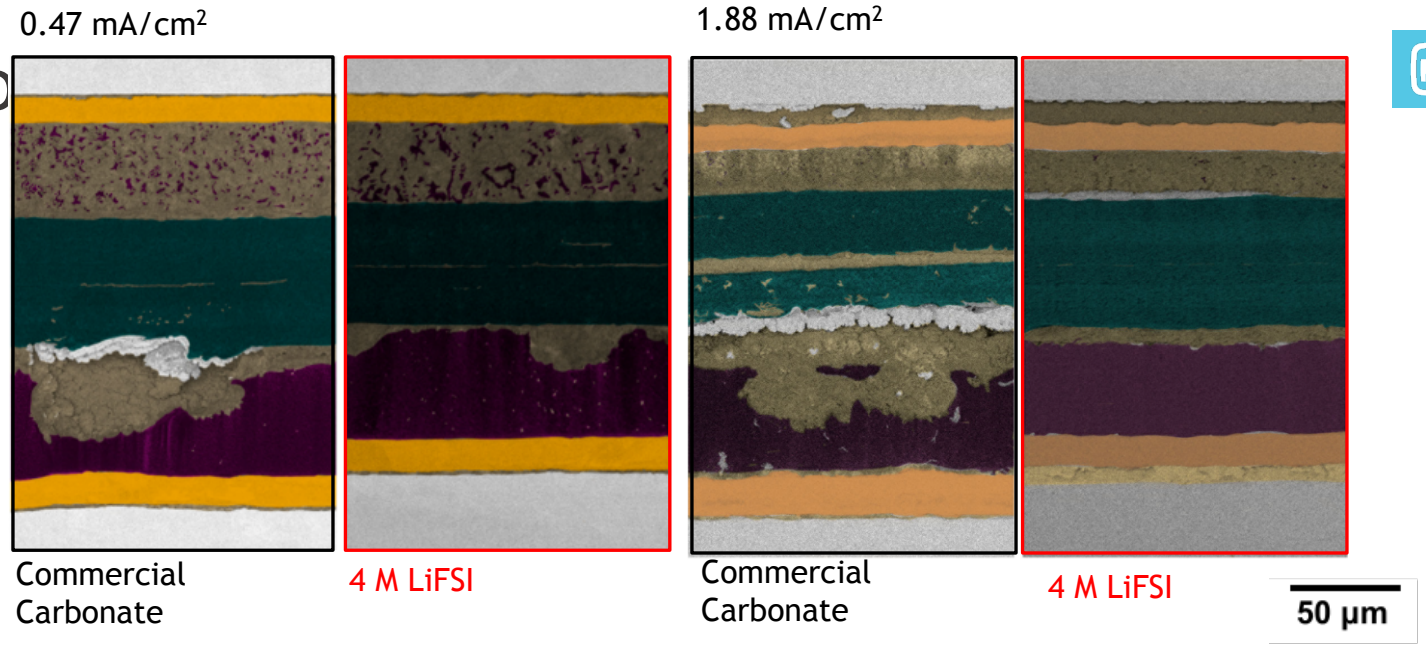
First Deposition Behavio

First deposition shows Li grains intermixed with SEI/electrolyte

Pitting observed in both counter electrodes at low rate

At high rate pitting only observed in Commercial Carbonate
→*Likely related to differences in mass transport/ionic conductivity*

Low rate deposits thicker than high rate deposits



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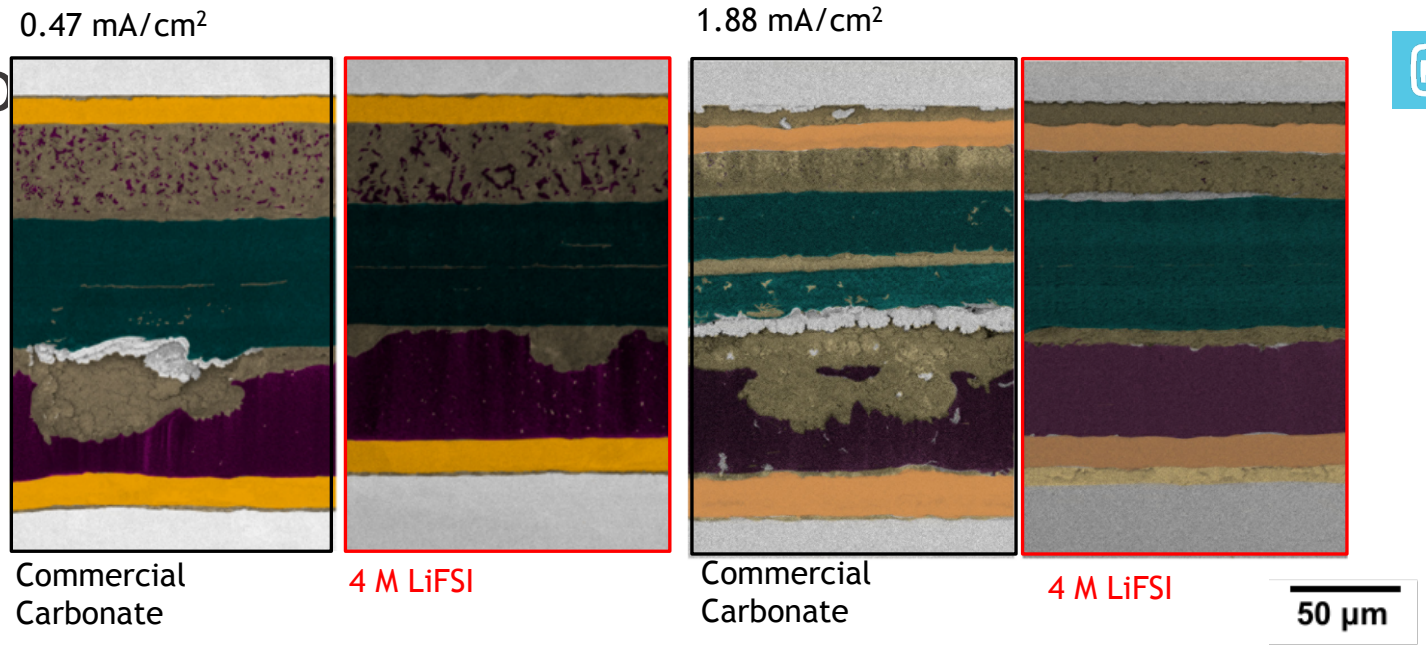
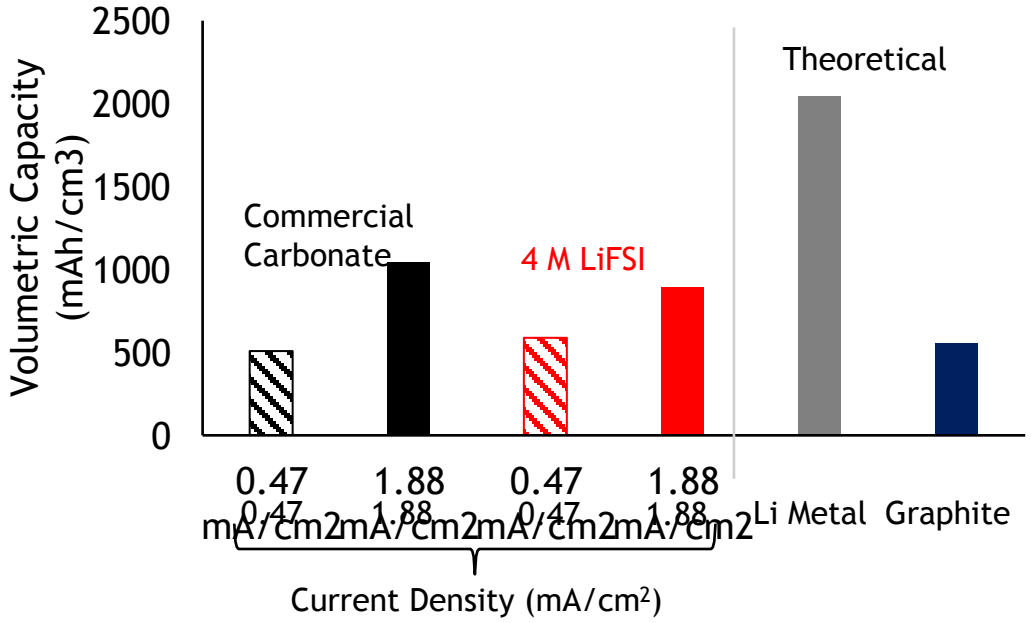
Practical capacities only reaching ½ of theoretical at *high rate*, nearing graphite at *low rate*.





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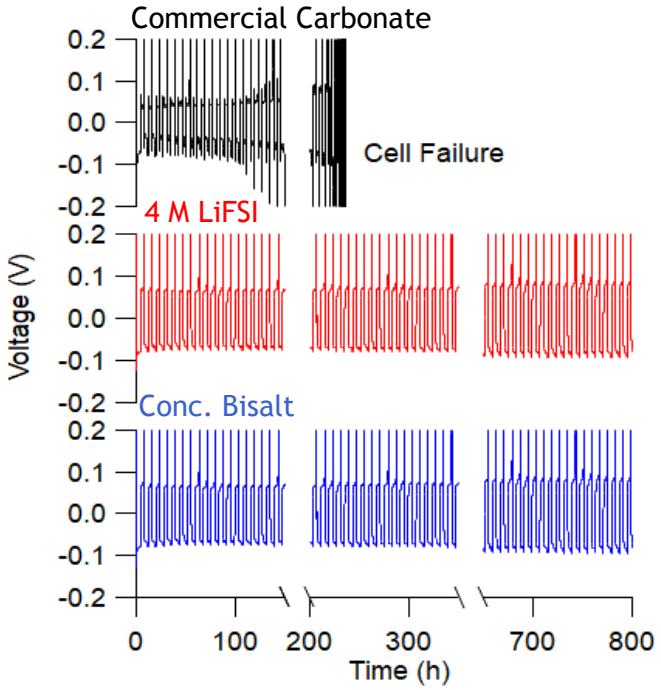
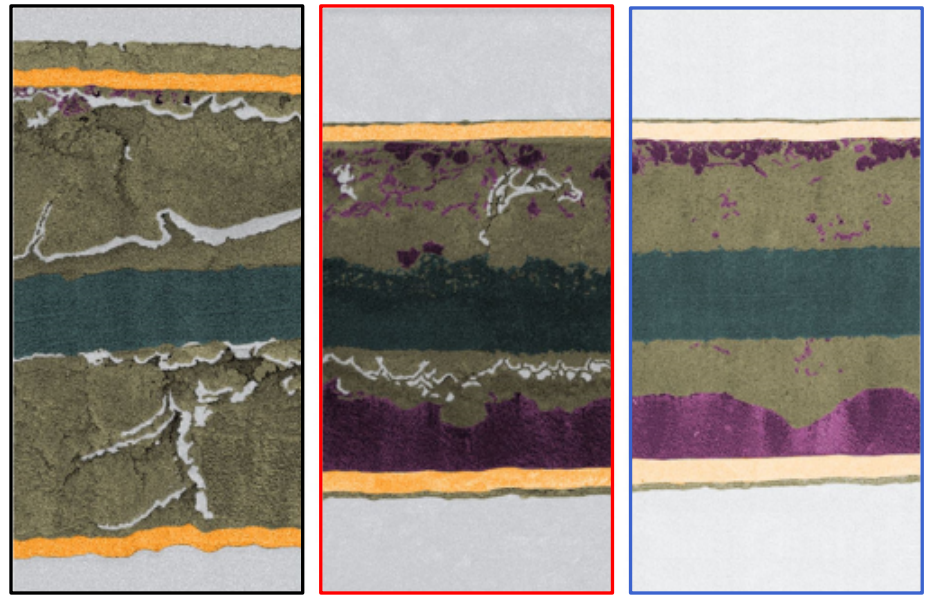
Extended Cycling Behavior

Cycling 100.5 cycles at 0.47 mA/cm^2 for 1.88 mAh/cm^2

Carbonate-based electrolyte fails early on in cycling

Both Concentrated Bisalt and 4 M LiFSI are able to cycle all 100 cycles





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Extended Cycling Behavior

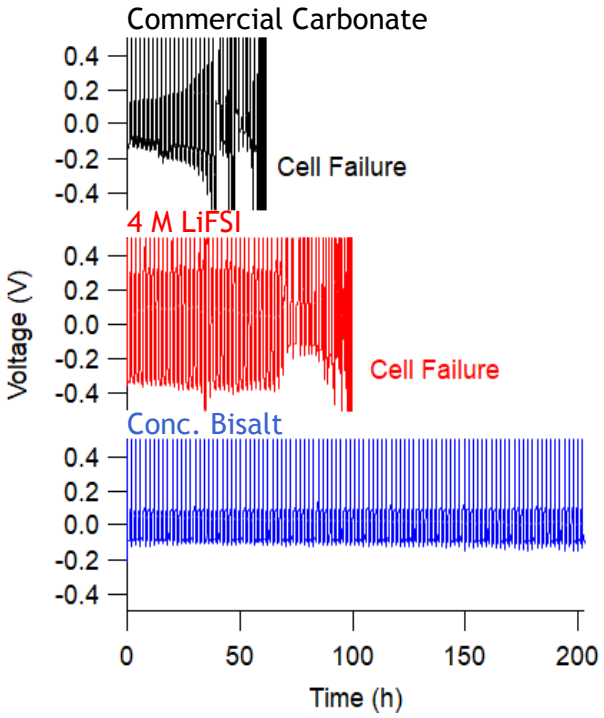
Cycling 100.5 cycles at 1.88 mA/cm^2 for 1.88 mAh/cm^2

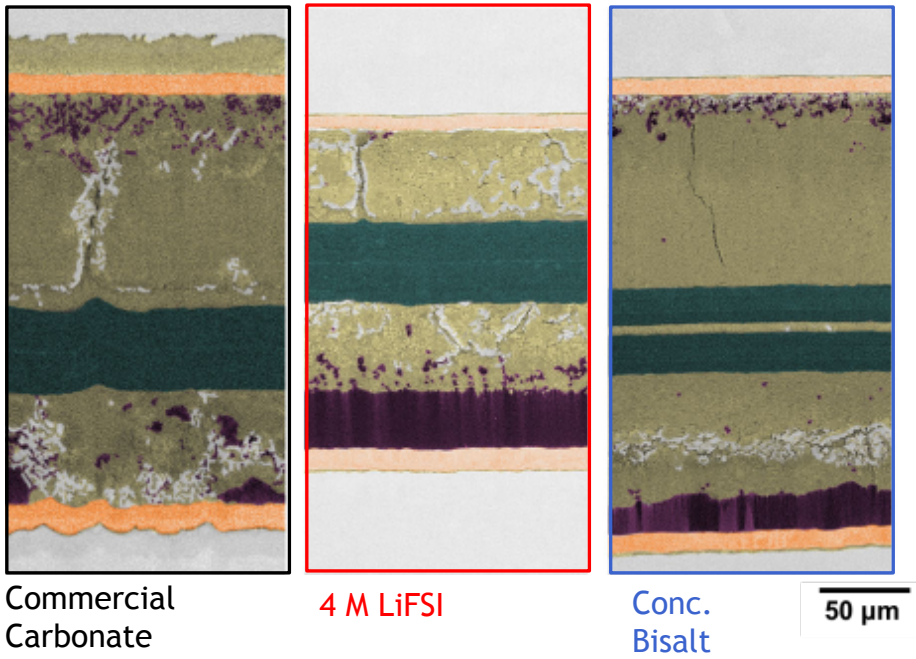
Both Commercial Carbonate and 4 M LiFSI fail at extended cycling (on average)

Concentrated Bisalt able to deliver all 100 cycles
- Average CE: 98.8 %

Extreme volume expansion with Concentrated Bisalt

Concentrated Bisalt also shows consumption of Li at counter electrode





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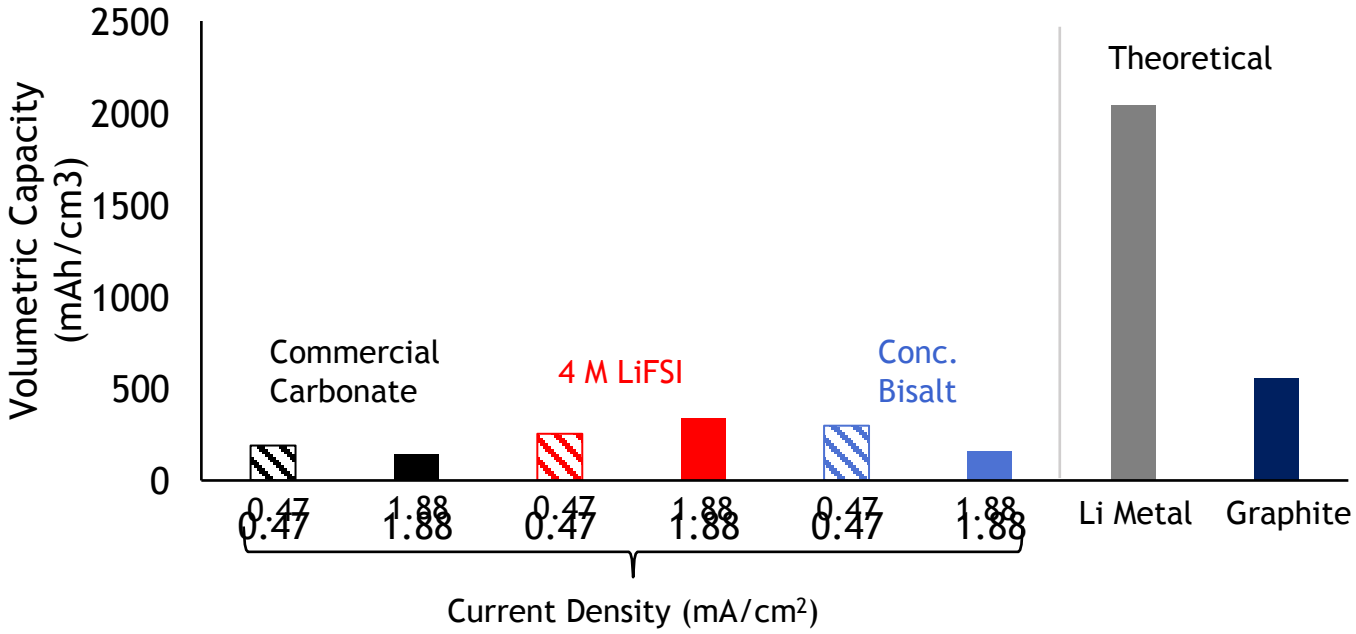
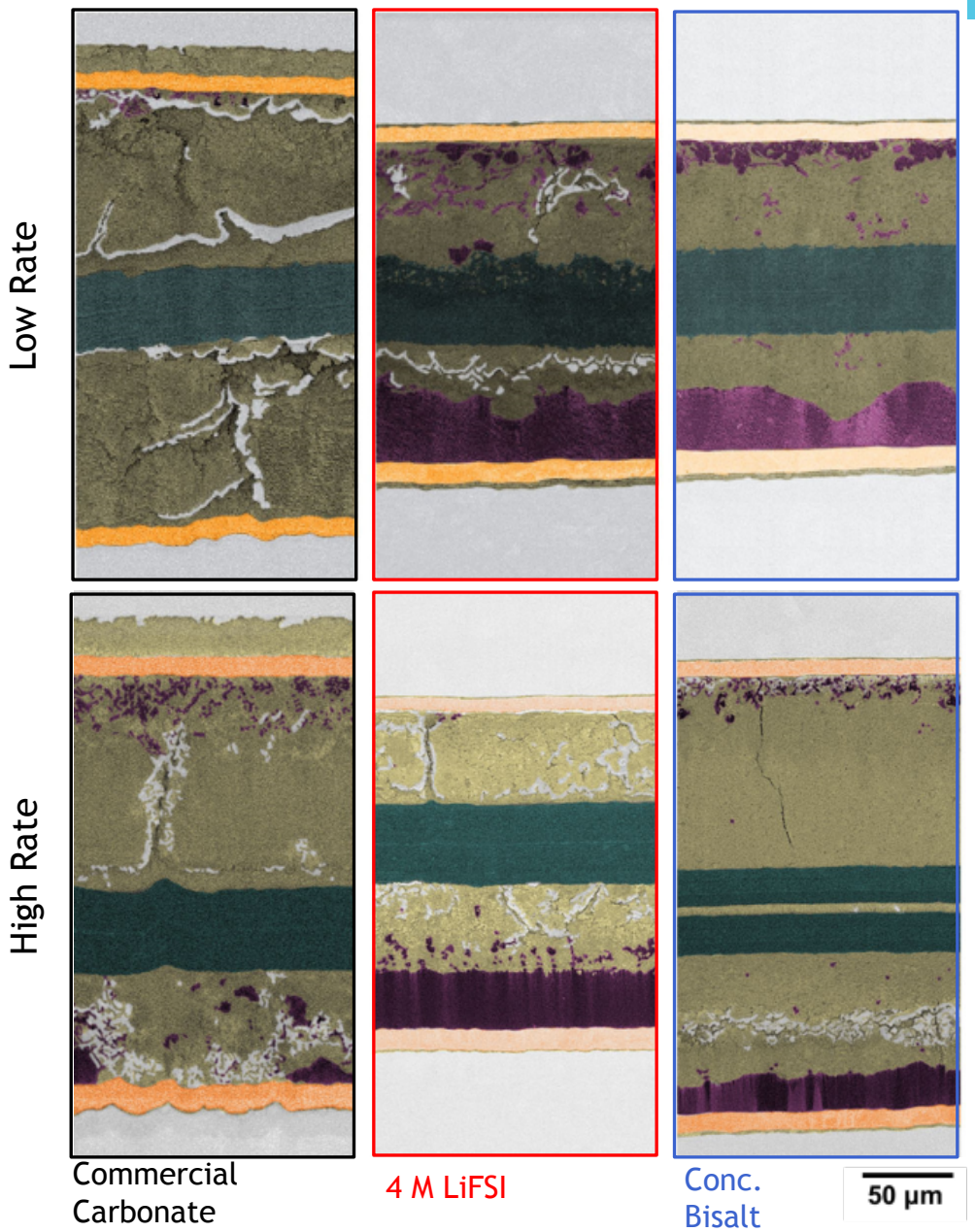
Extended Cycling Behavior

After extended cycling, practical capacity is *at best* 16 % of theoretical capacity

Best electrochemical performance has worst volumetric expansion (at high rate)

Coulombic efficiency measurements not sensitive to consumption of Li at counter electrode





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Summary

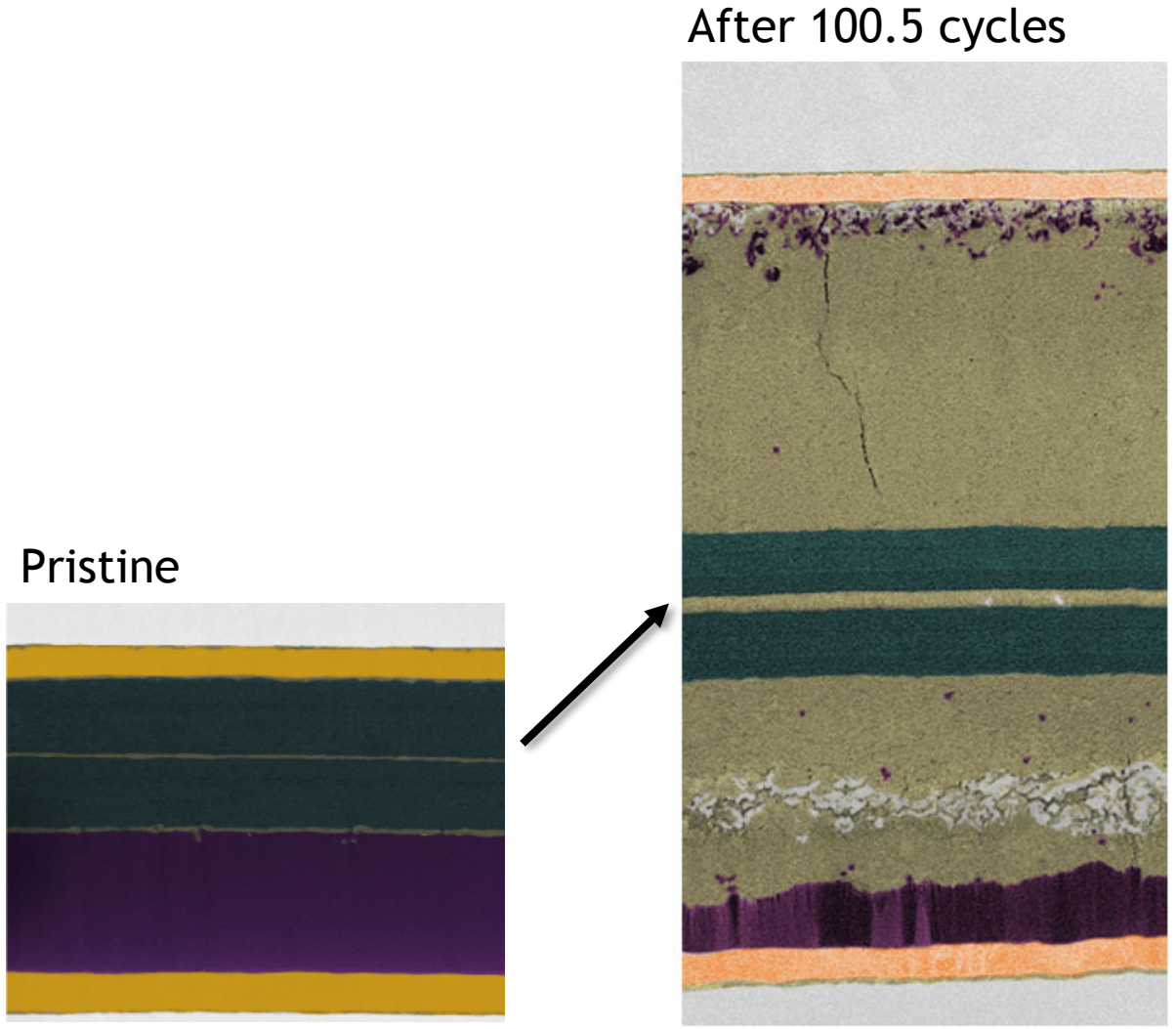
Coulombic efficiency:

- Not sensitive to counter electrode
- Not indicative of porosity of deposit

Volumetric expansion at anode might not be compensated by cathode

Anode volumetric changes likely localized during early cycling

How would this manifest in a fixed volume cell?



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- Katherine Jungjohann (NREL)
- Renae Gannon (Thermo Fisher)
- David Johnson (U Oregon)

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- Subrahmanyan Goriparti (General Motors)
- Kevin Zavadil
- Ben Warren

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Supplemental slides

First Deposition Behavior

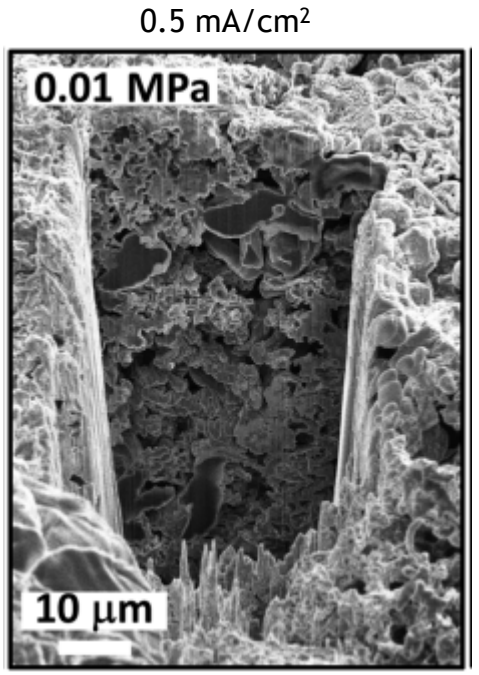
First deposition shows Li grains intermixed with SEI/electrolyte

Pitting observed in both counter electrode at low rate

At high rate pitting only observed in Commercial Carbonate
→*Likely related to differences in mass transport/ionic conductivity*

Low rate deposits thicker than high rate deposits
→ Consistent even in different form factor cells

1.



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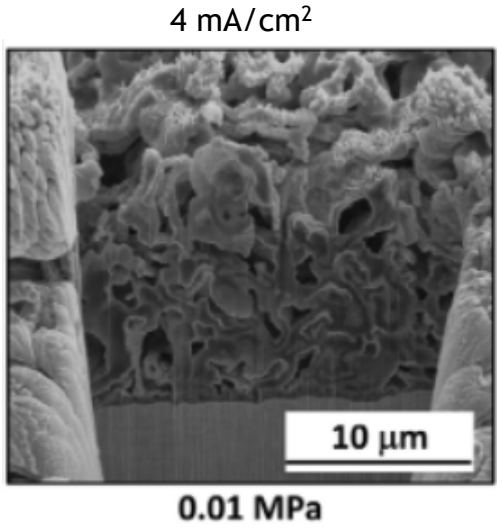


2.

Table 1. Approximate thicknesses of deposits from cross-sectional images after one deposition at 4 mA/cm² to 2 mAh/cm² at varied pressure

Pressure (MPa)	Thickness of deposit 4 mA/cm² (µm)	Thickness of deposit 0.5 mA/cm² (µm)
0	44	91
0.01	22	33
0.1	21	30
1	19	22

1. Harrison, Goriparti, Merrill *et al.*, *ACS Appl. Mater. Interfaces*, 2021, 13(27), 3166
2. Harrison, Merrill, *et al.*, *iScience*, 24(12), 103394

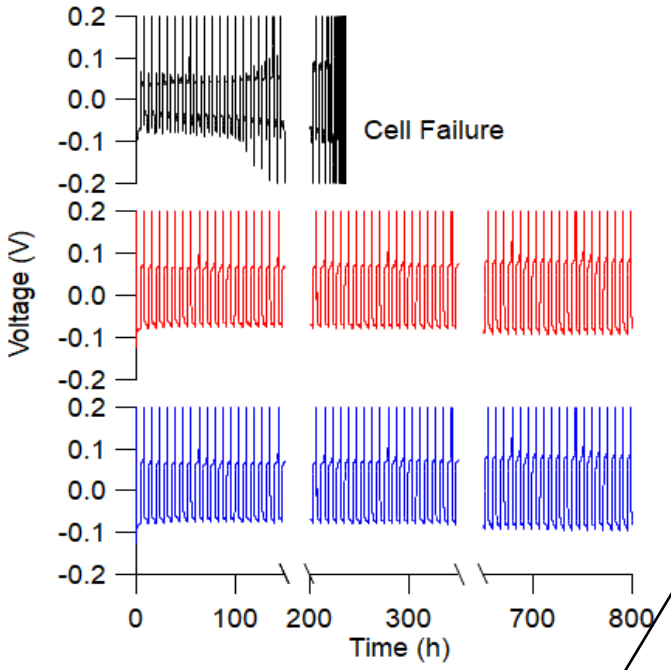
Extended Cycling Behavior

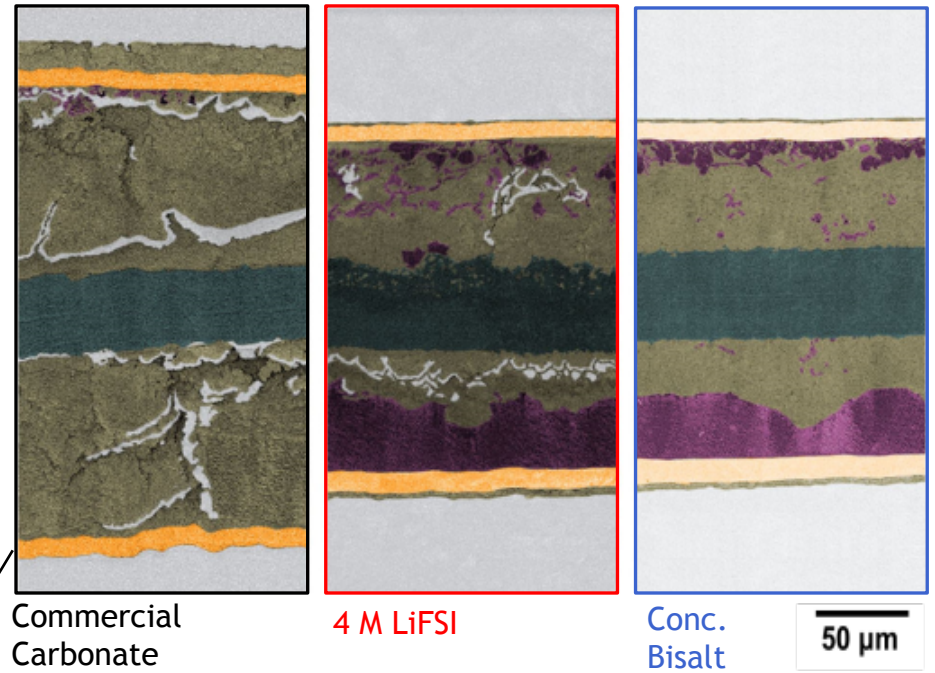
Cycling 100.5 cycles at 0.47 mA/cm^2 for 1.88 mAh/cm^2

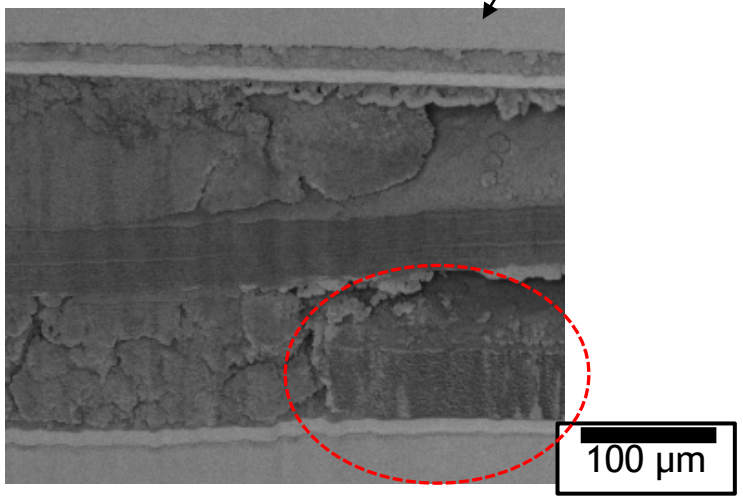
Carbonate-based electrolyte fails early on in cycling

Both Concentrated Bisalt and 4 M LiFSI are able to cycle all 100 cycles

Counter electrode not entirely consumed during cycling (Commercial Carbonate)
→ Pockets of Li remain but unable to deliver capacity







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