SAND2015-2568C

Sandia National Laboratories

Electrolyte Transport within Thermally-Activated Batteries

Thomas Humplik,

E. K. Stirrup, A.M. Grillet, D.E. Wesolowski, A. N. Allen, R.P. Grant,

B. McKenzie, C.C. Roberts, S.A. Roberts, & L.A. Mondy

Spring 2015 Materials Research Society Conference

April 9, 2015

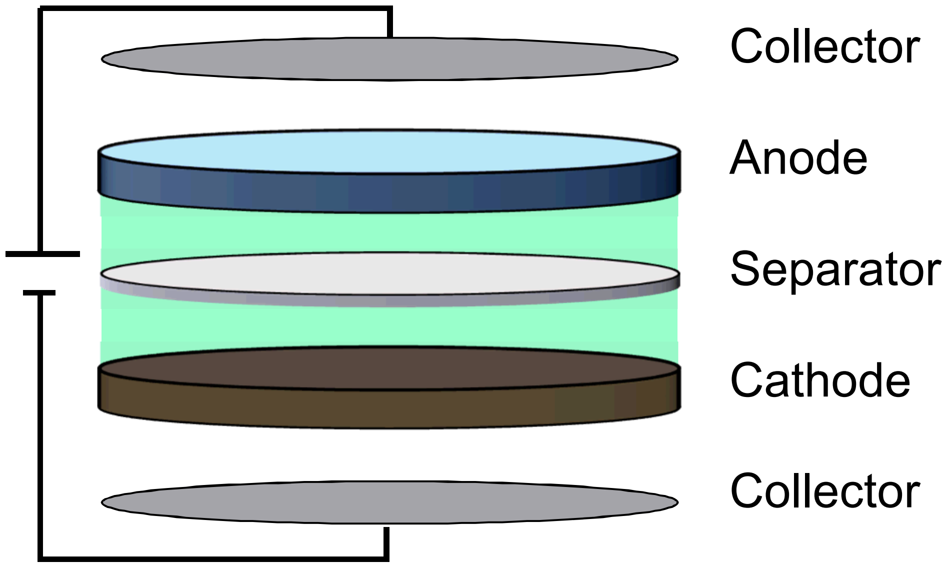
U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND2014-18205 PE

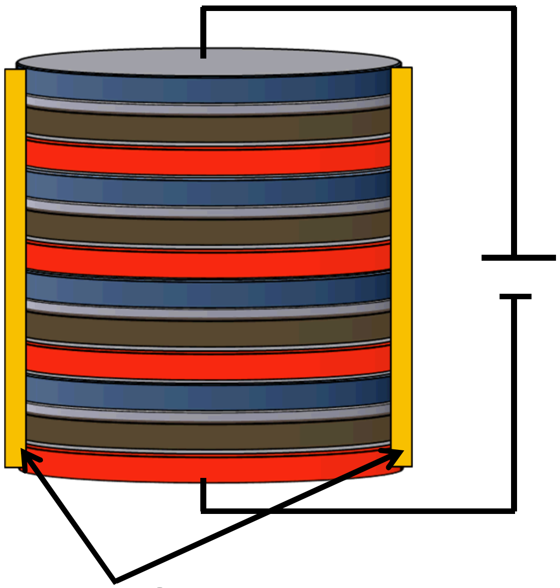
Basics of Thermally-Activated Batteries

Typical Lithium Ion Battery[1]



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

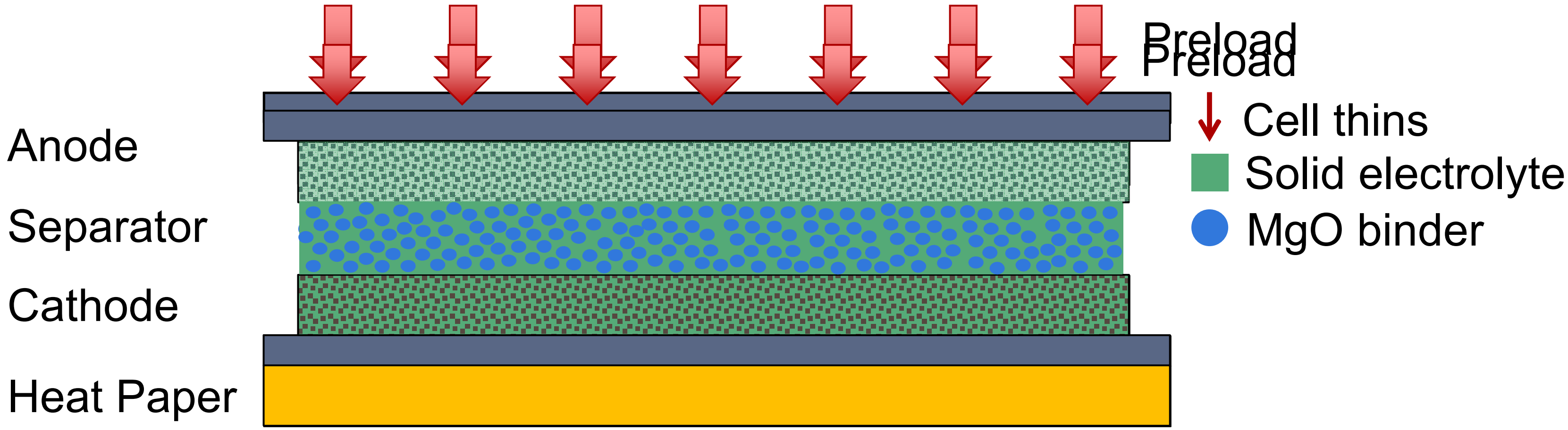
Molten Salt Battery



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

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

Thermal Battery Activation

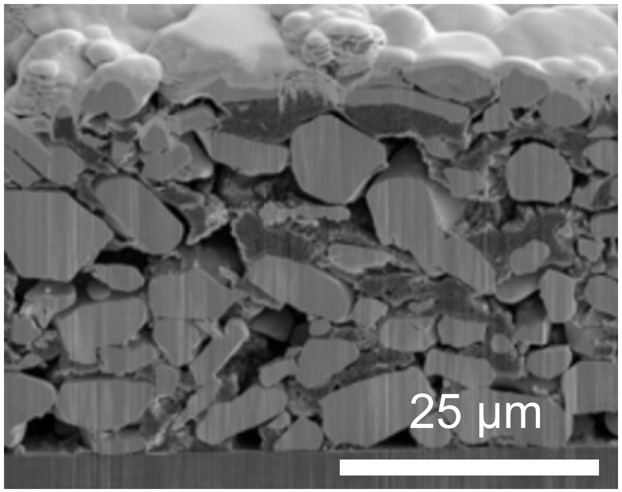


- Infiltration of electrolyte into cathode and anode reduces the internal impedance
- Excess electrolyte can cause shorting/collapse of the cell

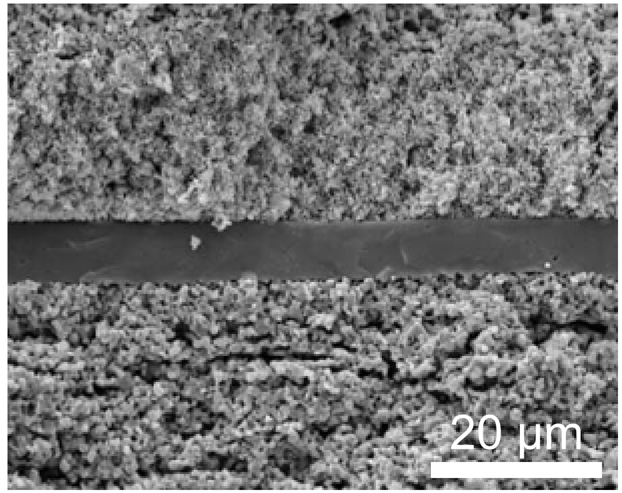
Improve the fundamental understand of electrolyte transport during activation

Quantifying Transport through Porous Components

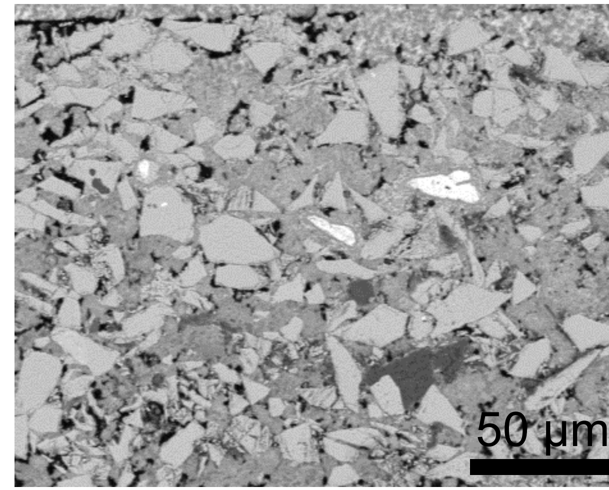
Li-Ion Battery[1]



Fuel Cell[2]



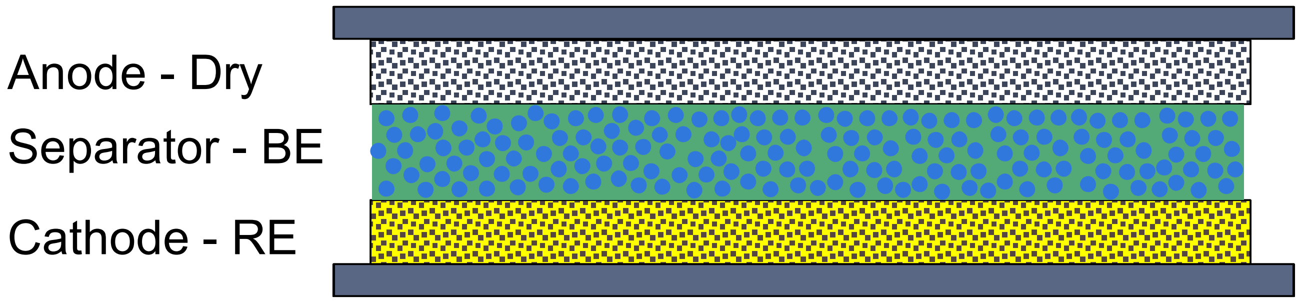
Thermal Battery



- 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 environments?**

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

Introduce Tracker to Probe Transport

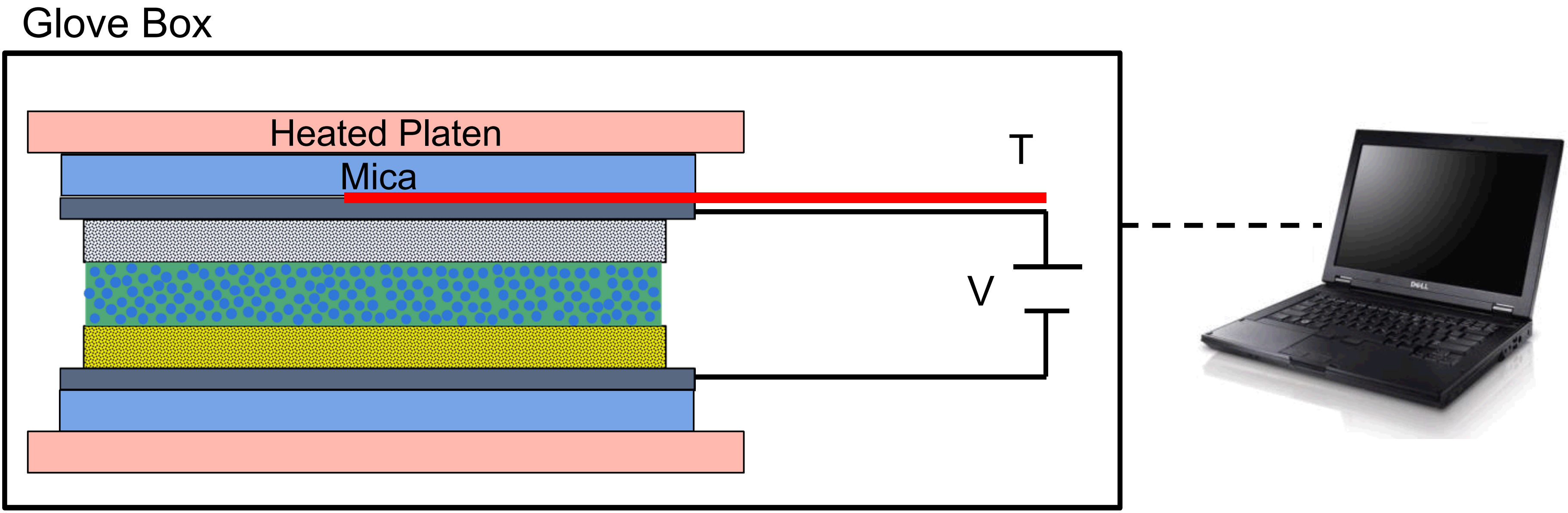


Bromine electrolyte (BE)
50wt% KBr
36wt% LiBr
12wt% LiCl
T_m=310˚C

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

T_m=352˚C

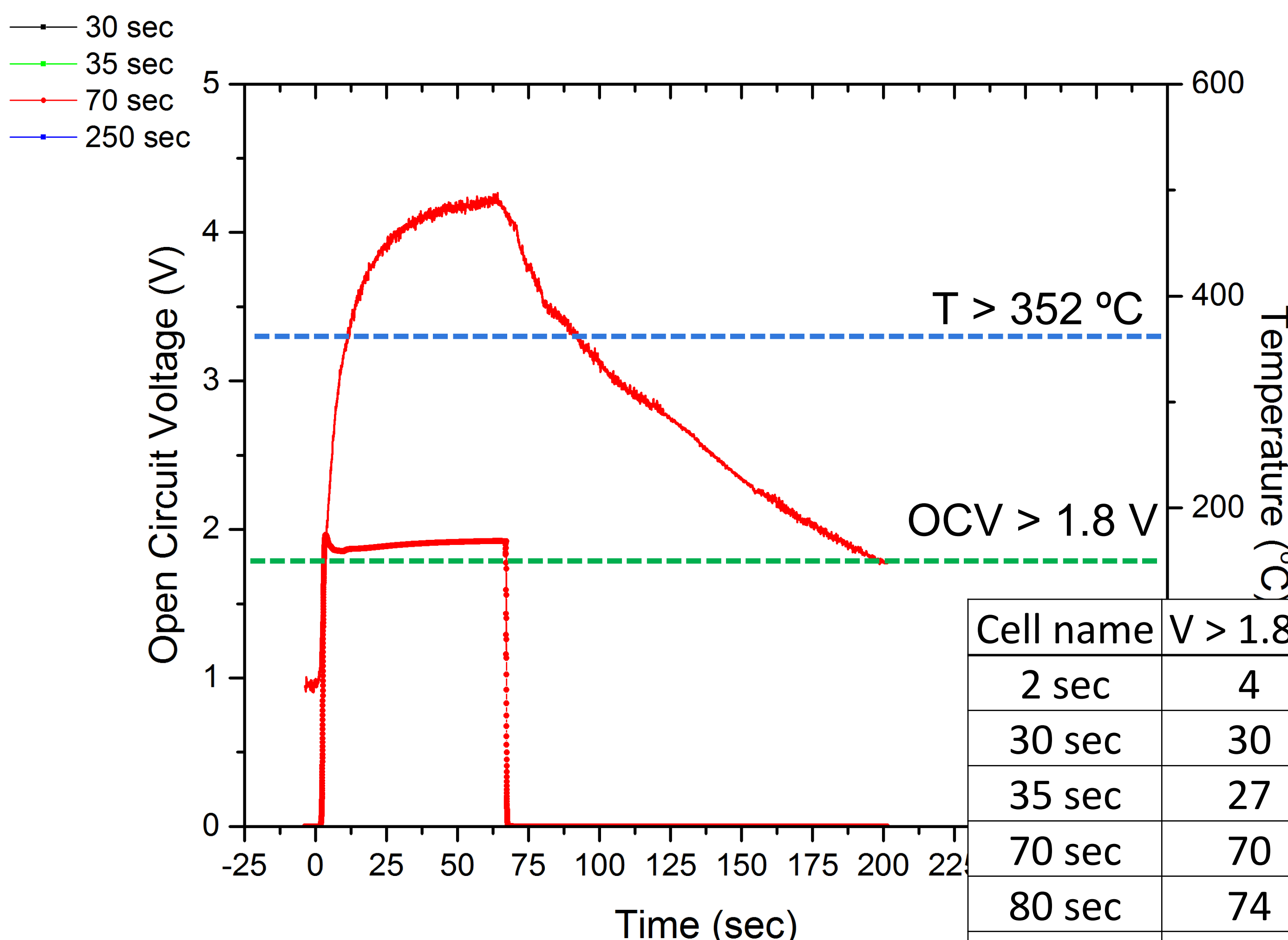
Experimental Setup



- 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

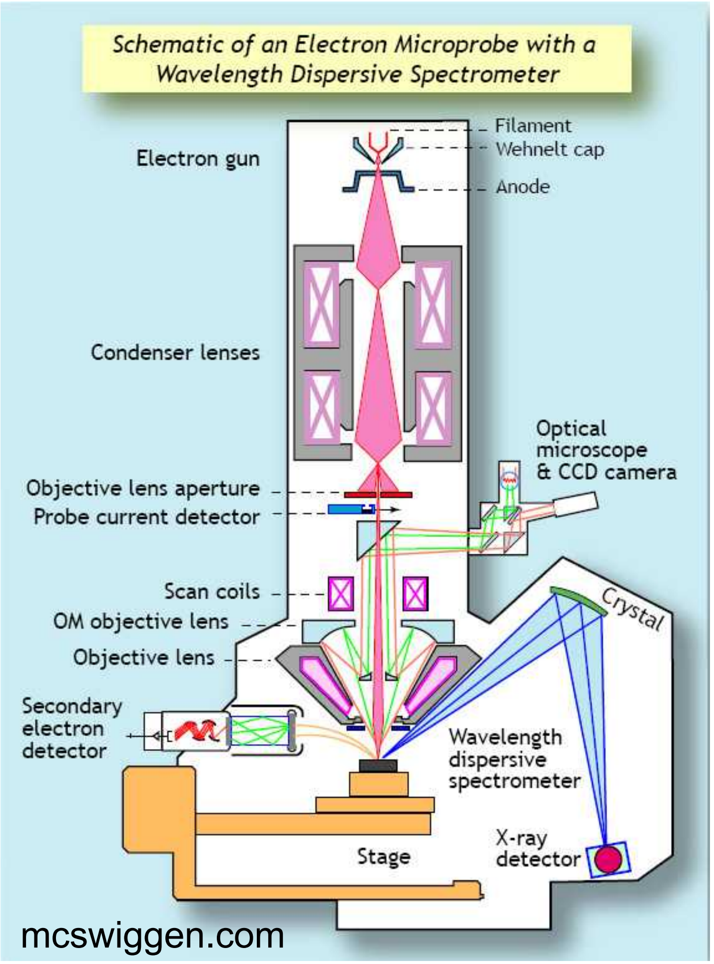
[1] Grillet *et al., Proc. 46th Power Sources Conference* (2014)

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

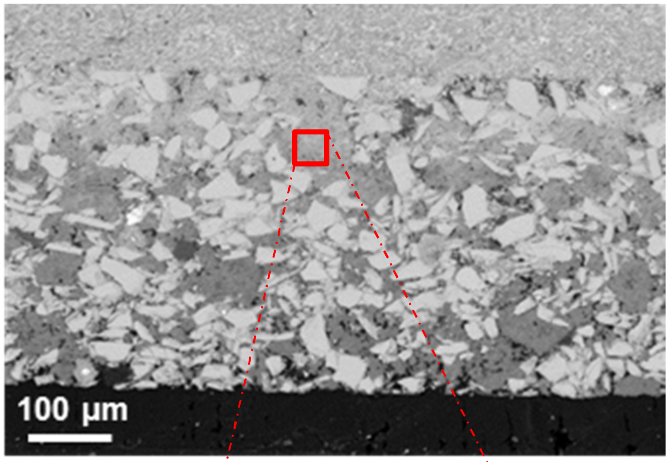
Electron Probe MicroAnalyzer (EPMA)



- 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 micron spatial resolution
  - Precision 0.1wt% elemental composition

Characterizing Electrolyte Concentration throughout Cell

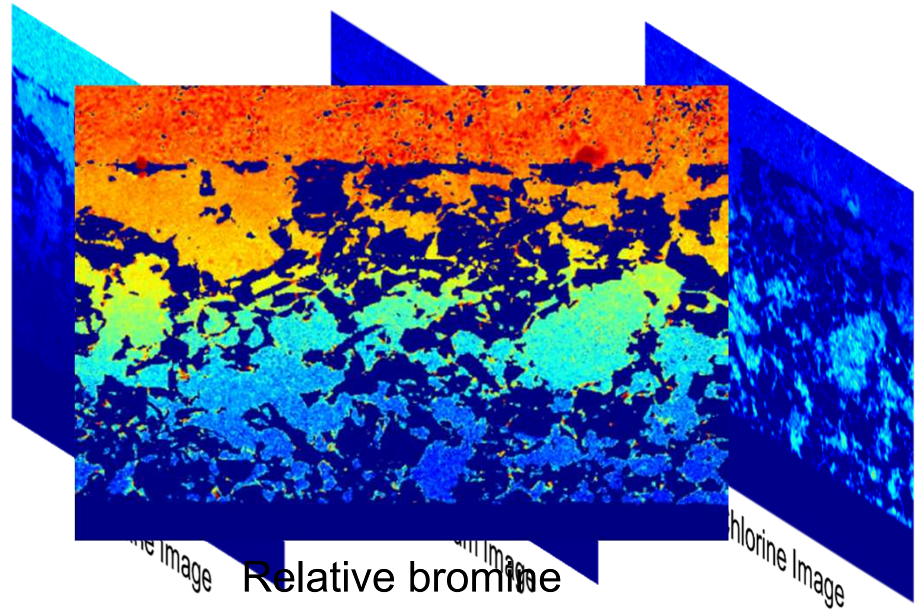
Backscatter Electron Image



44.2 wt% Br
10.8 wt% K
6.8 wt% Cl
...

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

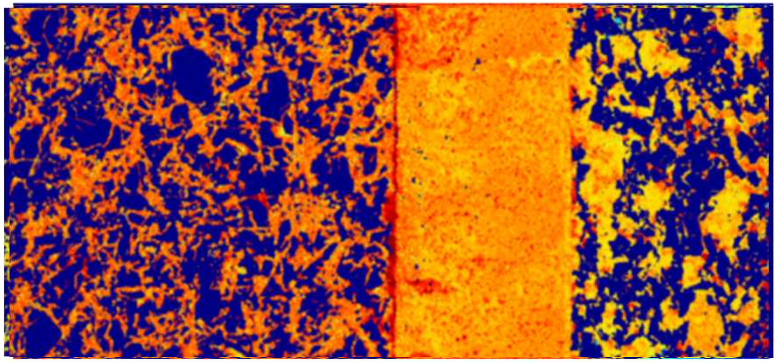
Using EPMA

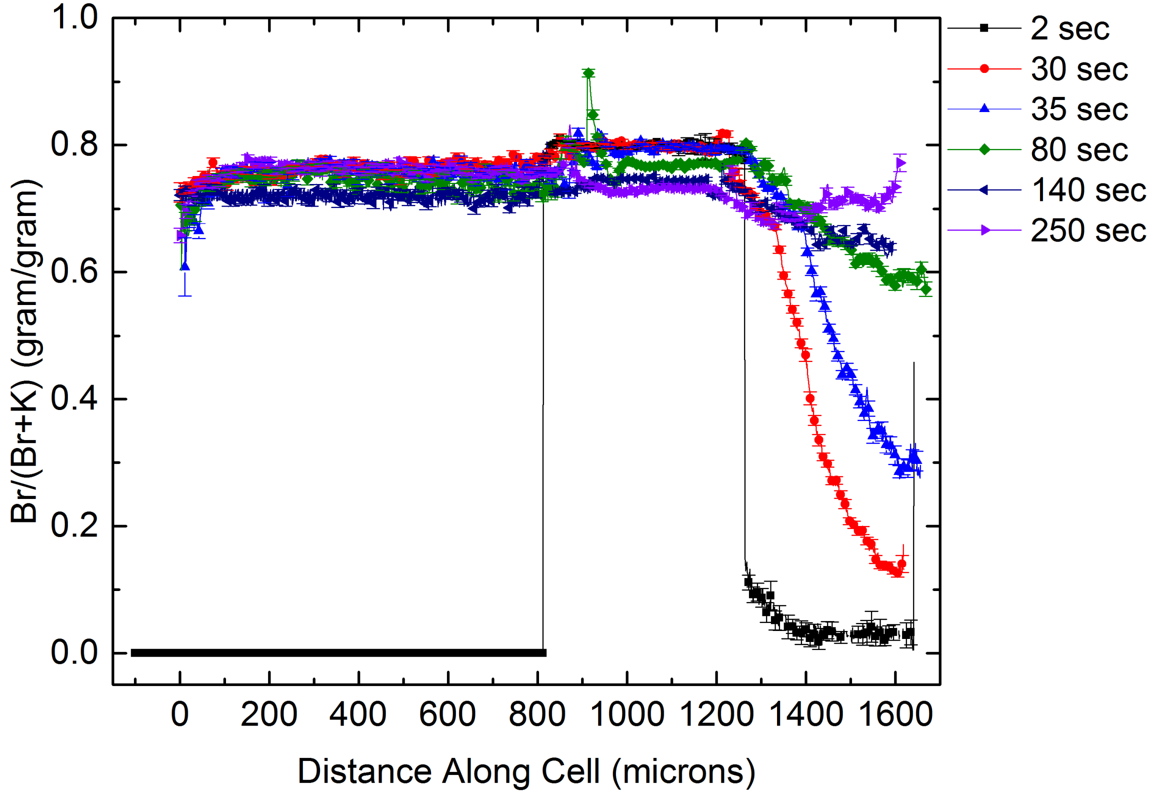


Relative bromine concentration

- 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

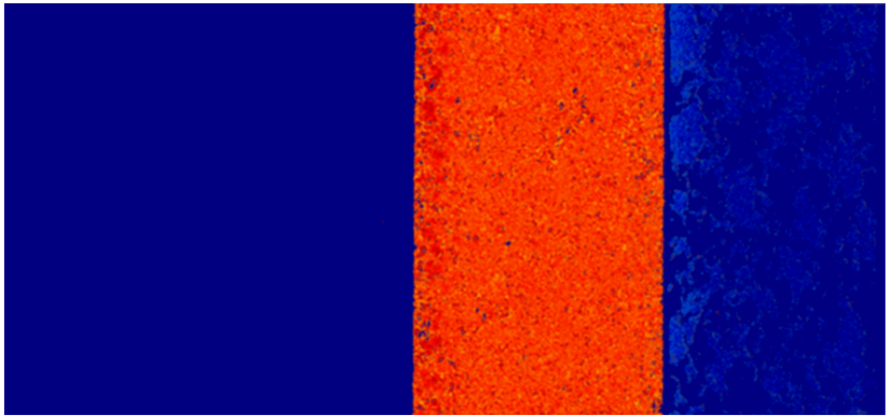




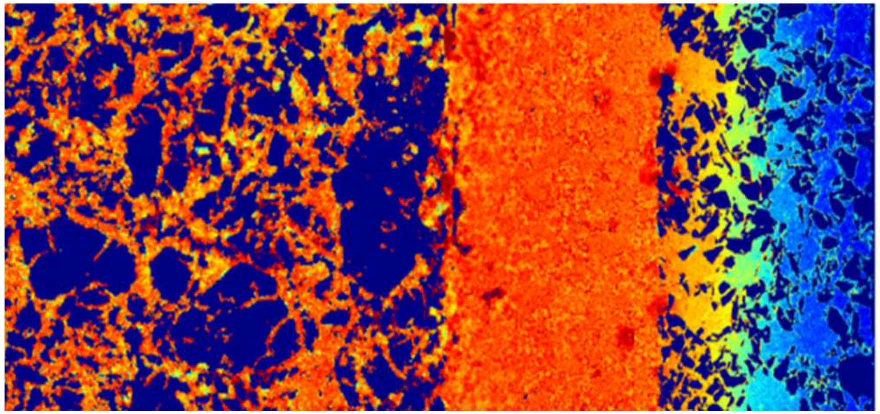
- Separator thins by ≈ 20 % (100 μm)
- Anode is flooded within 30 seconds
- Bromine is diffusing into cathode
- Equilibrium ≈ reached within 140 seconds after activation
- Activation process is finished within 250 seconds

Mechanisms of Transport

2 second

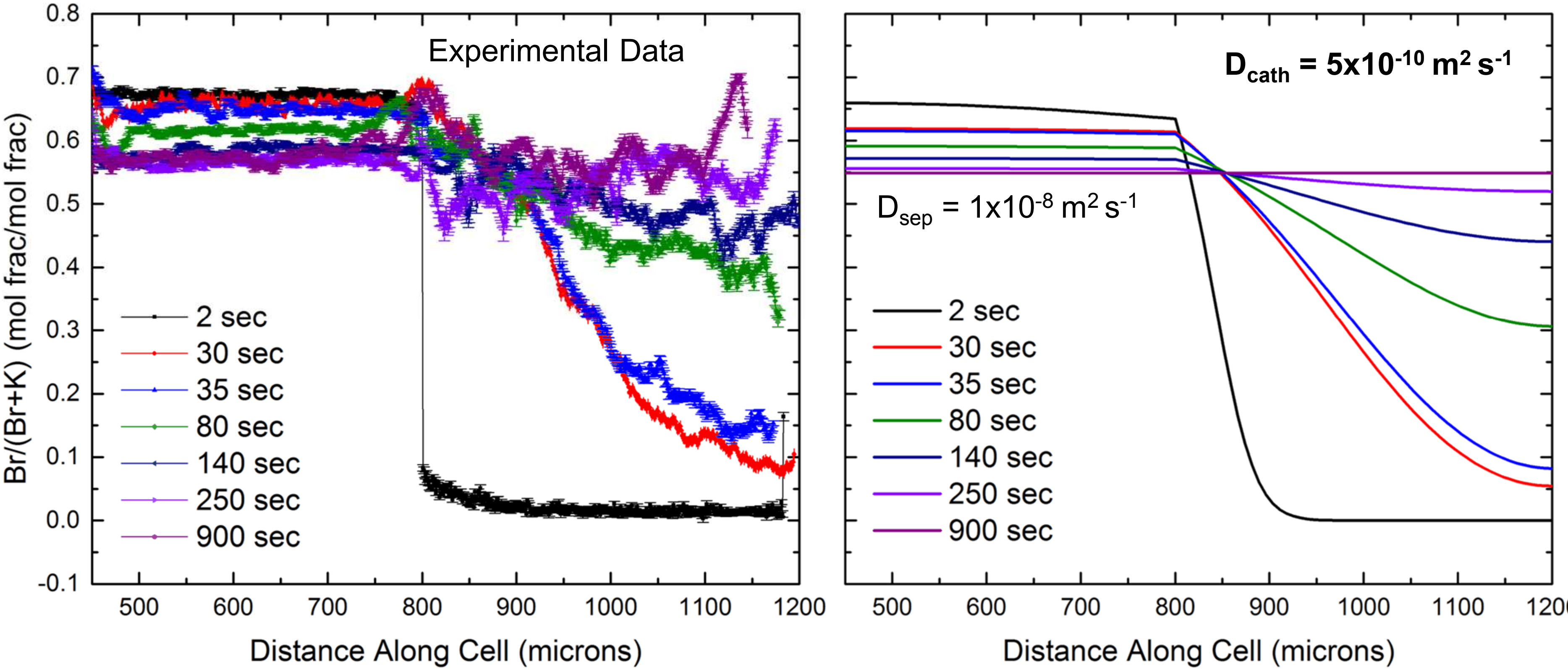


30 second



- 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

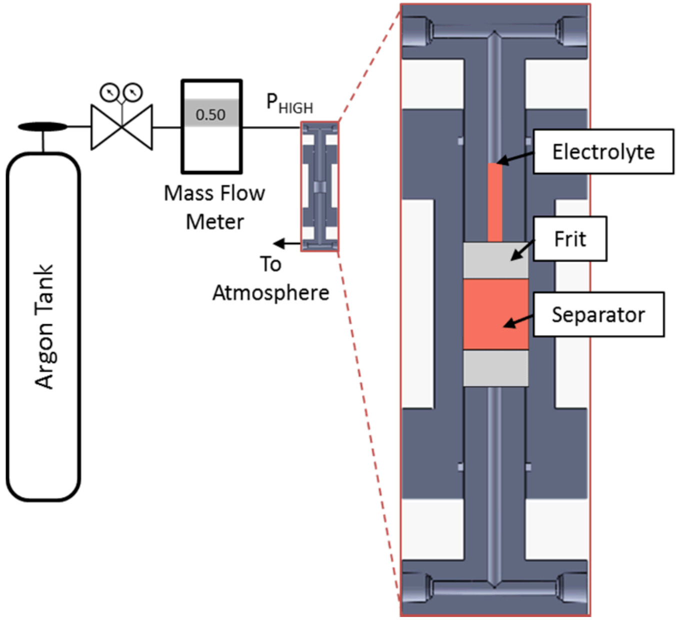


- Estimated diffusivity of bromine in cathode using COMSOL multiphysics modelling software
  - Indicates that tortuosity of FeS_2 network is between 3 – 6
- Investigating effects of porous flow and temperature-varying diffusivity with Sierra (Sandia's Multiphysics Modelling Software)

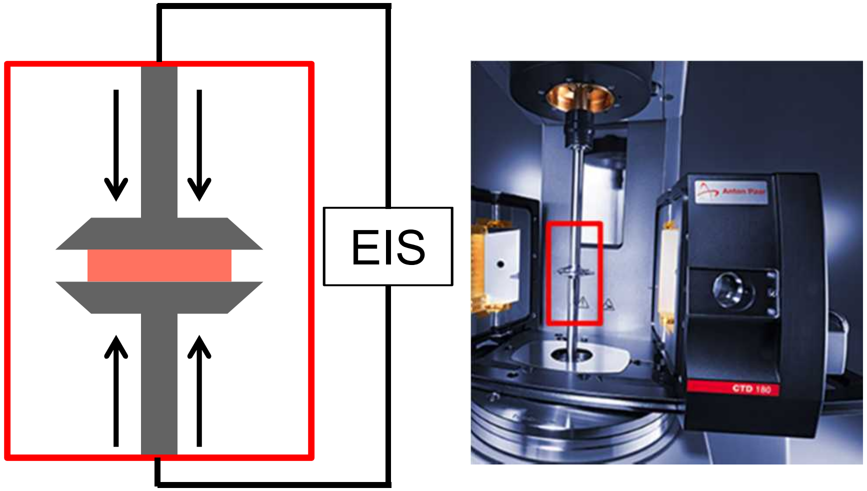
E.L. Cussler, "Diffusion: Mass Transfer in Fluid Systems" (1997)

Future Experiments Probing Transport

Permeability Cell



Combining Rheology with Impedance Spectroscopy



Building high temperature (> 300 °C) permeability cell to measure mass flow through individual components

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

Conclusions

- Developed new methodology exploiting high spatial resolution and resolution of electron probe microanalysis (EPMA) to probe electrolyte mobility within thermally activated batteries
- 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
- Utilizing insights to better tune input parameters to thermal battery modelling efforts at SNL