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Ionic Permeability within Thermally-Activated Batteries

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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Basics of Thermally-Activated Batteries

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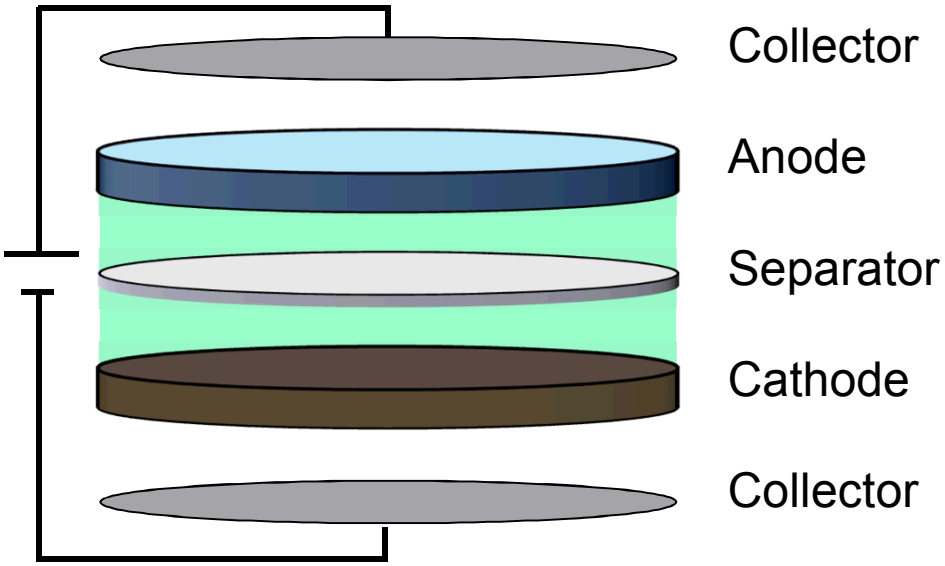
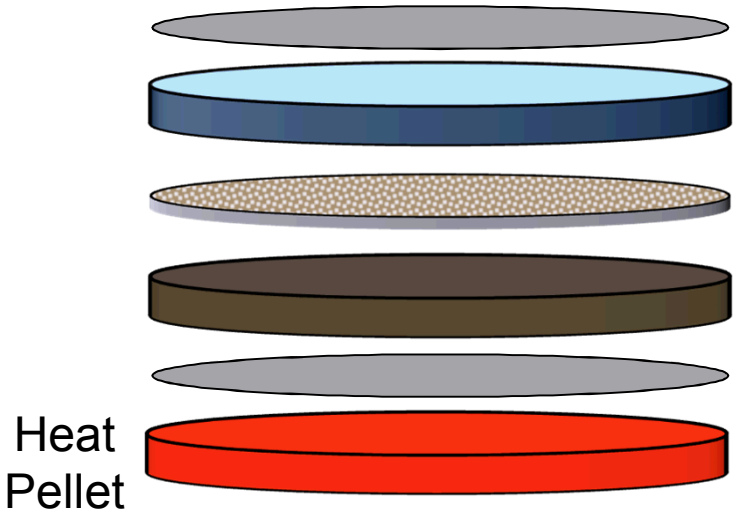
Typical Lithium Ion Battery[1]



- 1-3 year shelf life
- Low voltage/low current
- **Liquid** electrolyte dispersed throughout battery cell

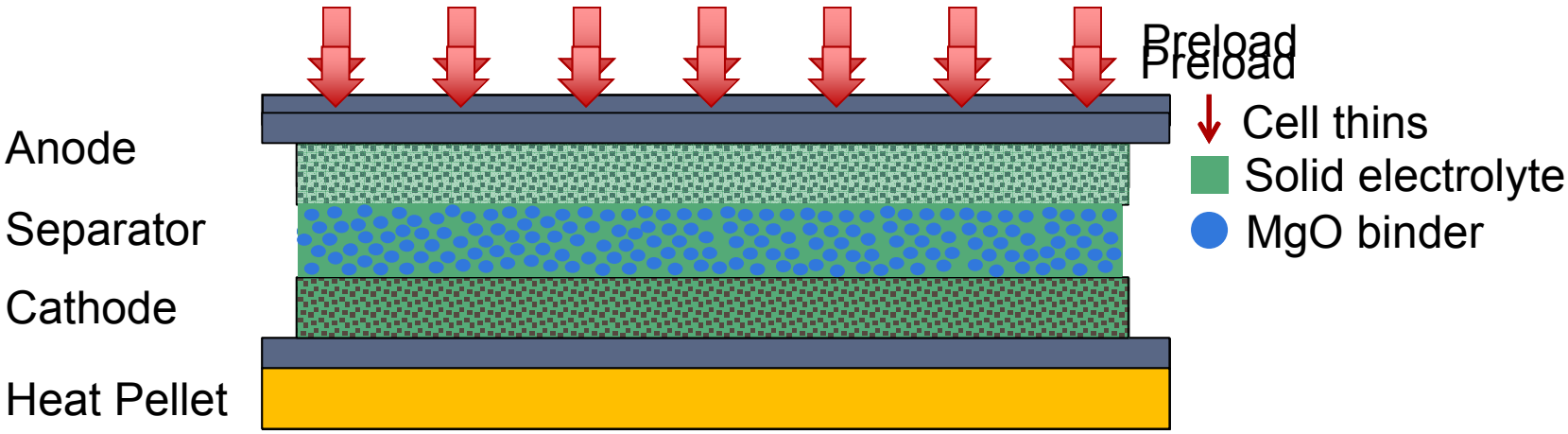
Molten Salt Cell



- 20+ years shelf life
- High voltage/high current
- **Solid** electrolyte initially stored in separator – battery must be heated to >300°C to draw power

[1] Yoshio and Brodd, "Lithium-Ion Batteries" (2009)

Thermal Battery Activation



- Infiltration of electrolyte into cathode and anode reduces the internal impedance
- Excess electrolyte can cause shorting/collapse of the cell

Improve the fundamental understanding of electrolyte transport during activation

Quantifying Transport through Porous Components

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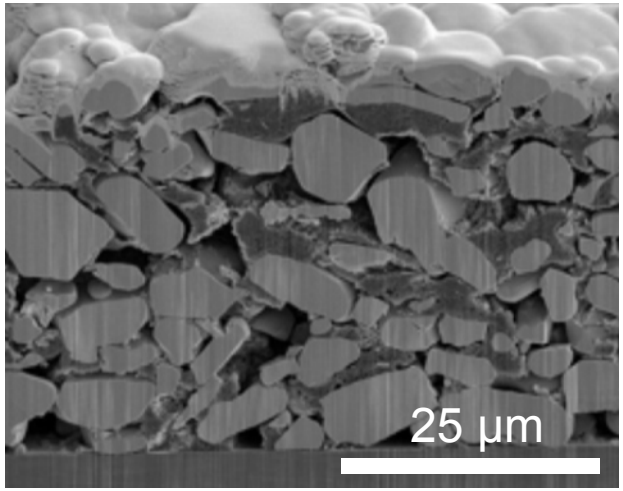
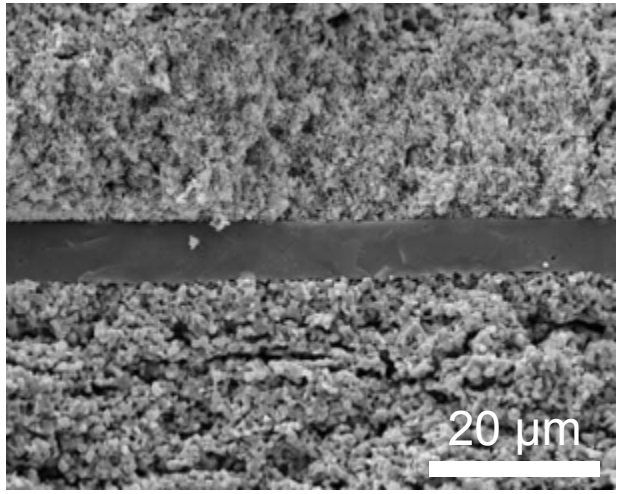
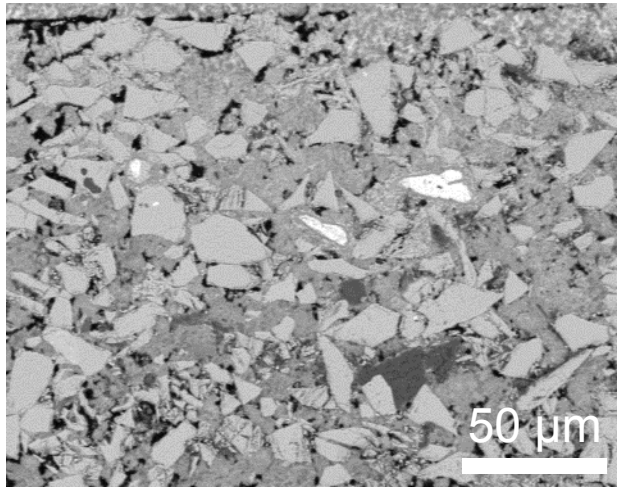
Li-Ion Battery[1]



Fuel Cell[2]



Thermal Battery



- Transport through porous materials is ubiquitous amongst electrochemical cells
- Improved understanding of limiting transport processes can lead to improvements in performance and lifetime
- **How to experimentally study transport at these length scales and in these challenging environments?**

[1] Stephenson *et al.*, *J. Elec.Chem. Soc.* (2011), [2] Birss *et al.*, *J. Elec.Chem. Soc.* (2010)

Introduce Tracker to Probe Transport

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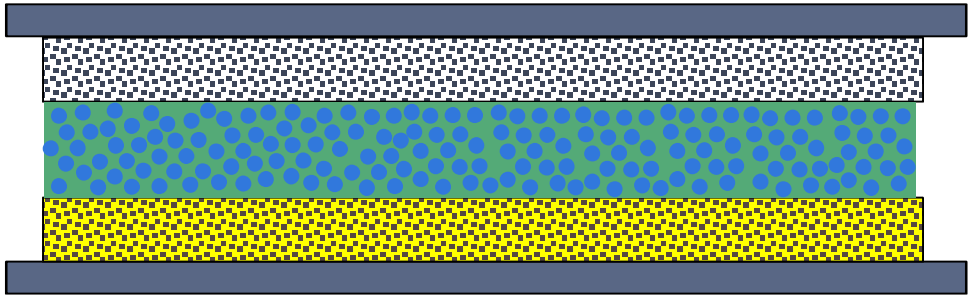
Anode - Dry

Separator - BE

Cathode - RE



Bromine electrolyte (BE)
50wt% KBr
36wt% LiBr
12wt% LiCl
T_m=310˚C

Regular electrolyte (RE)
45wt% LiCl
55wt% KCl

T_m=352˚C

Experimental Setup

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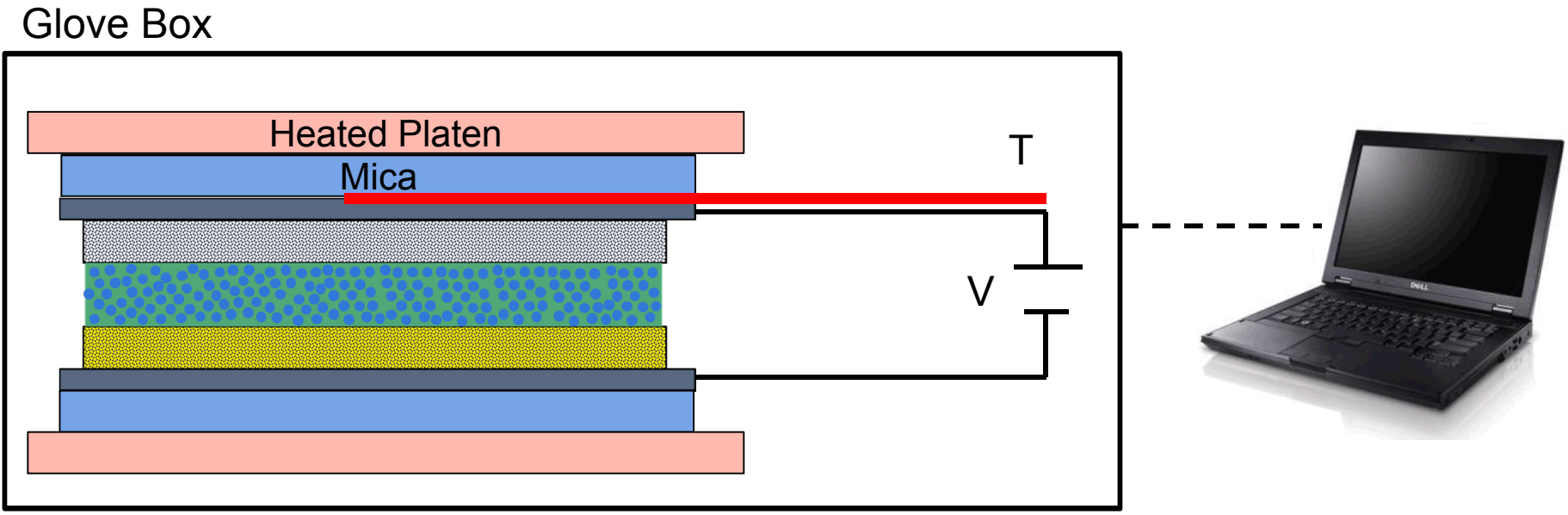
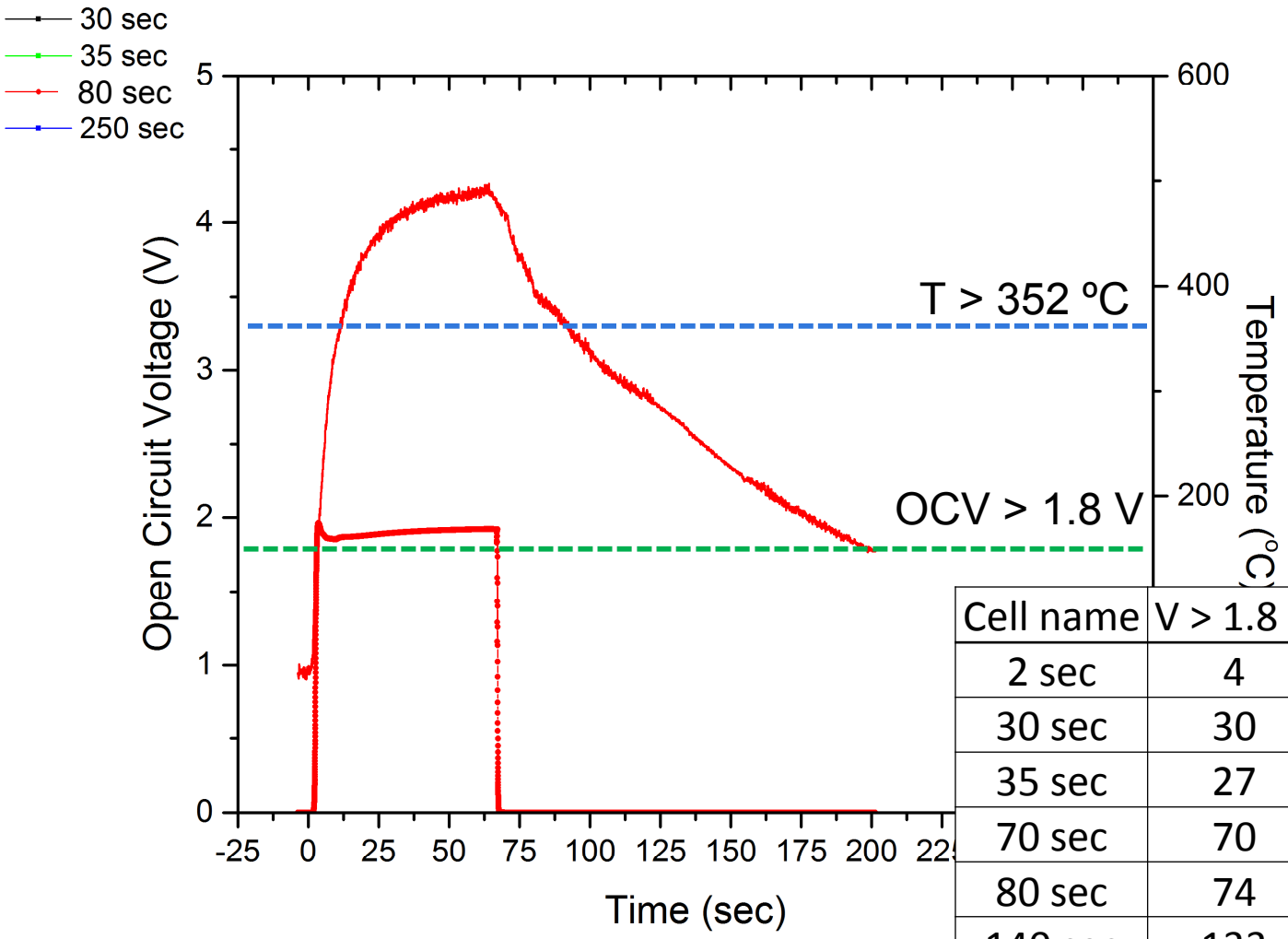


- Cells were compressed to 12 psi (uniaxial compression) between heated platens (500 ^{0}C) for various time durations
- Quenched to room temperature
- Temperature and open circuit voltage (OCV) data was recorded

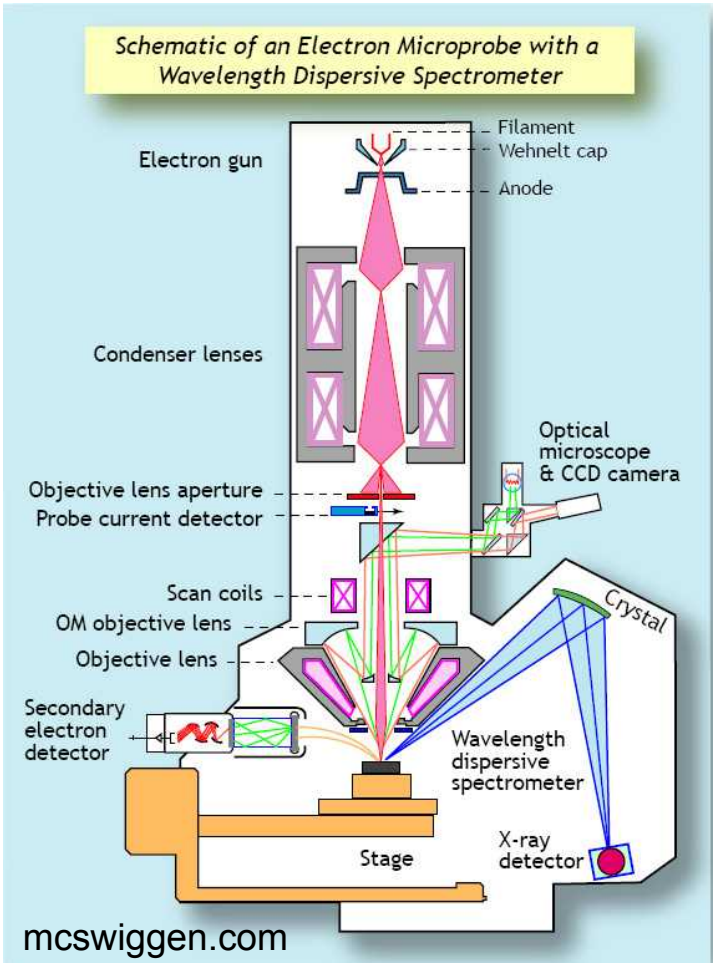
[1] Grillet *et al., Proc. 46th Power Sources Conference* (2014)

Sample Preparation



Cell name	V > 1.8 V	T > 350 C
2 sec	4	0
30 sec	30	33
35 sec	27	39
70 sec	70	72
80 sec	74	84
140 sec	133	151
250 sec	238	263

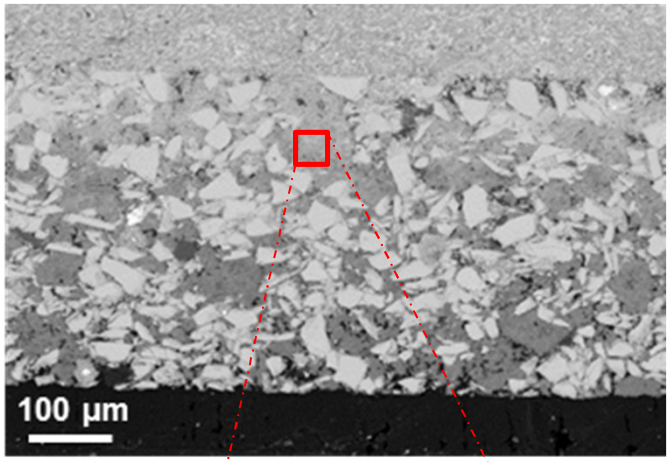
Electron Probe MicroAnalyzer (EPMA)



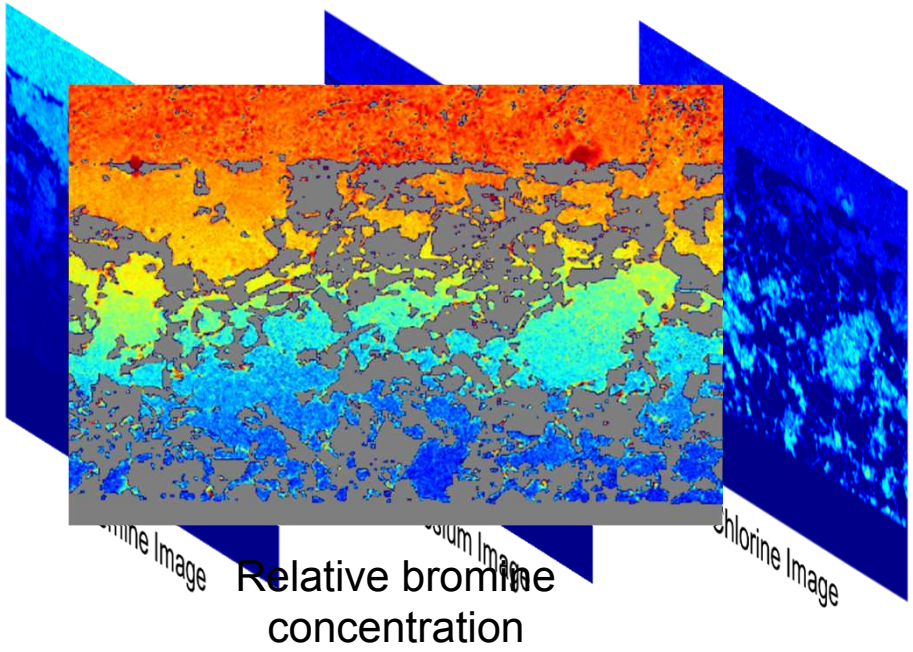
- X-rays emitted by a sample under electron bombardment
  - Extremely stable beam current
- Specific X-ray wavelengths or energies are selected and counted by wavelength dispersive X-ray spectroscopy (WDS)
- Comparison of generated x-rays to elemental standard of known concentration
  - Flow proportional X-ray counter
- **Quantitative Chemical Analysis**
  - 1 μm^3 spatial resolution
  - Precision 0.1wt% elemental composition

Characterizing Electrolyte Concentration throughout Cell

Backscatter Electron Image



Using EPMA



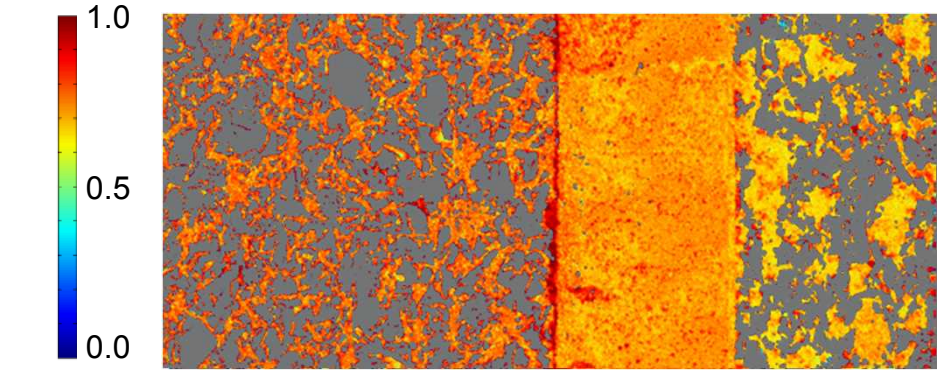
Relative bromine concentration

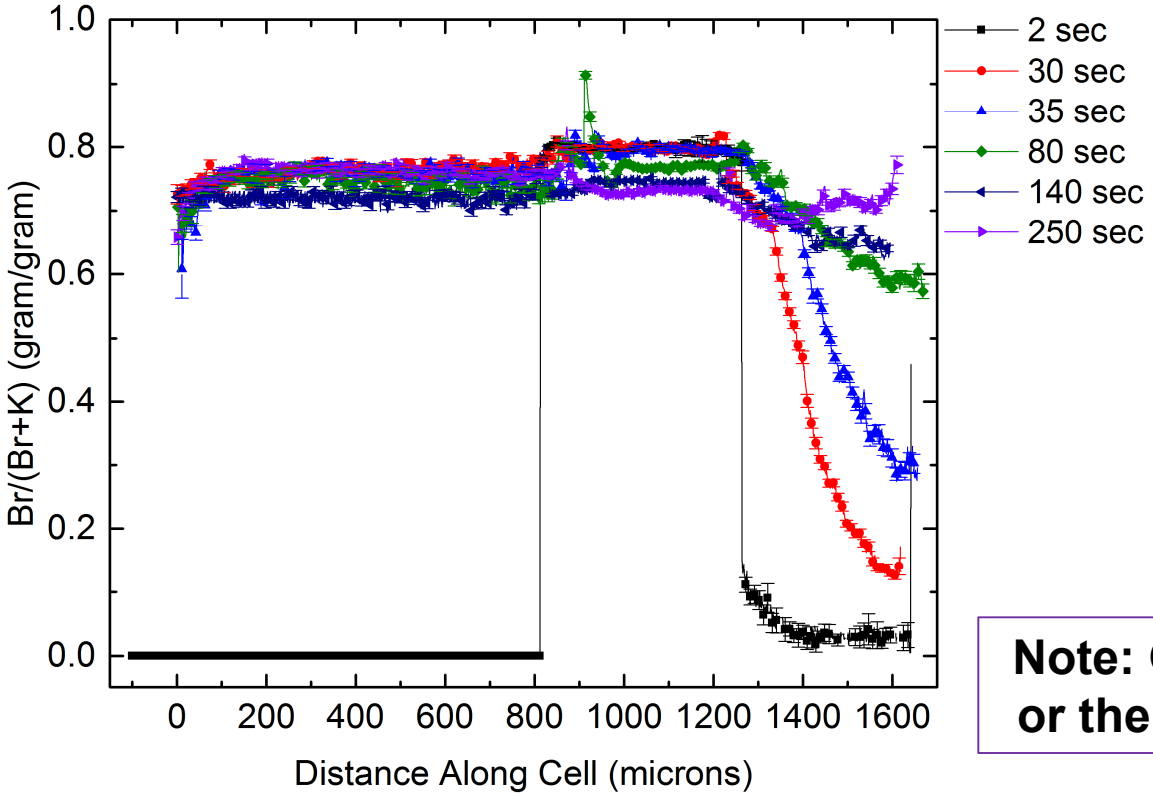
44.2 wt% Br
10.8 wt% K
6.8 wt% Cl
…

$$\frac{Br\ (wt\%)}{Br(wt\%) + K\ (wt\%)}$$

- Images are thresholded to 2 wt% (K or Br) such that only the electrolyte/binder mixture is analyzed
- Each pixel normalized by amount of Br and K (to account for variations in amount of electrolyte per pixel)

Bromine Transport into Components



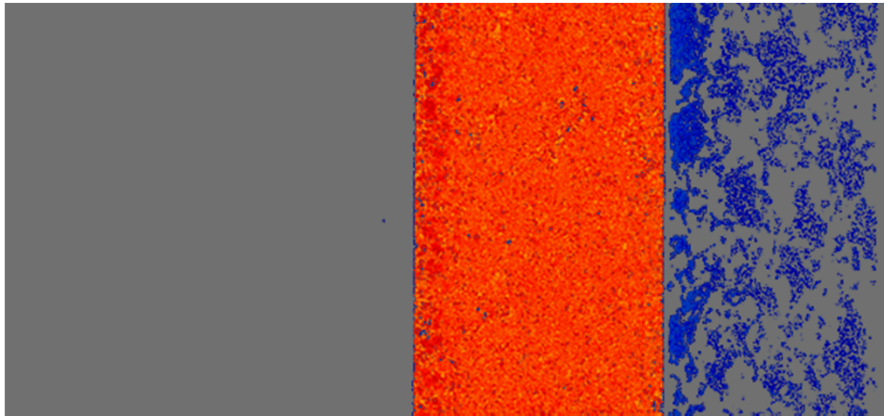


- Separator thins by ≈ 20 % (100 μm)
- Anode is flooded within 30 seconds
- Bromine is diffusing into cathode
- Equilibrium ≈ reached within 140 seconds after activation
- Activation process is finished within 250 seconds

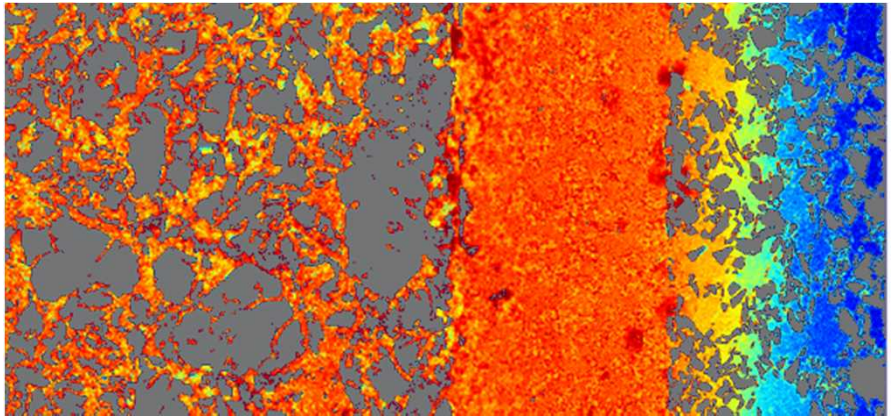
Note: Grey areas are void space or the solid network (LiSi, FeS_2)

Mechanisms of Transport

2 second

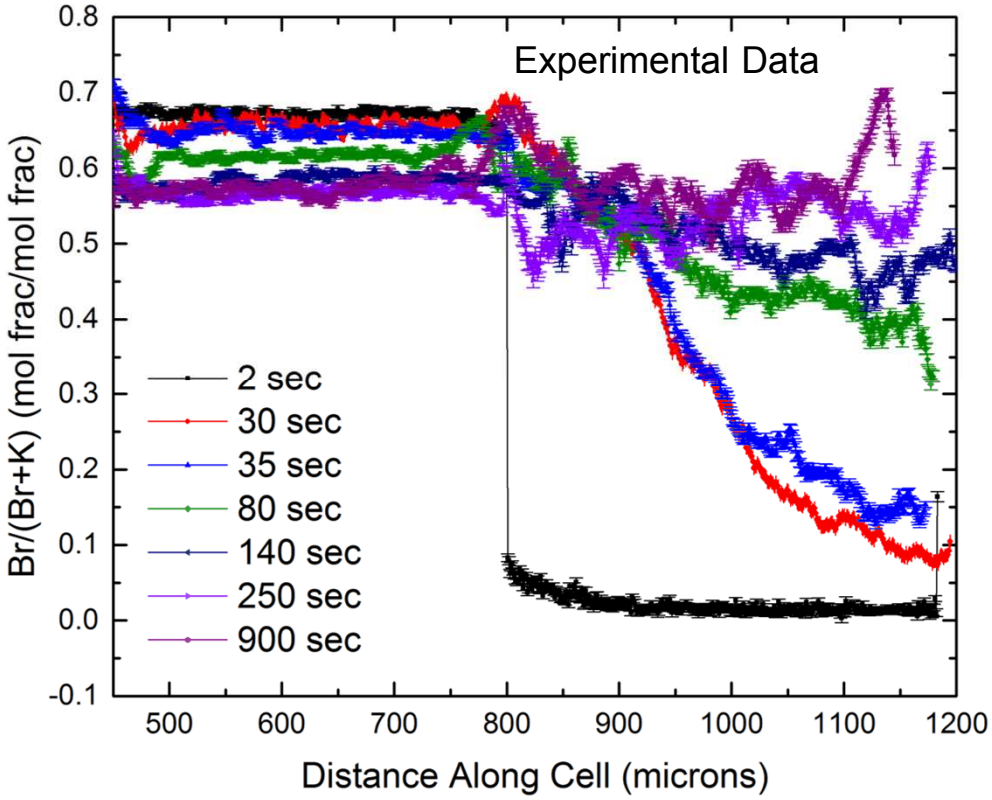


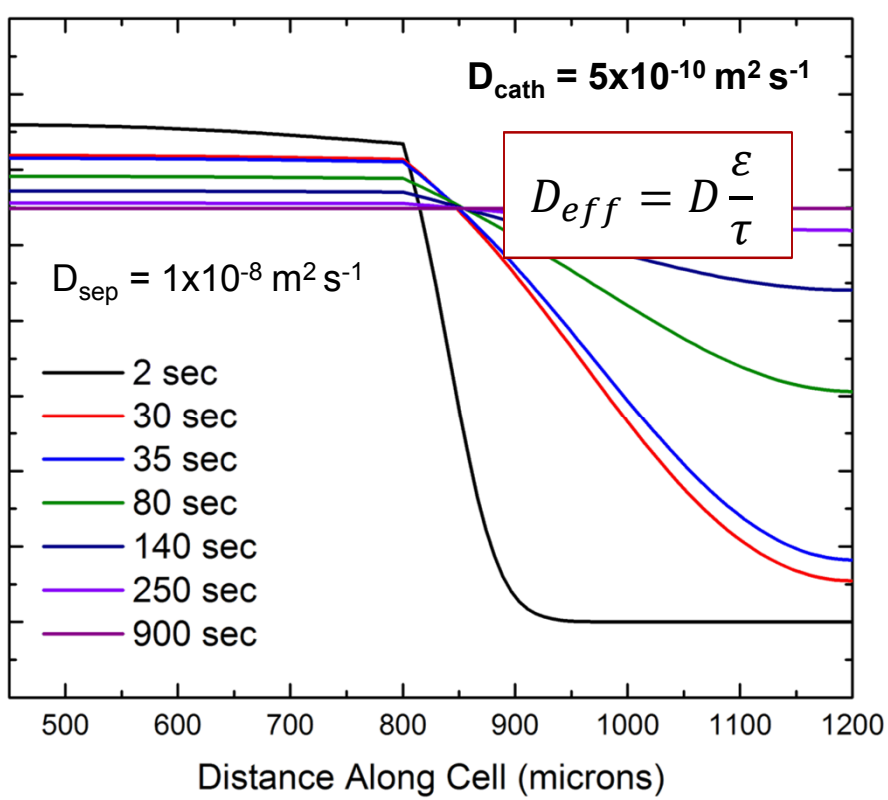
30 second



- Within first 30 seconds, electrolyte flows and fills dry anode structure
  - **Capillary-pressure driven flow** into micron – submicron pore structure of lithium-silicon anode
- Transport into cathode is slower, requires ≈ 250 seconds to reach equilibrium
  - **Diffusion-limited transport** into tortuous iron disulfide cathode

Quantifying Diffusivity of Bromine

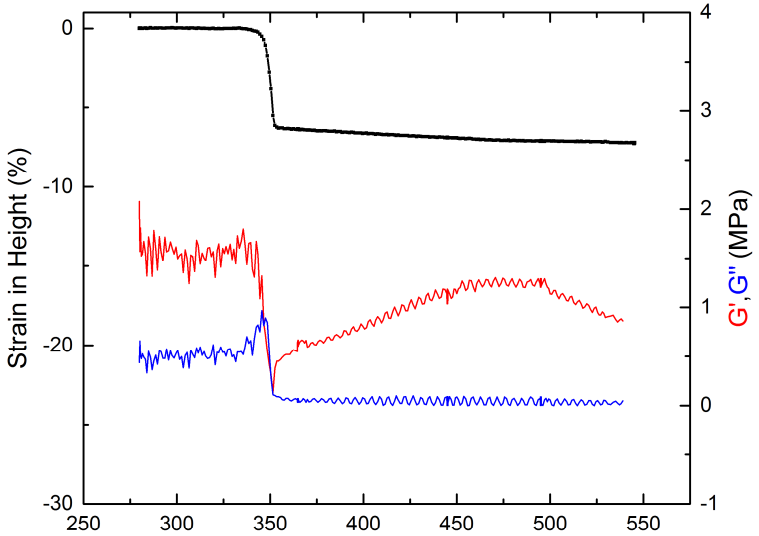


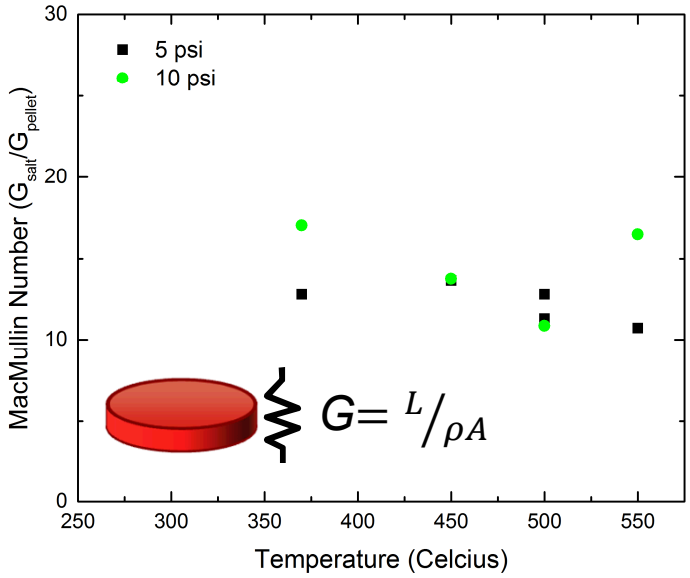


- Estimated diffusivity[2] of bromine in cathode using COMSOL multiphysics modelling software
  - Indicates that tortuosity[2] of FeS_2 network is between 3 – 6
- Investigating effects of porous flow and temperature-dependent diffusivity with Sierra (Sandia's Multiphysics Modelling Software)

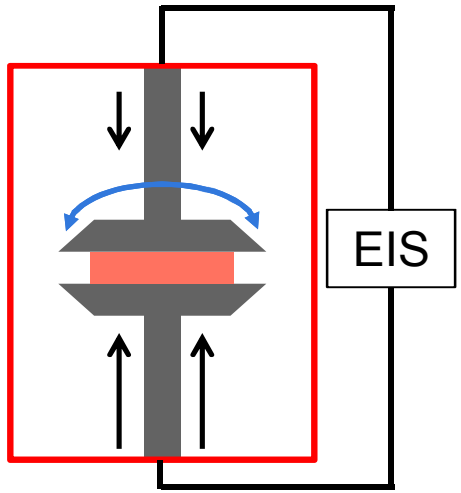
[1] Janz and Bansal, *J. Phys. Chem. Ref. Data* (1982) [2] E.L. Cussler, "Diffusion: Mass Transfer in Fluid Systems" (1997)

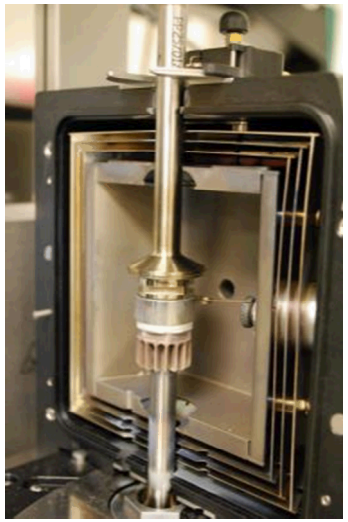
More Data Still Needed…





Combining Rheology with Impedance Spectroscopy

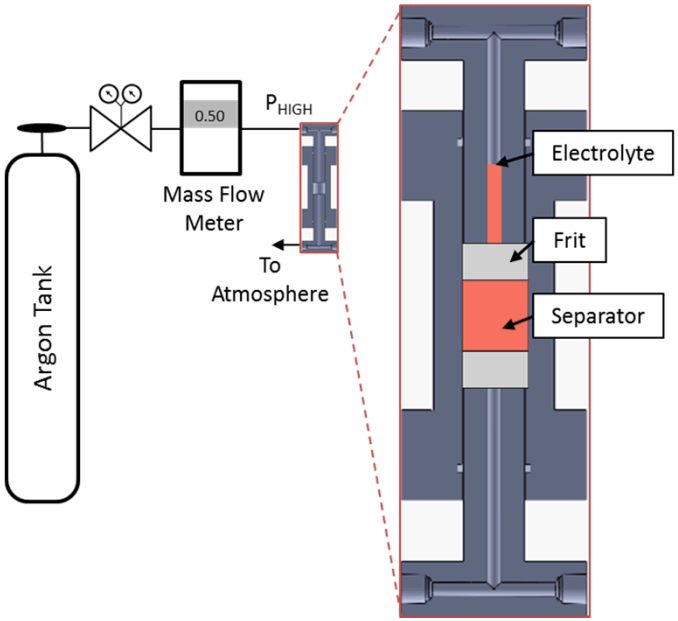


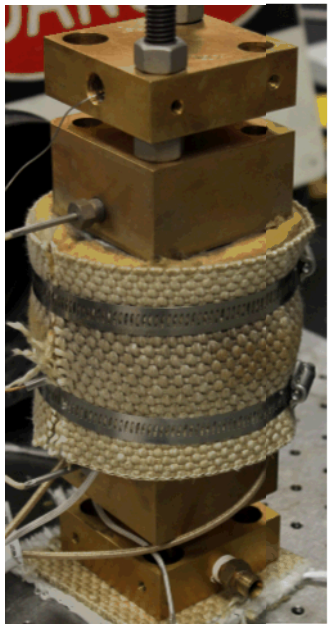


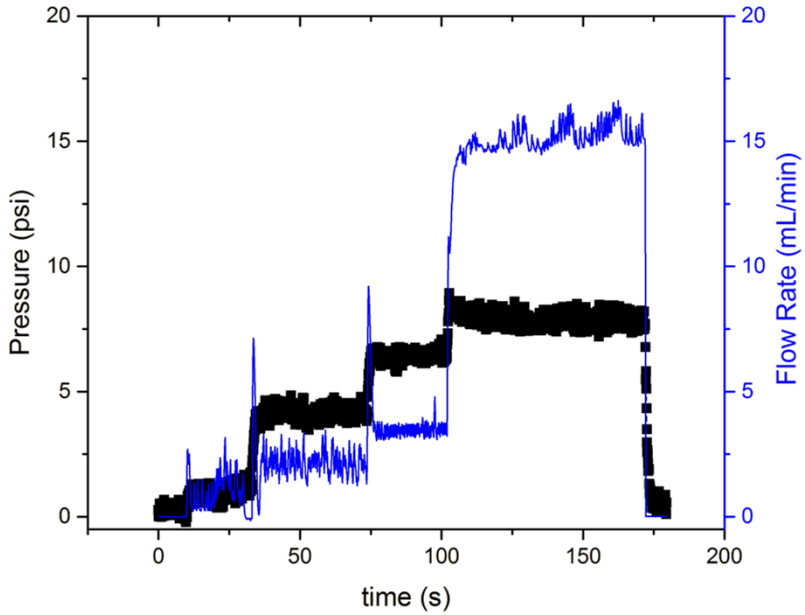
Investigating impedance, shear strength and compression of components during activation under various temperature and loading conditions

More Data Still Needed…

Permeability Cell



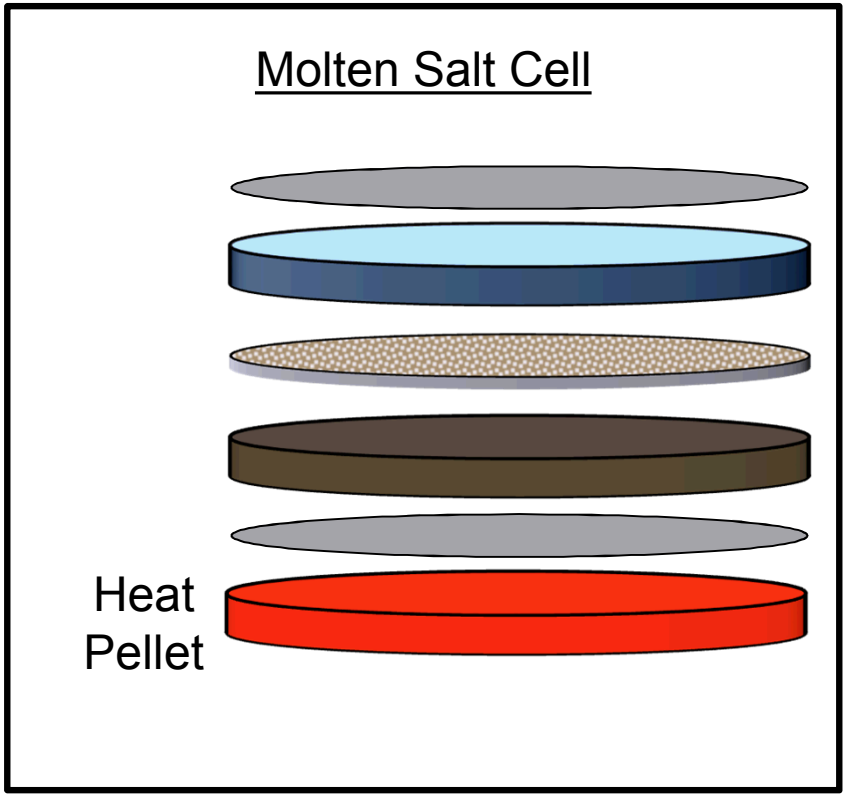


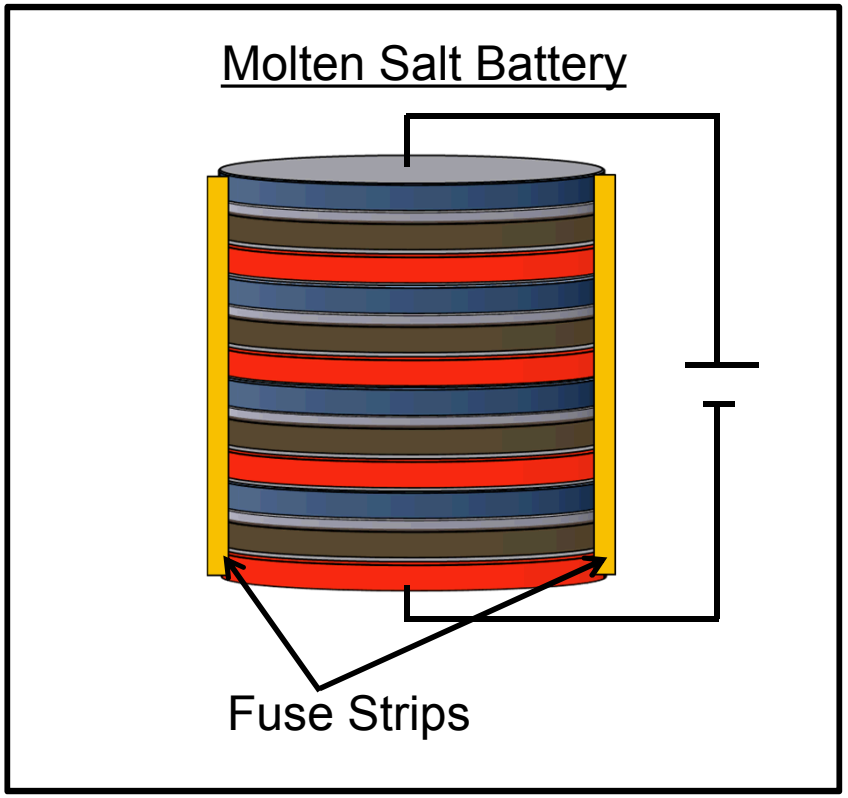


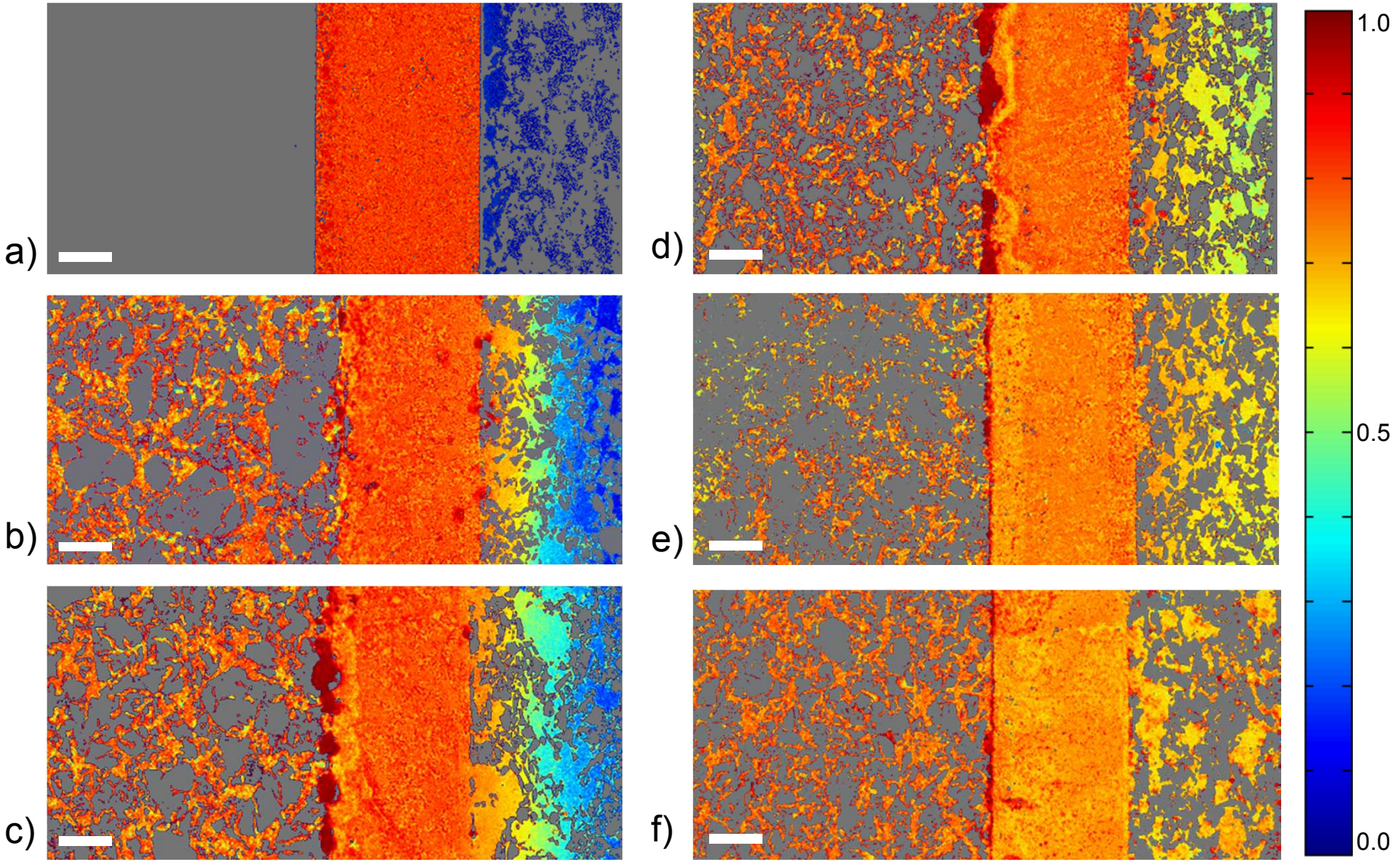
Building high temperature (> 350 ^{0}C) permeability cell to measure electrolyte flow through individual components as a function of applied load and temperature

Conclusions

- Developed new methodology exploiting high spatial resolution and resolution of electron probe microanalysis (EPMA) to probe electrolyte mobility within electrochemical systems
- Estimated an approximate order of magnitude decrease in the diffusivity of bromine into the cathode which we suspect is due to the large tortuosity (3 – 6) of the cathode structure
- Observed fast capillary-pressure driven flow into the micron – submicron pore structure of the anode
- Configuring new experiments to obtain more direct measurements for more accurate input parameters to aid thermal battery modelling efforts at SNL


Molten Salt Cell
Heat Pellet


Molten Salt Battery
Fuse Strips


a)
b)
c)
d)
e)
f)
1.0
0.5
0.0

Future Experiments Probing Transport

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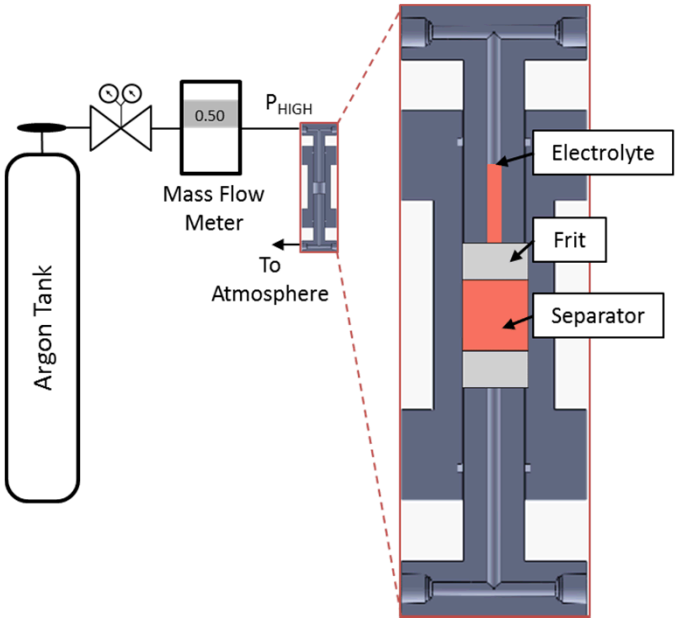
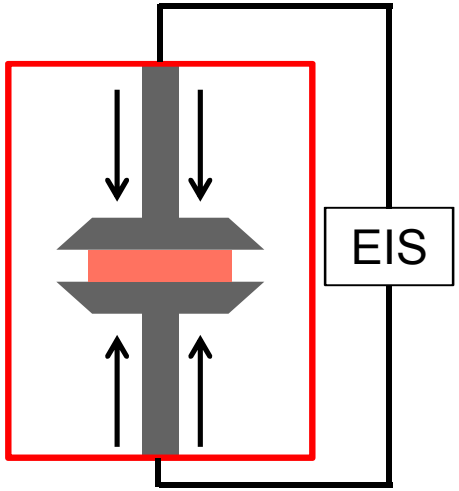
Permeability Cell

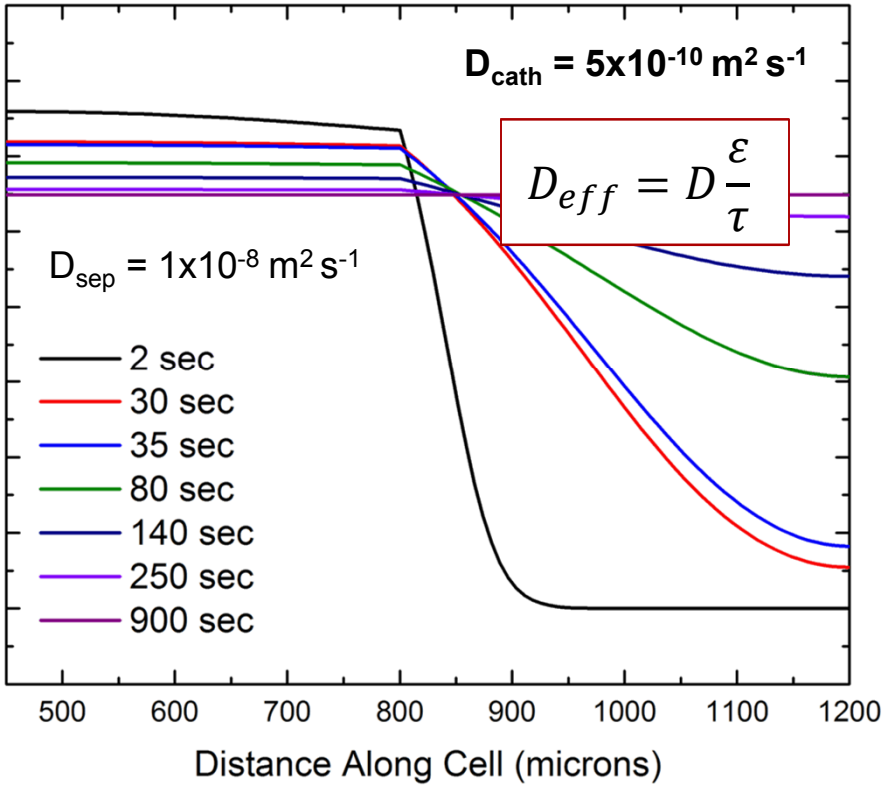


Building high temperature (> 300 ^{o}C) permeability cell to measure mass flow through individual components

Combining Rheology with Impedance Spectroscopy



Investigating impedance characteristics of components during activation under various temperature and loading conditions


D_{cath} = 5x10^{-10} m^2 s^{-1}
$D_{eff} = D\frac{\varepsilon}{\tau}$
D_{sep} = 1x10^{-8} m^2 s^{-1}
2 sec
30 sec
35 sec
80 sec
140 sec
250 sec
900 sec
500
600
700
800
900
1000
1100
1200
Distance Along Cell (microns)