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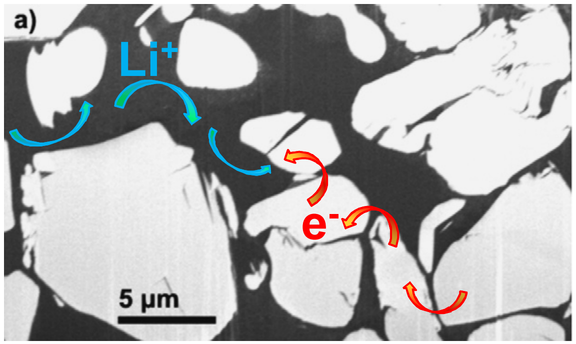


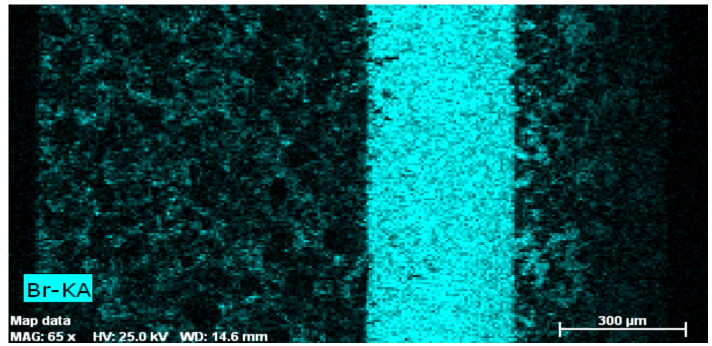


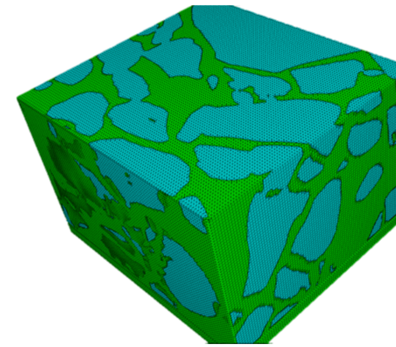

# Ion transport in porous battery electrodes

**Anne M. Grillet**,
Scott A. Roberts, Christine C. Roberts, Daniel E. Wesolowski,
Ashley N. Allen, Lisa A. Mondy, Richard P. Grant, & Bonnie McKenzie

86th Annual Meeting of Society of Rheology

October 7, 2014

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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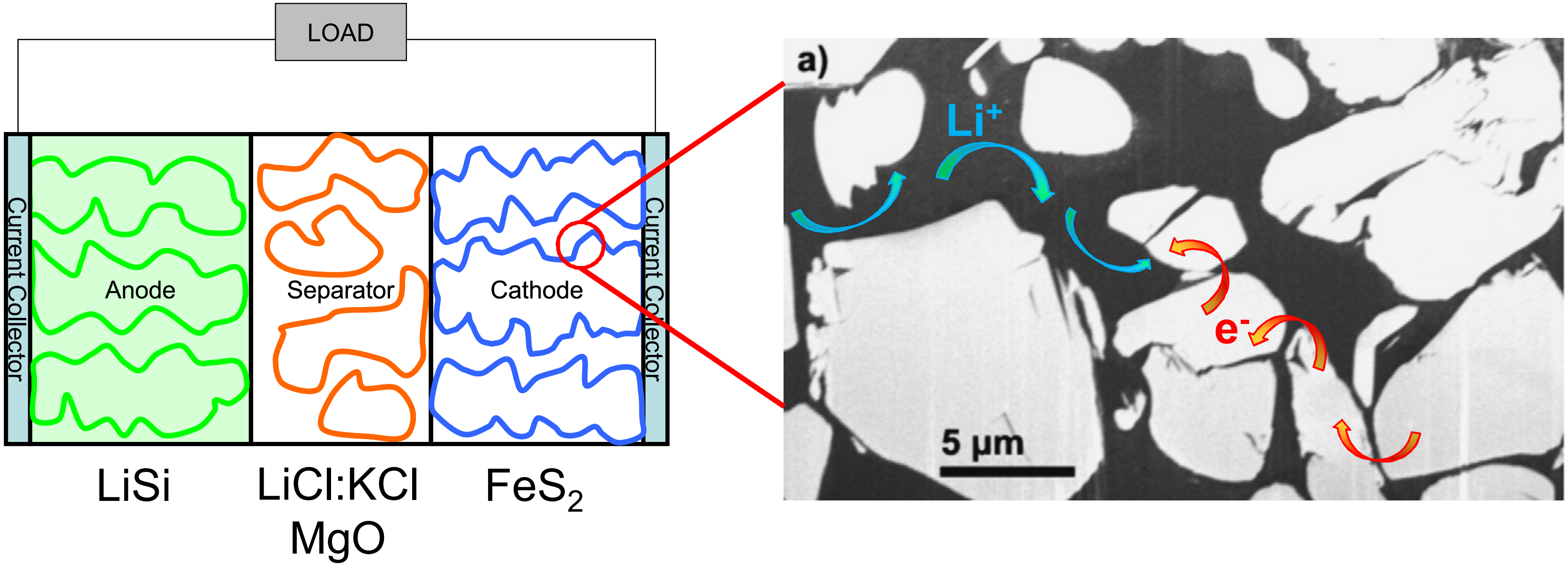
# Battery Introduction

- Batteries convert stored chemical energy into electrical energy
  - Lithium is stored in the anode at high chemical potential
  - Molten salt batteries use an electrolyte that is solid at room temperature
  - Battery electrodes are particle composites which form bicontinuous percolated network

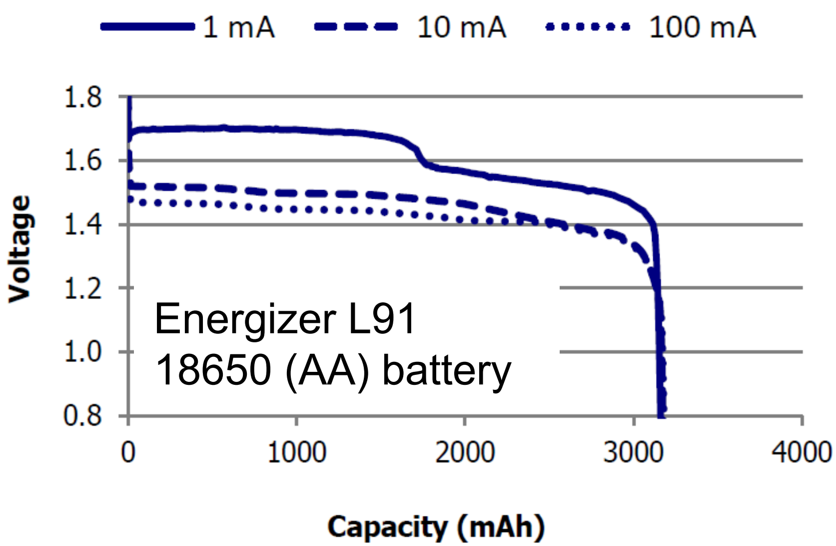


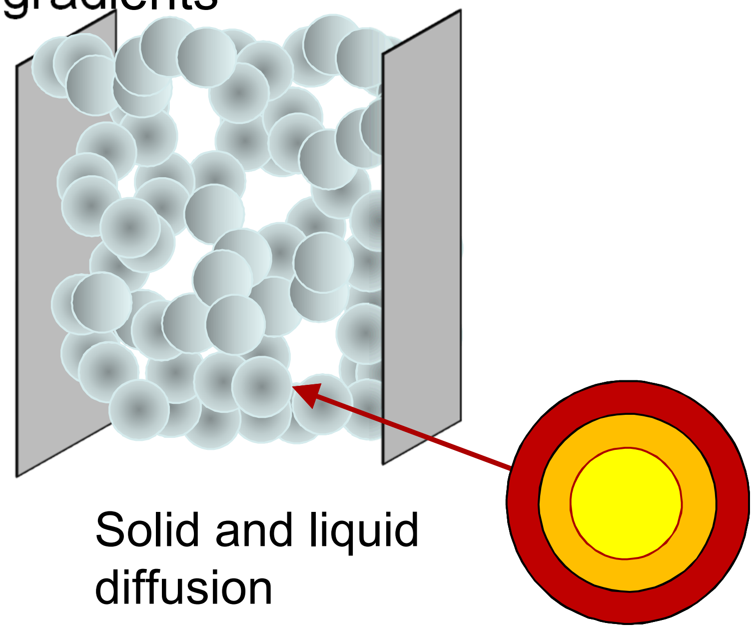

Actual voltage depends on how efficiently lithium is transported

Wilson *et al.* (2011)

# High Power Limited by Ion Transport

- Voltage drops caused by battery internal resistance
  - Reaction rate limitations
  - Transport limitations – concentration gradients



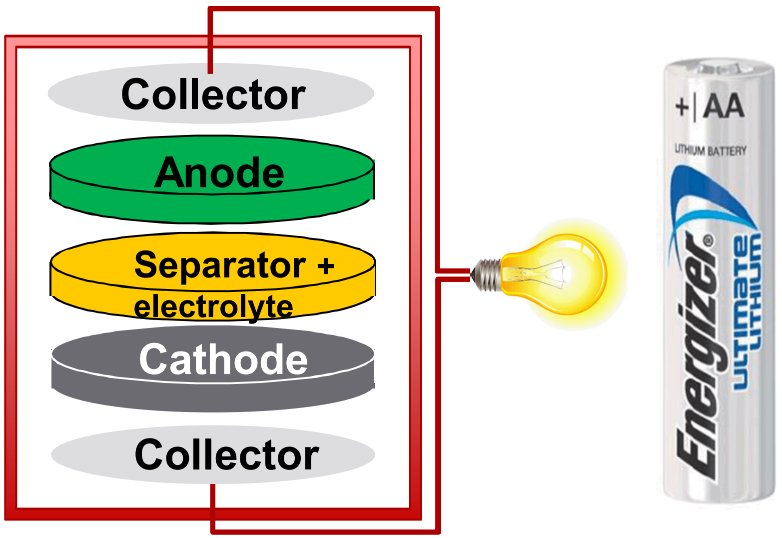
Solid and liquid diffusion

- Part of a larger effort at Sandia to develop predictive model for battery performance
  - Electrochemical, mechanical, and thermal dependence

# Molten Salt Battery Basics

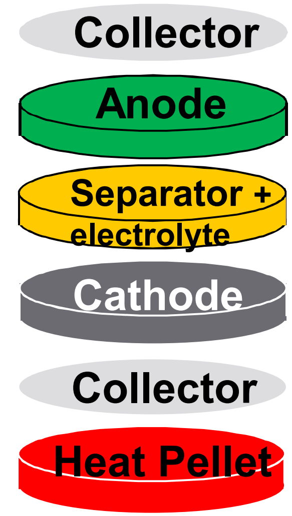
Sandia National Laboratories

Commercial AA Cell Battery




- 2-3 year shelf life
- Low voltage/low current
- Liquid electrolyte dispersed in a separator support material

Molten Salt Battery




- 20+ years shelf life
- High voltage/high current
- Solid electrolyte dispersed a separator – electrolyte must be melted for battery to work

By quenching a molten salt battery, we can analyze the electrolyte & ion distributions as a function of active time

# Outline

- **Goal: Understand ion transport in an active battery**
  - Quenching of single cell molten salt batteries
  - Scanning Electron Microscopy with Energy Dispersive Spectroscopy - qualitative imaging of distribution
  - Electron Probe Microanalyzer - quantitative concentration mapping
  - Mechanisms of electrolyte movement
  - Meso-scale modeling of transport in lithium battery electrodes

# New Approach for Electrolyte Transport

- **Goal: Understand movement of electrolyte in molten salt battery**
- Use bromine tracer to track electrolyte transport through thermal battery
  - Scanning Electron Microscopy Energy Dispersive Spectroscopy qualitative imaging of distribution
  - Electron Probe MicroAnalyzer - quantitative concentration mapping

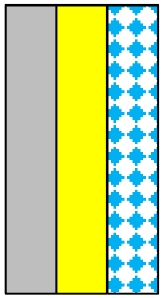
Bromine electrolyte
50wt% KBr
36wt% LiBr
12wt% LiCl
$T_m$=310˚C

Regular electrolyte
45wt% LiCl
55wt% KCl
$T_m$=352˚C

Anode
LiSi
Dry

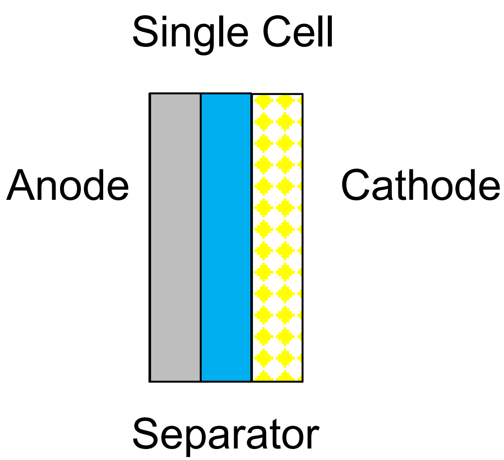
Separator
MgO binder +
electrolyte

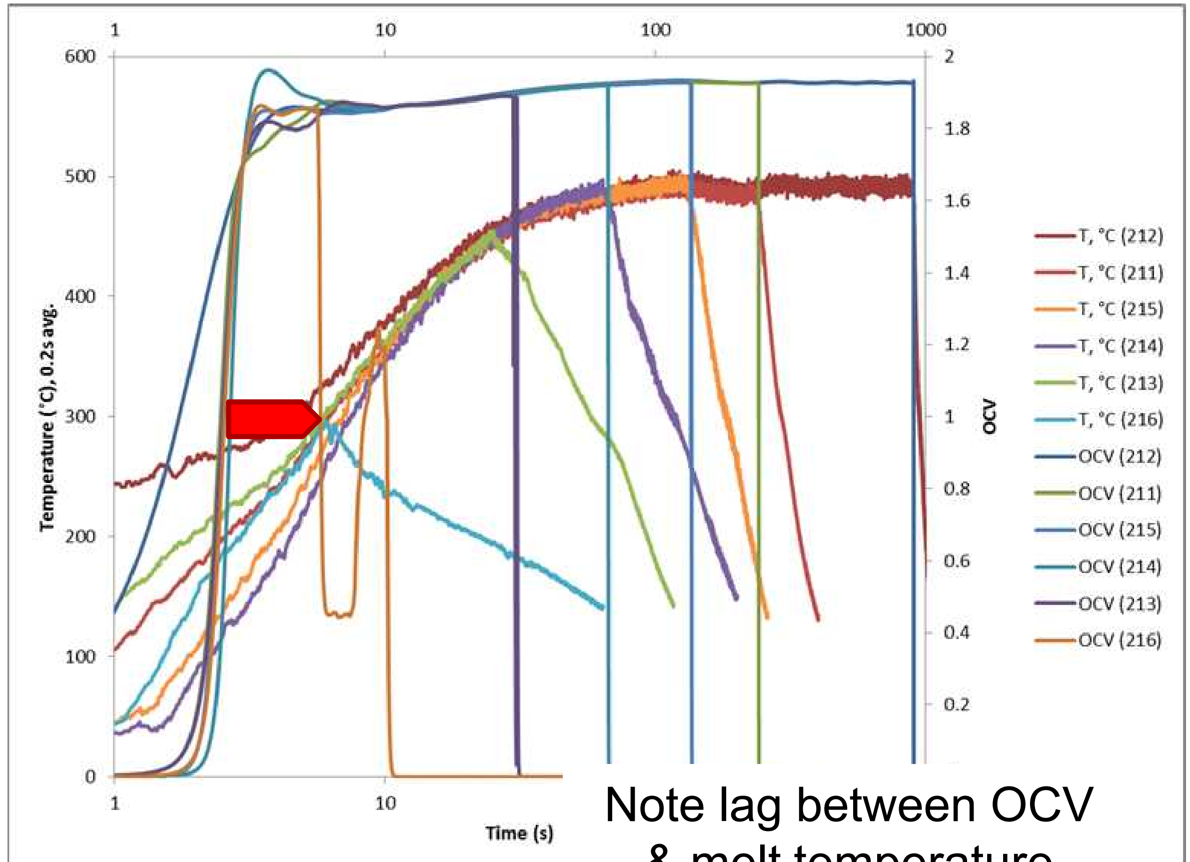
Cathode
$FeS_2$
+ separator
+ $Li_2O$



# Quenching of Single Cell

- Single cells are tested at 500˚C under 12psi force
- Temperature monitored by a thermocouple on top of the cell
- Cooled cells were mounted & cross-sectioned for analysis



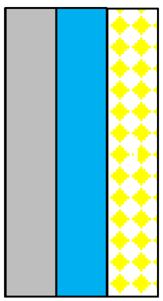



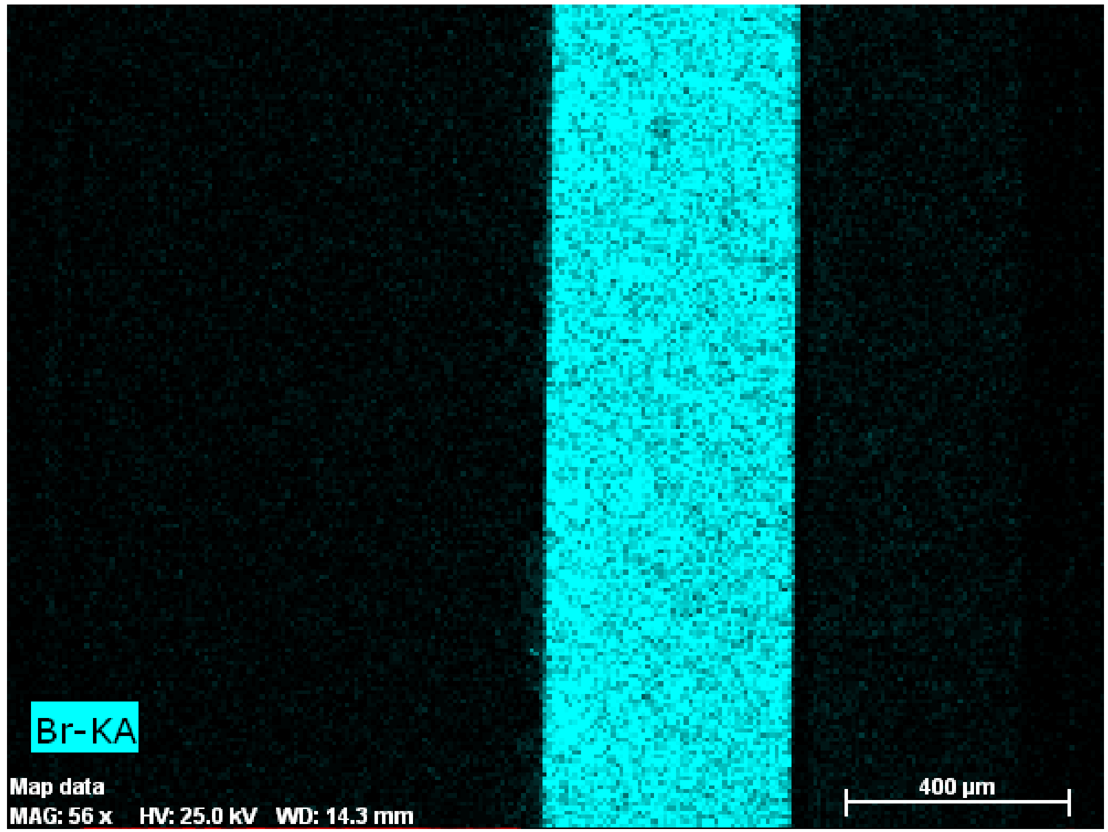

Note lag between OCV & melt temperature

# What's Inside a Molten Salt Battery?

- Scanning Electron Microscopy with Energy Dispersive Spectroscopy can qualitatively map distributions of various elements

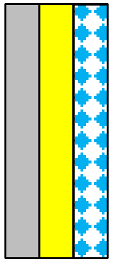
Single Cell



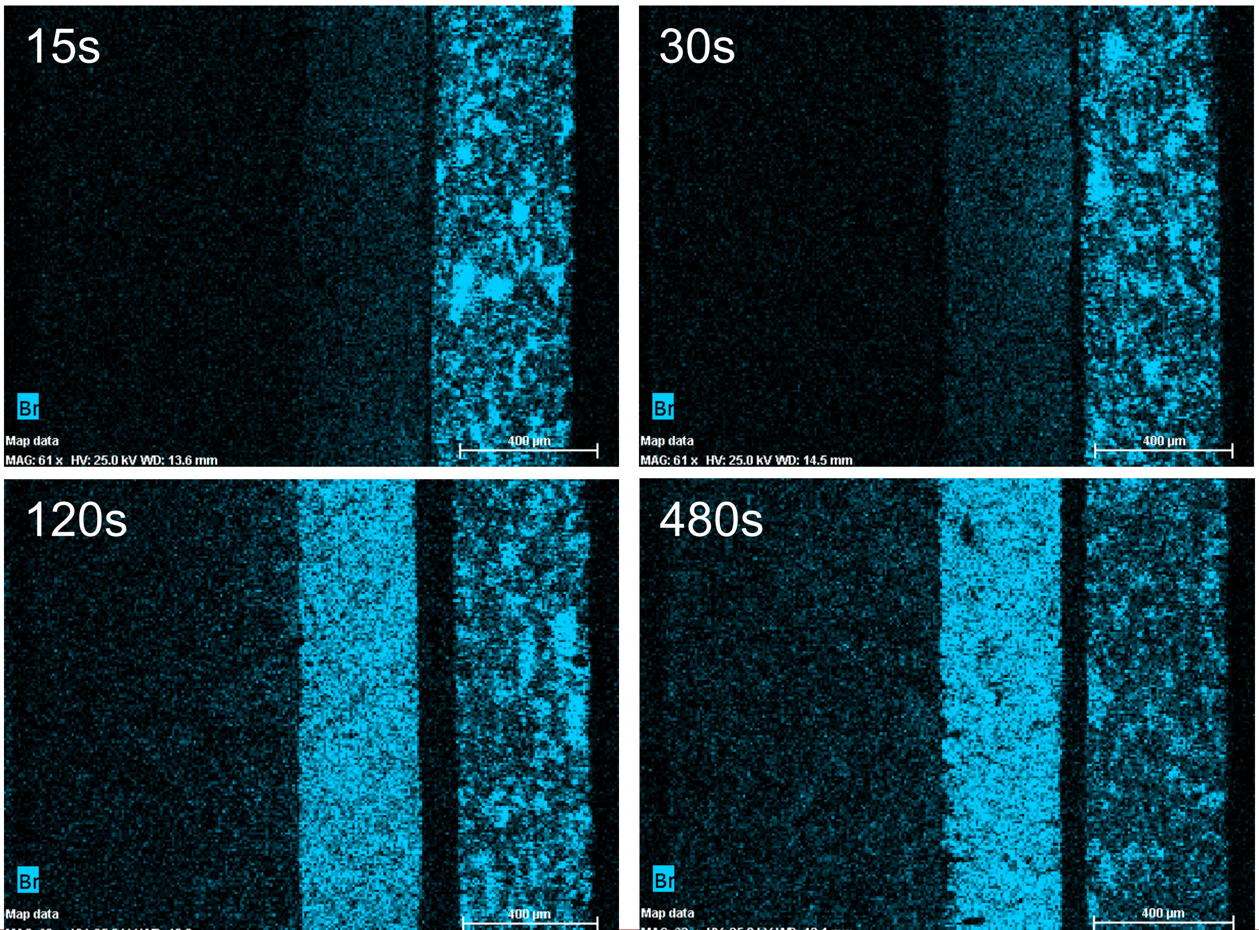




Anode Separator Cathode

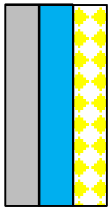
# Tracking Electrolyte from the Cathode



- On activation,
  - separator get thinner
  - Bromine diffuses from cathode across the cell.

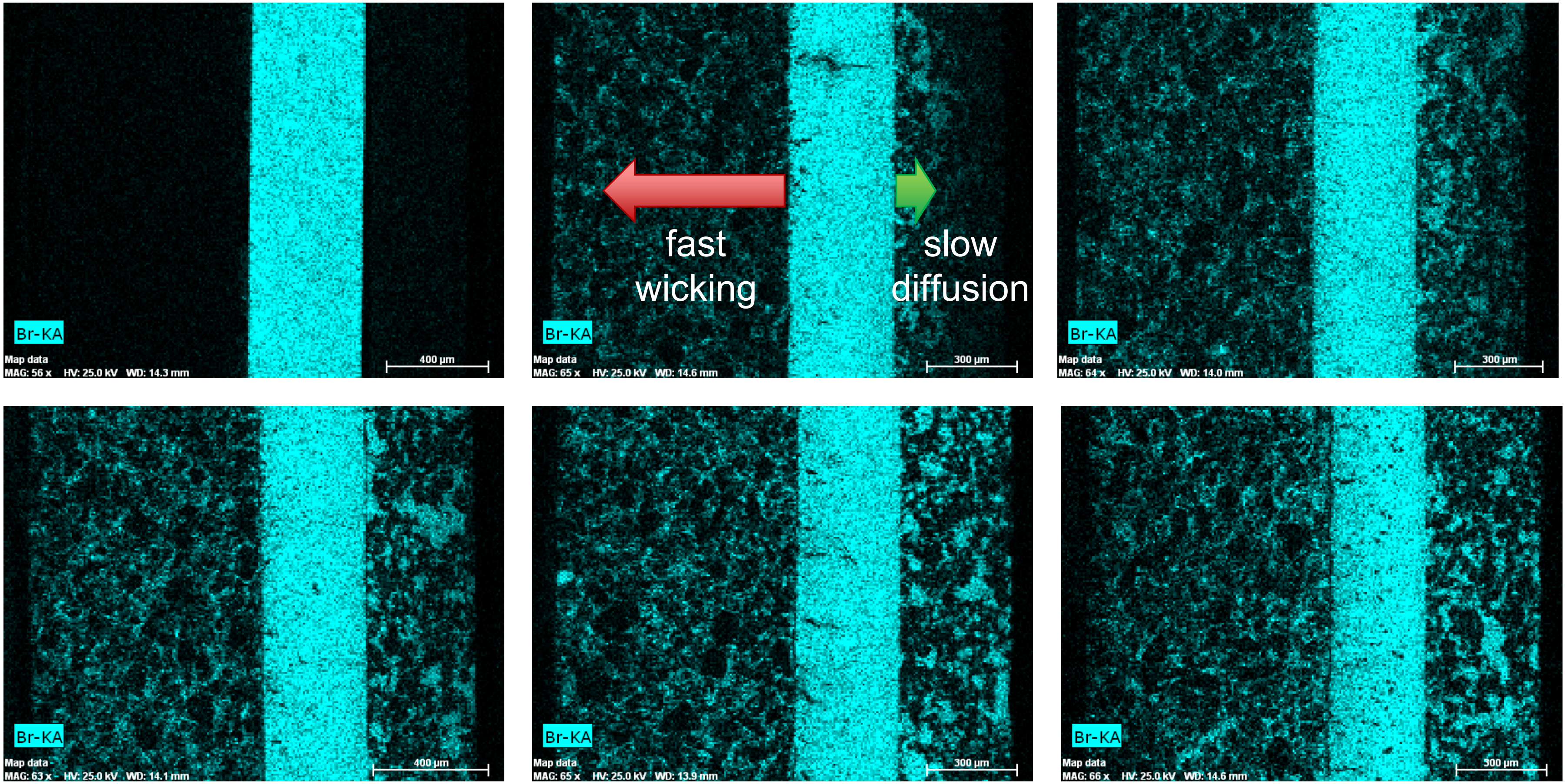


# Tracking Electrolyte from the Separator



- Energy dispersive spectroscopy images of electrolyte transport out of separator

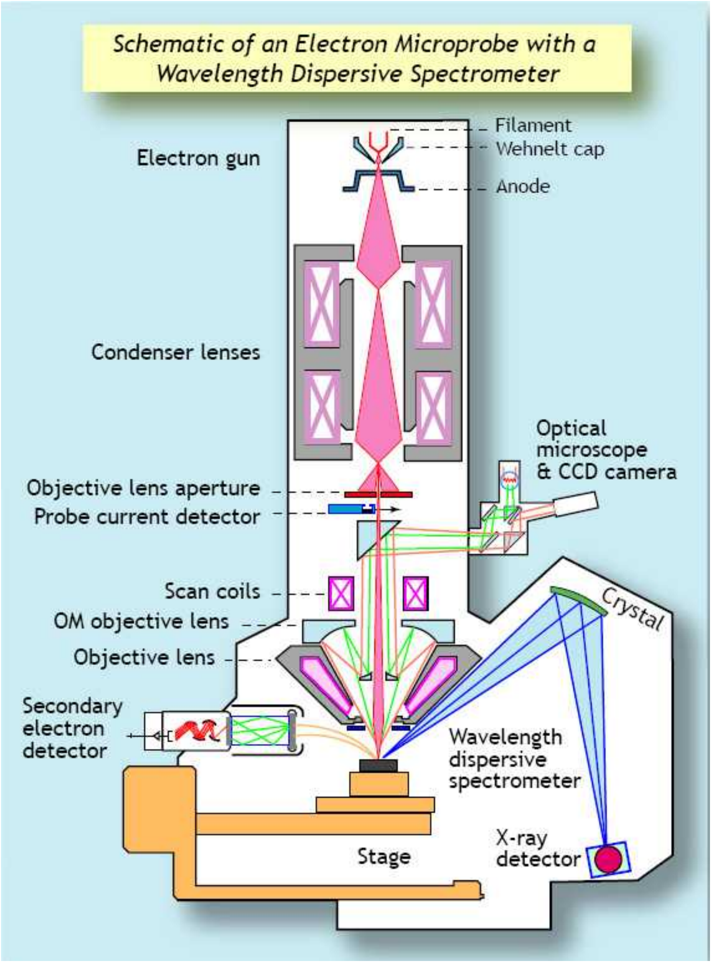
t=2s (not melted) t=30s t=60s




t=120s t=400s t=900s

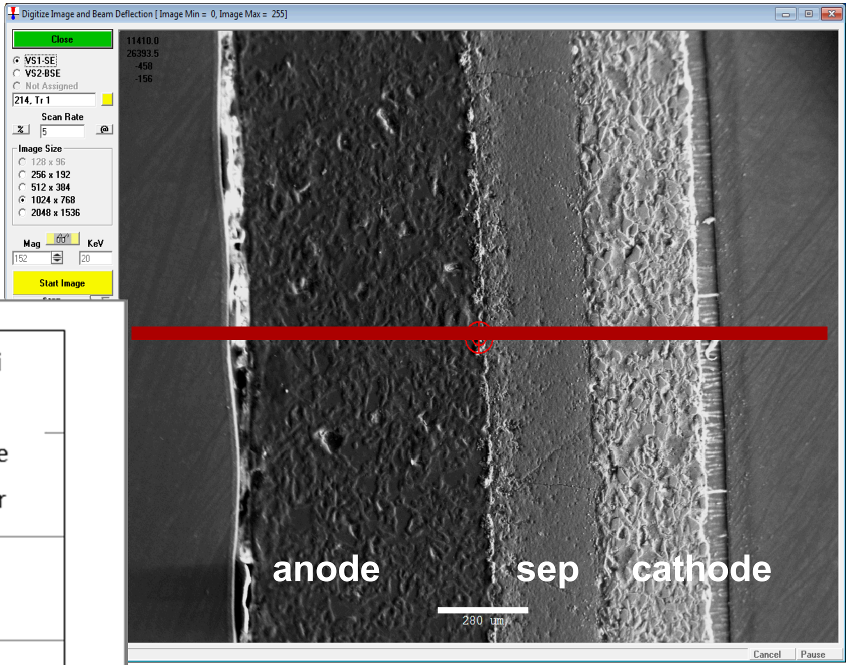
# Electron Probe Microanalyzer (EPMA)

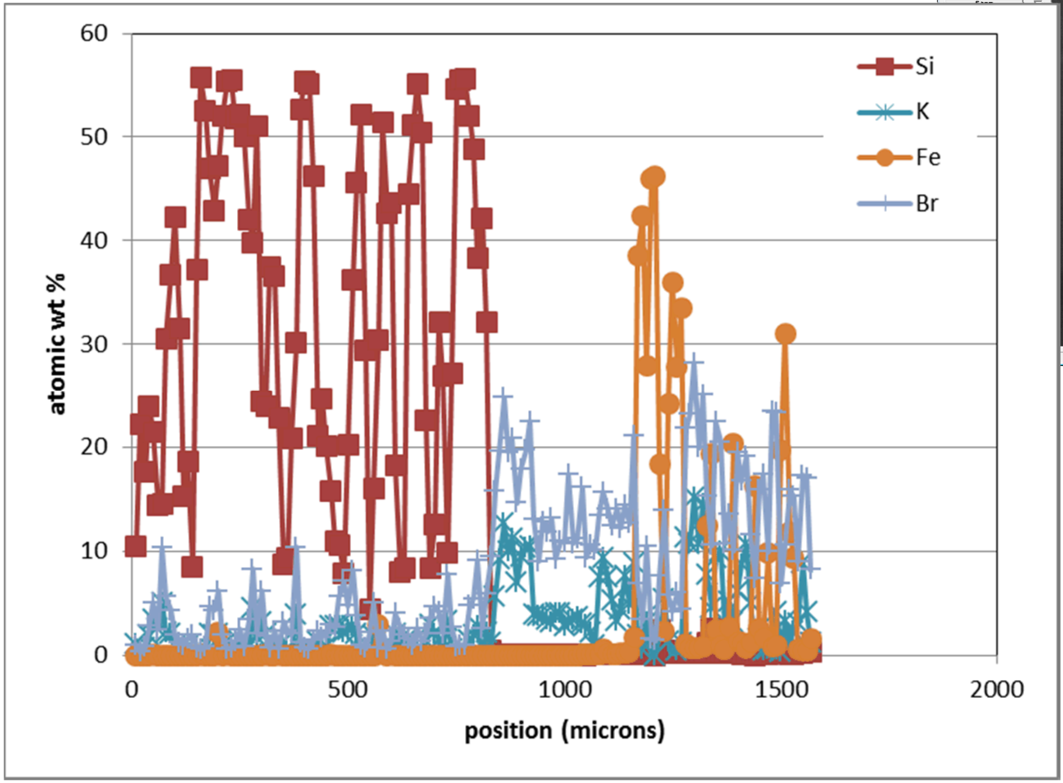
- X-rays emitted by a sample under electron bombardment
- Spectral analysis allows element detection
- Comparison to elemental standard of known concentration
- **Quantitative Chemical Analysis**
  - 1 micron spatial resolution
  - Precision 0.1wt% elemental composition

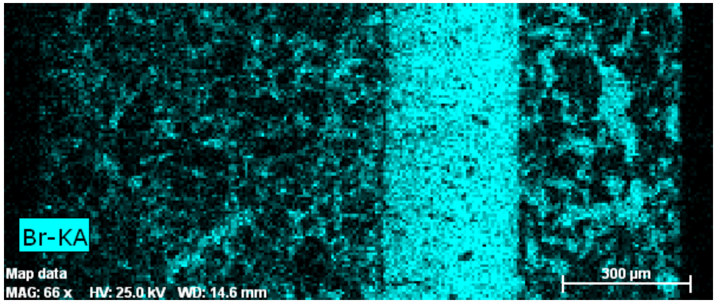


# Meso-scale Structure of Electrode

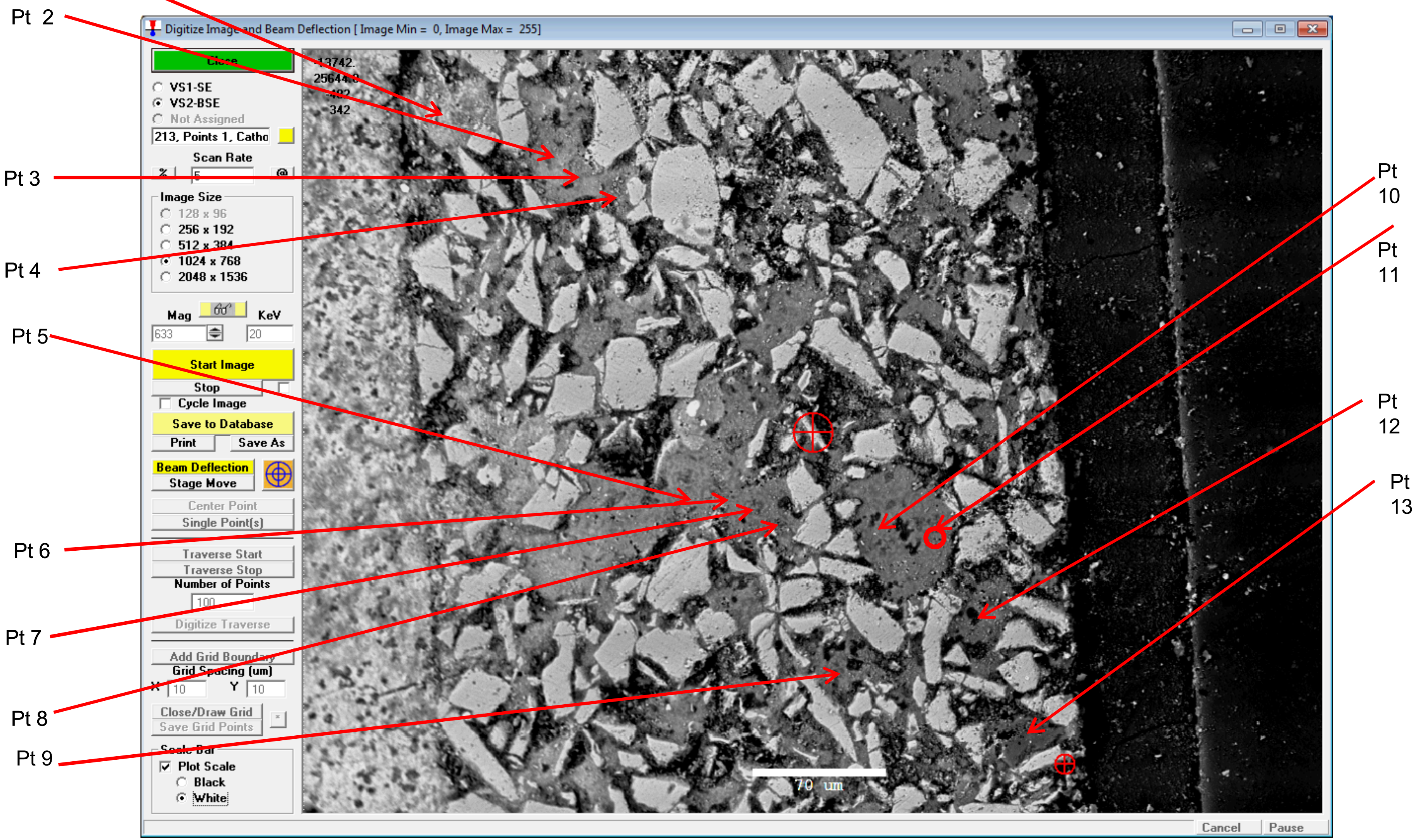
- Heterogeneous structure of battery complicates chemical analysis



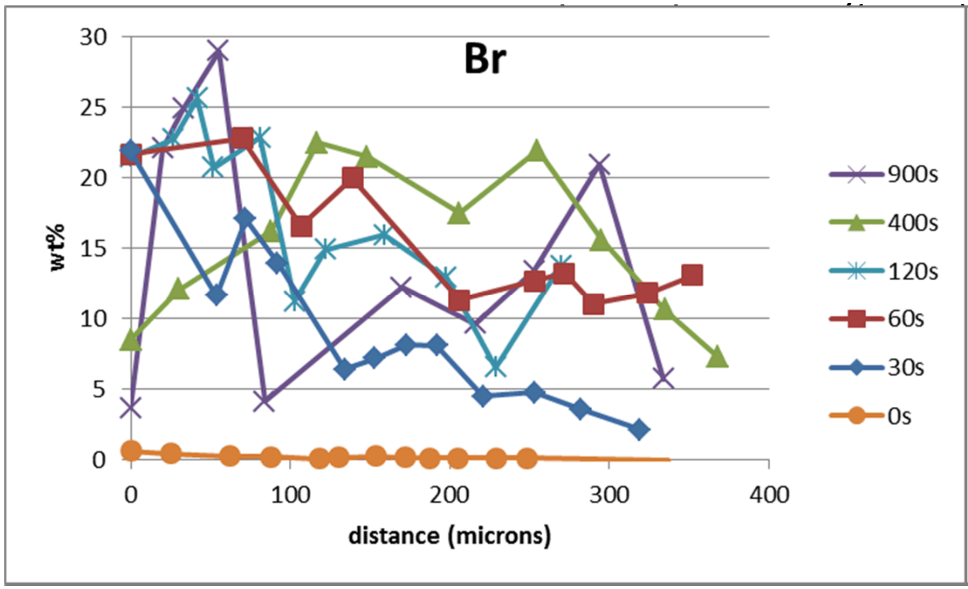
# Point-wise measurements in cathode

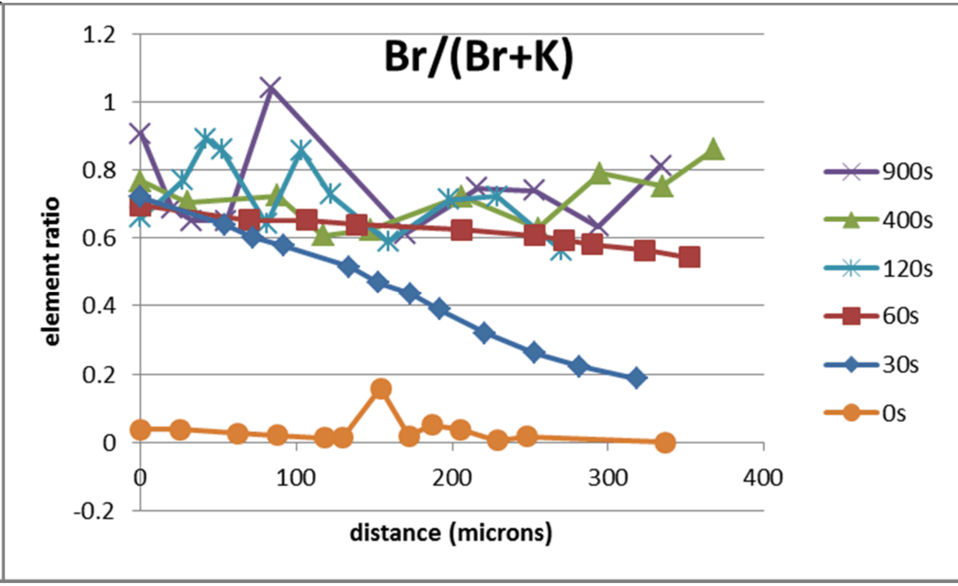



Average over 10 micron beam size at distinct points across the cathode

# Microprobe for Quantitative Chemical Imaging

- Even isolating the electrolyte rich regions, bromine concentration data is very noisy
  - Using element ratio with potassium gives cleaner, quantitative data

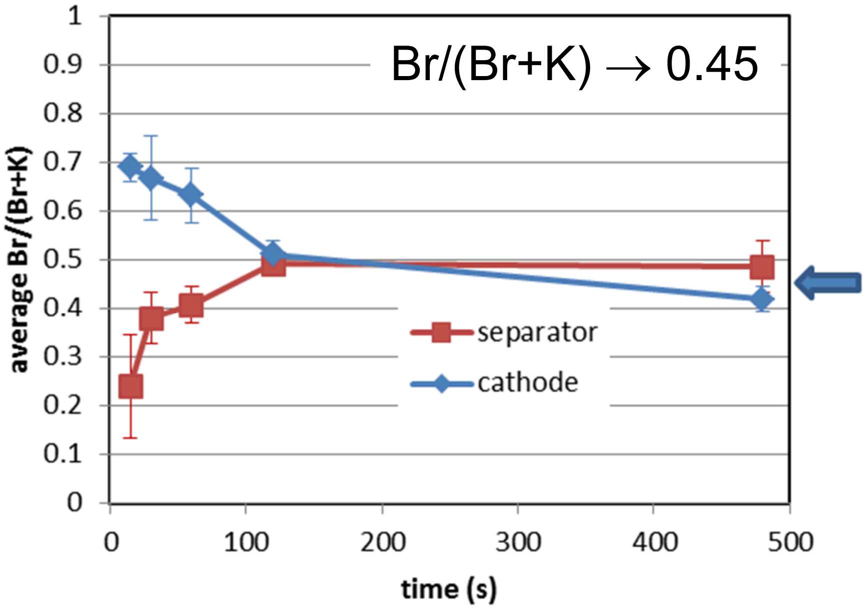


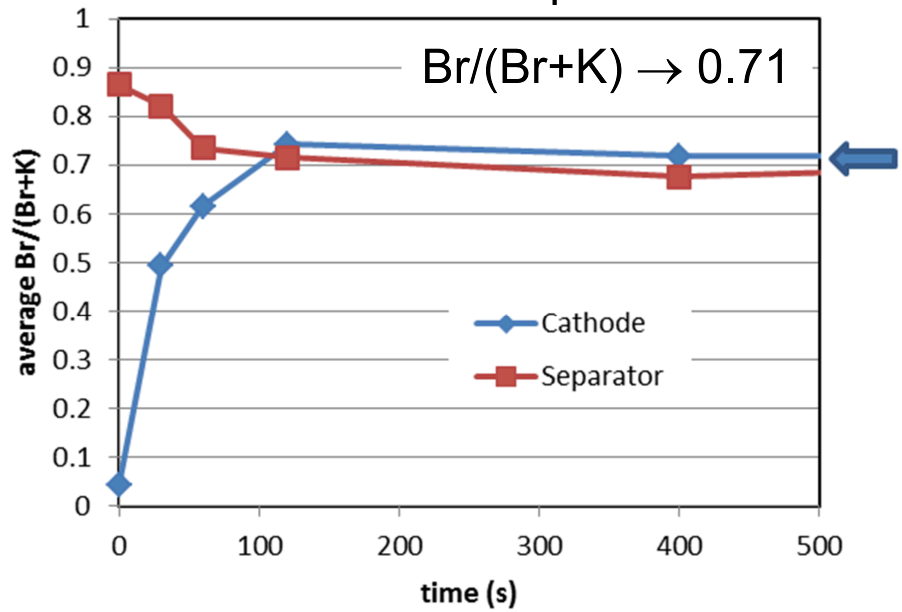
# Bromine Diffusion into Cathode

- Bromine diffusion between separator and cathode is complete within 120 seconds
- Calculated equilibrium bromine ratio based on initial electrolyte concentrations

Br from the cathode

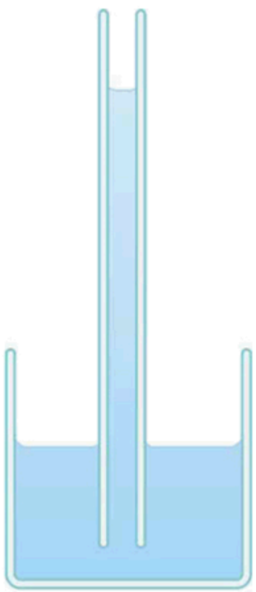


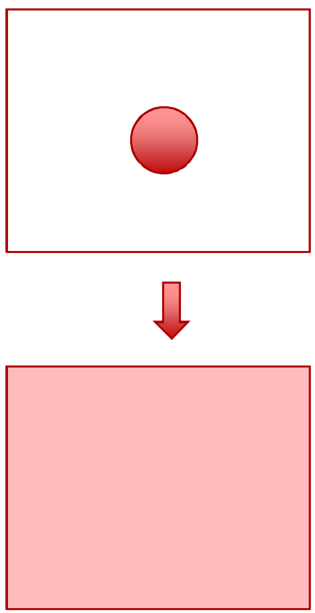

Br from the separator

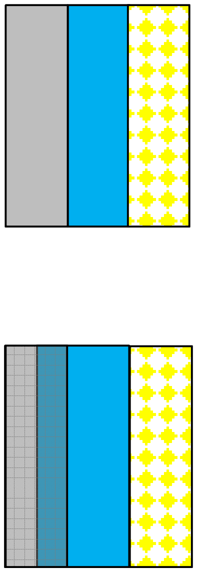


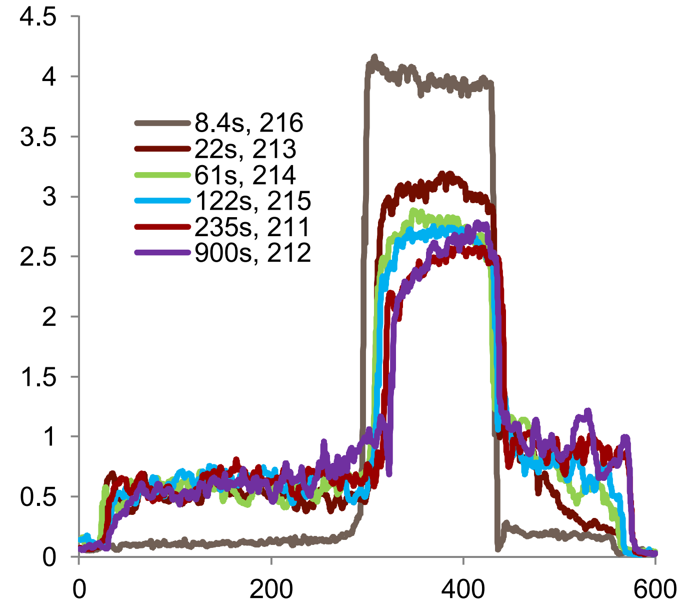
# Transport mechanisms

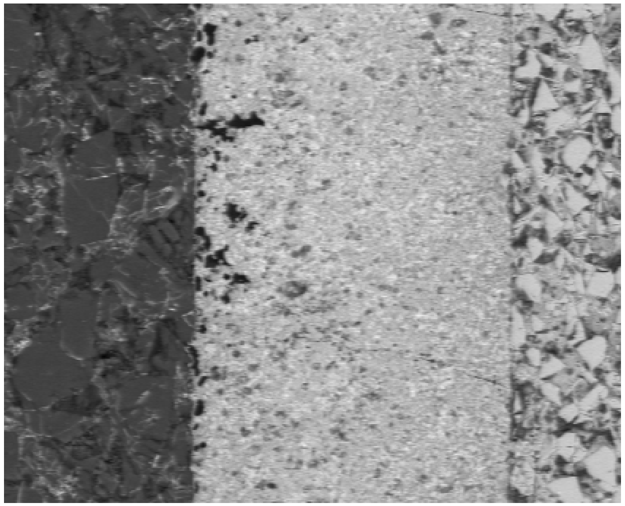
- 3 Potential transport mechanisms
  - Capillary wicking
  - Diffusion
  - Pressure driven flow





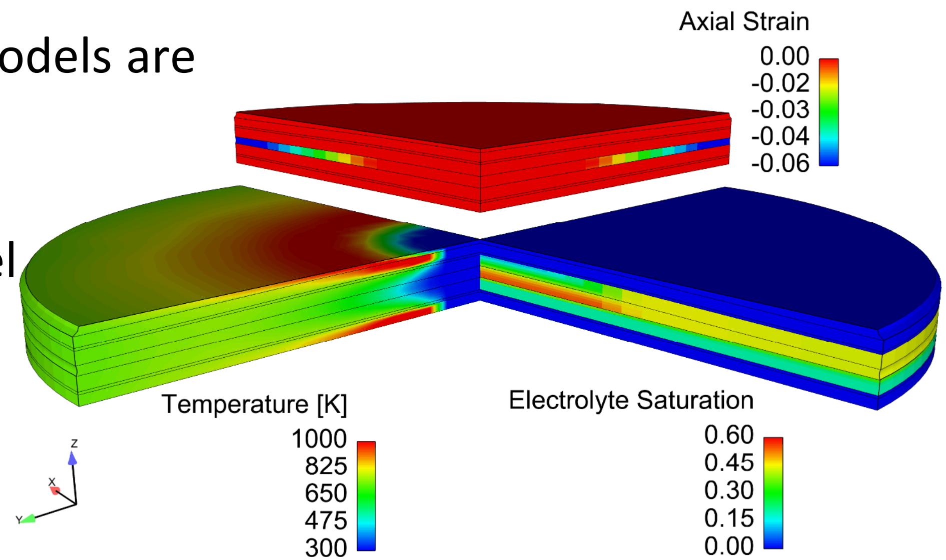




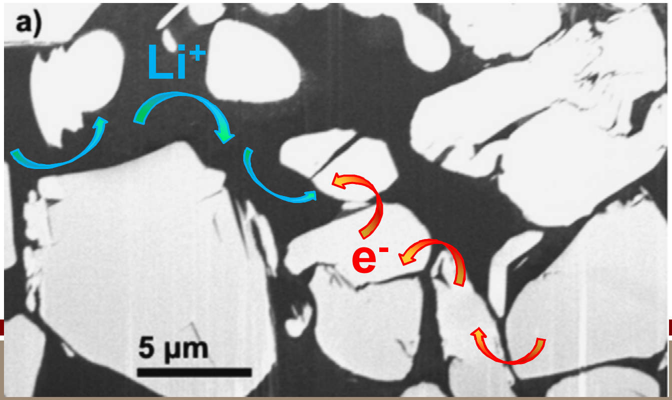



# Better Predictions of Battery Performance

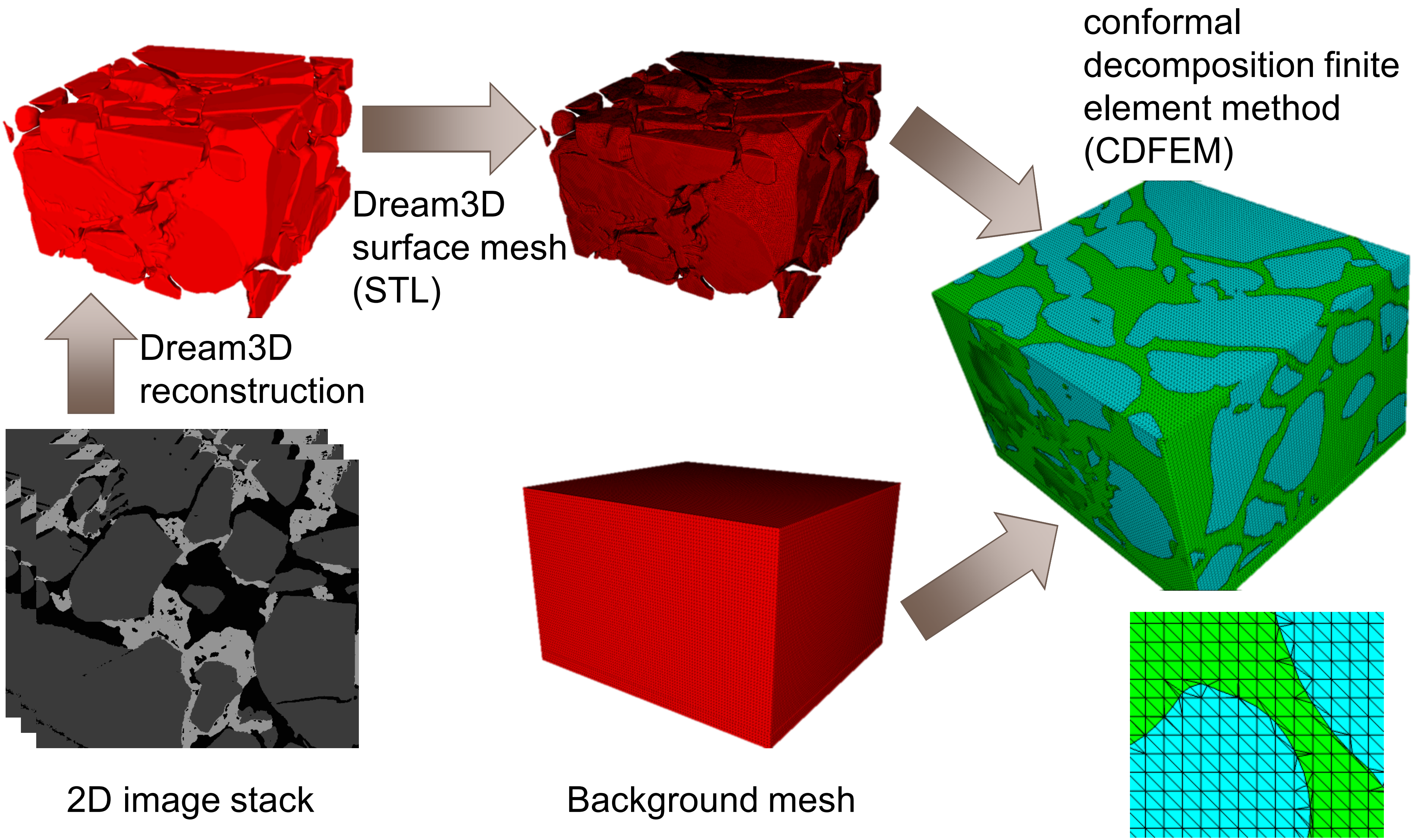
- Good models need high fidelity experiments
  - Determine parameters
  - Validate the predictions
- Most of our multi-physics battery models are based on continuum assumptions
  - Coupled thermal, mechanical deformation & porous flow model of molten salt battery




- New effort: Microstructure of battery electrodes
  - Ionic conduction
  - Electronic conduction



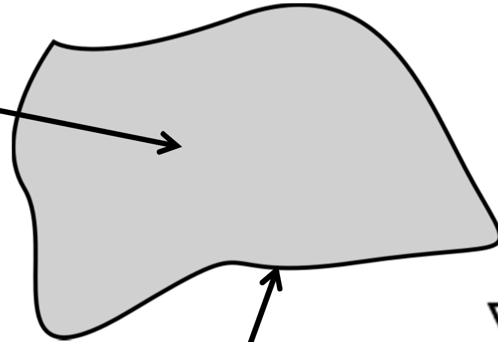
# Representation of electrode microstructure






Hutzenlaub *et al* (2012) Electro Chem Solid State Let., Lechman *et al.* (2012) Int. J Numerical Methods in Fluids

# Physics models: Electrochemistry



**In the particle**

- Ohm's Law

$$\underline{\nabla} \cdot \left(\sigma \underline{\nabla} \phi_{\mathrm{s}}\right) = 0$$

- Intercalated Li conservation

$$\frac{\partial C_{\mathrm{Li}}}{\partial t} + \underline{\nabla} \cdot \left(-D_{\mathrm{Li}} \underline{\nabla} C_{\mathrm{Li}}\right) = 0$$

**In the electrolyte**

- Current conservation

$$\underline{\nabla} \cdot \left[F\left(\underline{J}_{\mathrm{Li}^+} - \underline{J}_{\mathrm{PF}_6^-}\right)\right] = 0$$

- Nernst-Planck fluxes

$$\underline{J}_i = -D_i\left(z_i C_i \frac{F}{RT}\underline{\nabla}\phi_{\mathrm{l}} + \underline{\nabla} C_i\right)$$

- Li+ conservation

$$\frac{\partial C_{\mathrm{Li}^+}}{\partial t} + \underline{\nabla} \cdot \underline{J}_{\mathrm{Li}^+} = 0$$

- Electroneutrality

$$C_{\mathrm{PF}_6^-} = C_{\mathrm{Li}^+}$$

**At the interface**

- Butler-Volmer reaction rate

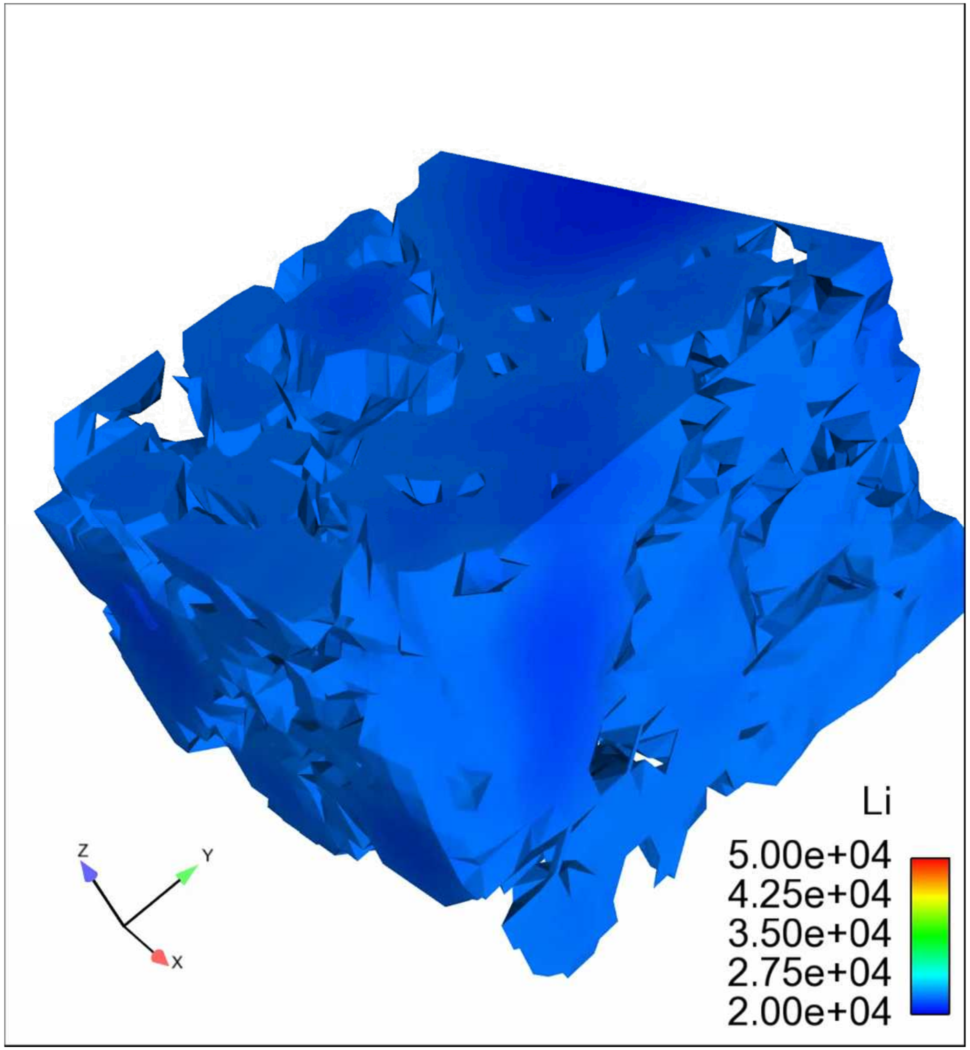
$$\underline{J} \cdot \underline{n} = j_0\left[\exp\left(\frac{\alpha_a F\left(\phi_{\mathrm{s}} - \phi_{\mathrm{l}} - \phi_{\mathrm{eq}}\right)}{RT}\right) - \exp\left(\frac{-\alpha_c F\left(\phi_{\mathrm{s}} - \phi_{\mathrm{l}} - \phi_{\mathrm{eq}}\right)}{RT}\right)\right]$$

- Plus, a few other boundary conditions



Roberts *et al.* (2014) J Electrochemical Society

# Lithium Concentration During Discharge






Roberts *et al.* (2014) J Electrochemical Society

# Conclusions

- New method to analyze ion transport in batteries
  - Molten salt batteries allow quenching during operation
  - Bromine allows visualization of movement and mixing of electrolyte
  - Electron Probe Microanalyzer gives quantitative chemical analysis
- Two mechanisms
  - Fast wicking into dry anode
  - Slower diffusion between layers
- Beginning to probe the impact of electrode microstructure

- Develop a better understanding of battery performance

# Conclusions

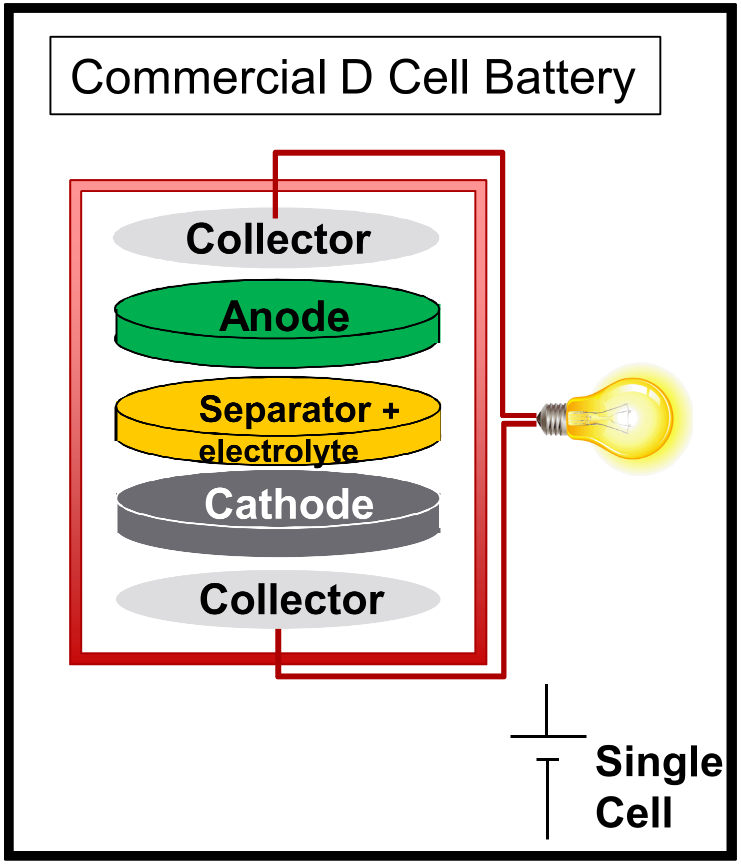
- Department of Energy: Energy Efficiency & Renewable Energy program & Vehicle Technology Office initiatives, EERE Report of Energy Storage Research Needs:

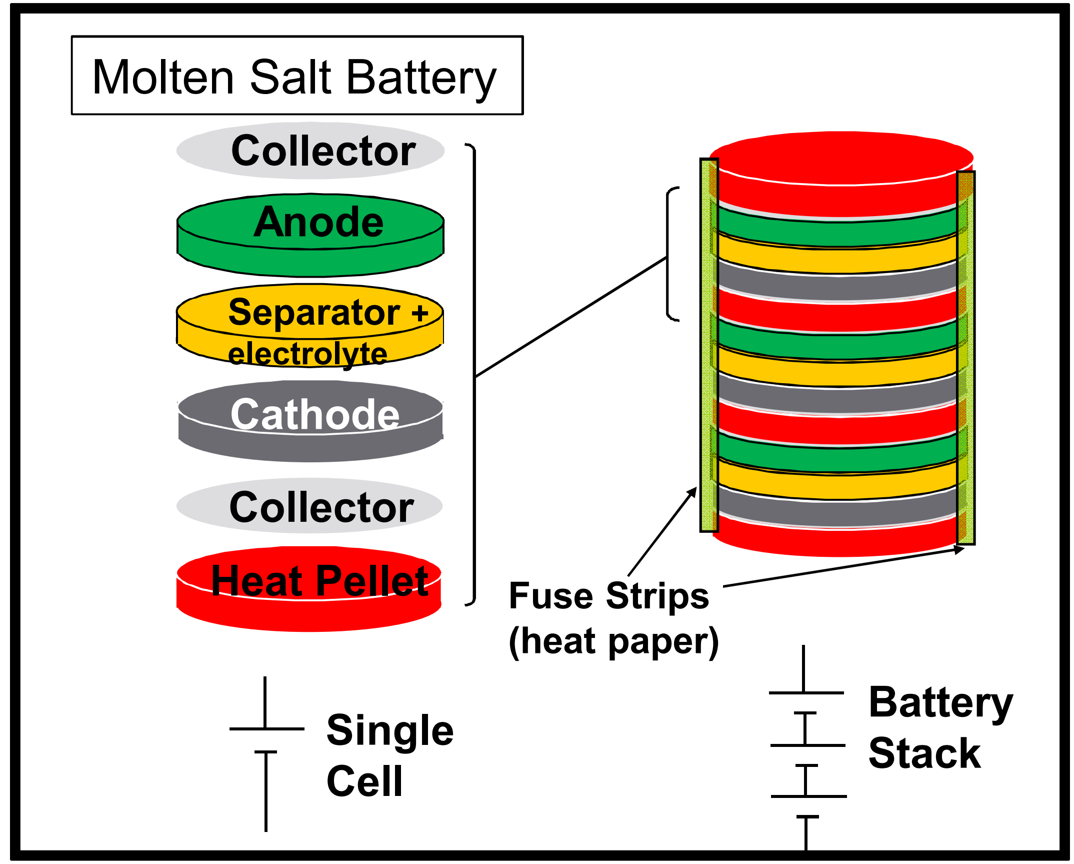
  *"A fundamental understanding of the relationships between structure and function of energy storage materials … can move capacity, power and lifetime improvements to electrical energy storage devices beyond the incremental to the transformational – a result with the potential to dramatically change the energy landscape of the United States."*

Backup Slides

# Molten Salt Battery Basics

- Batteries convert stored chemical energy into electrical energy



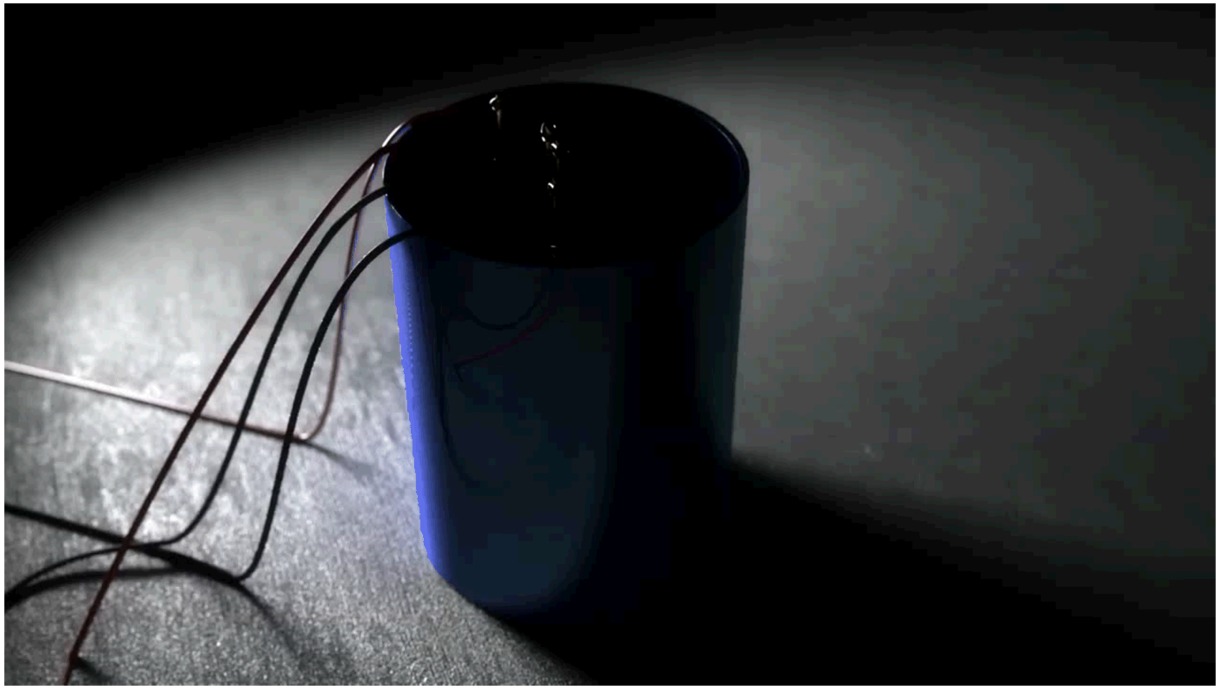




- 2-3 year shelf life
- Low voltage/low current
- Liquid electrolyte dispersed in a separator support material

- 20+ years shelf life
- High voltage/high current
- Solid electrolyte dispersed a separator support material – electrolyte must be first melted in order for battery to work

# Molten Salt Battery Activation

Demonstration of side-fired pyrotechnic activation



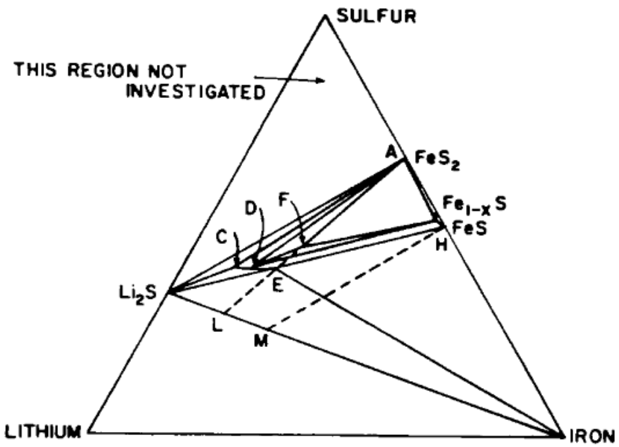
**Requirements**
- Thermal management: Rise time, life time, avoid thermal decomposition
- Electrochemical: Steady voltage through variable current loads
- Mechanical: Stable performance under environments

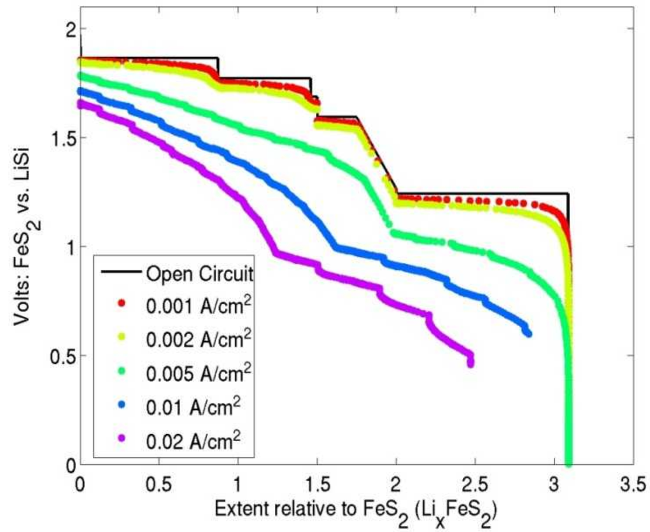
# Electrochemistry Reaction Cascade

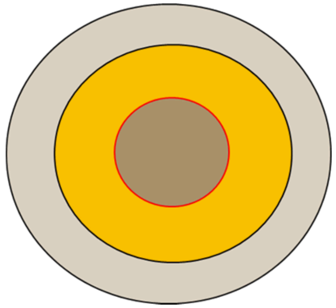
- Reaction pathways, especially for the cathode, are stoichiometrically complicated.

Cathode: $FeS_2 \rightleftarrows Li_3Fe_2S_4 \rightleftarrows Li_{2+x}Fe_{1-x}S_2 + Fe_{1-y}S \rightleftarrows Li_2FeS_2 \rightleftarrows Li_2S + Fe$

Anode: $Li_{13}Si_4 \rightleftarrows Li_7Si_4 \rightleftarrows 4\ Si$



Shrinking Core Model

- Multiple plateaus can react simultaneously
- Diffusional losses with transport

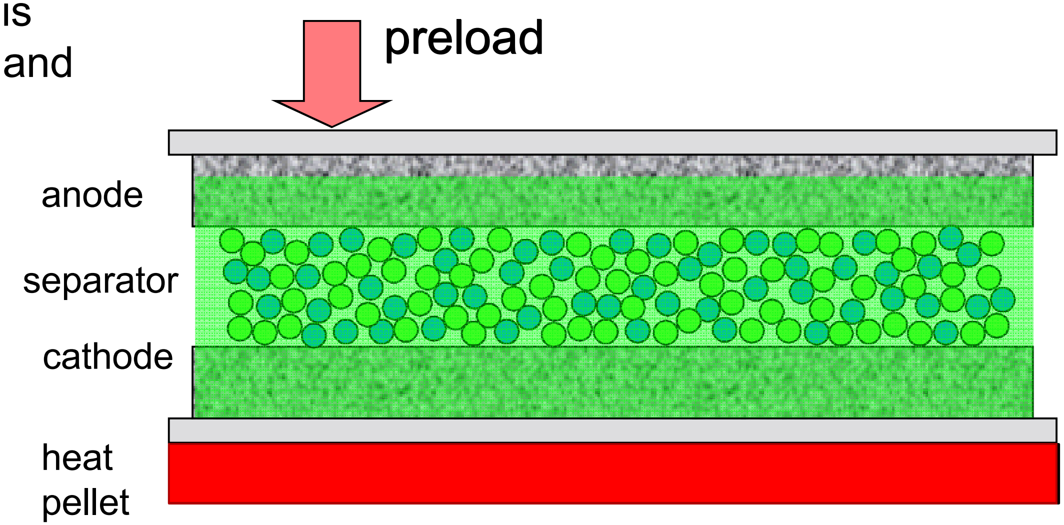
# Molten Salt Battery Activation

- Melting of electrolyte activates a molten salt battery

Porous separator layer is
65wt% solid electrolyte and
35wt% MgO binder

On battery activation, electrolyte melts initiating current

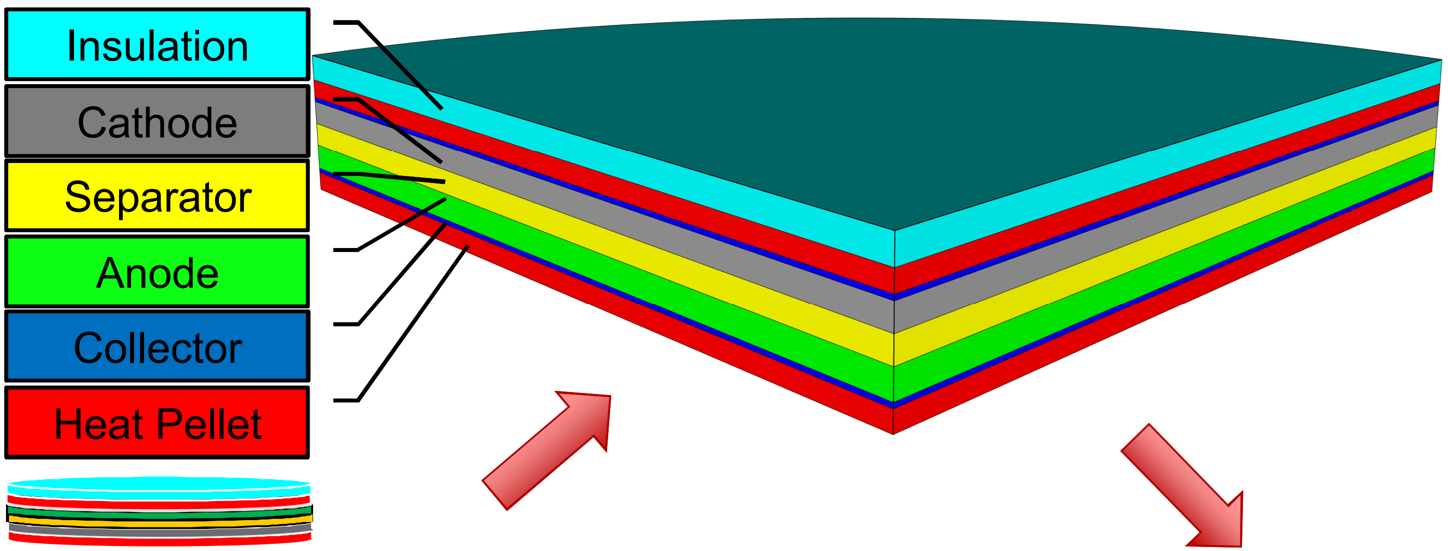
Pellet compacts until remaining force is supported by binder



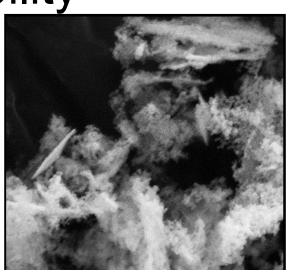

- Freezing the electrolyte halts ion transport
  - By quenching the battery, we can analyze the ion distribution as a function of active time

# Demonstration of Thermo-Mechanics Model

- Pyrotechnic Thermal models, Mechanical Deformation, & Porous Flow of Electrolyte



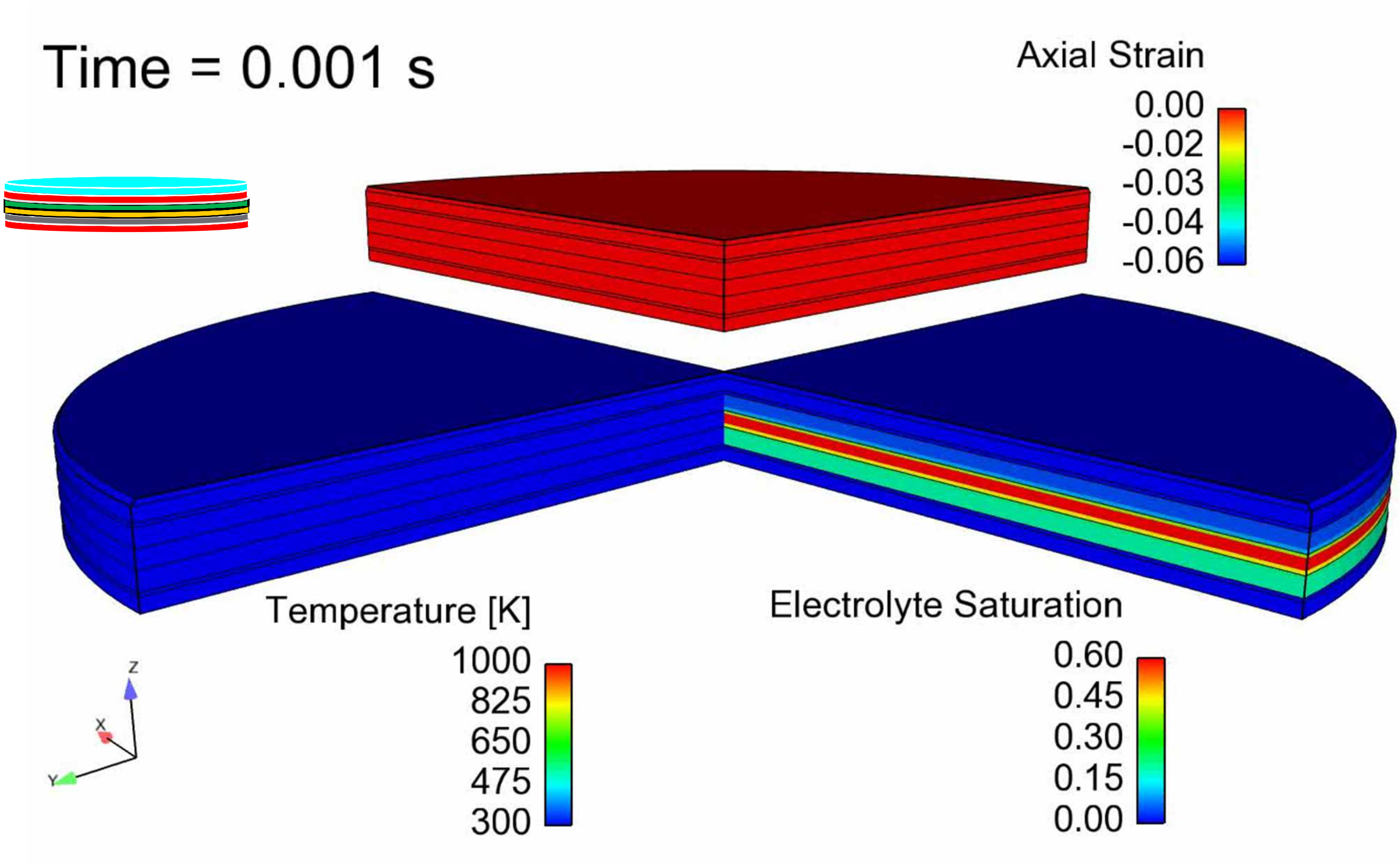

densities, viscosity of molten salt, contact angle, particle size distribution, air permeability



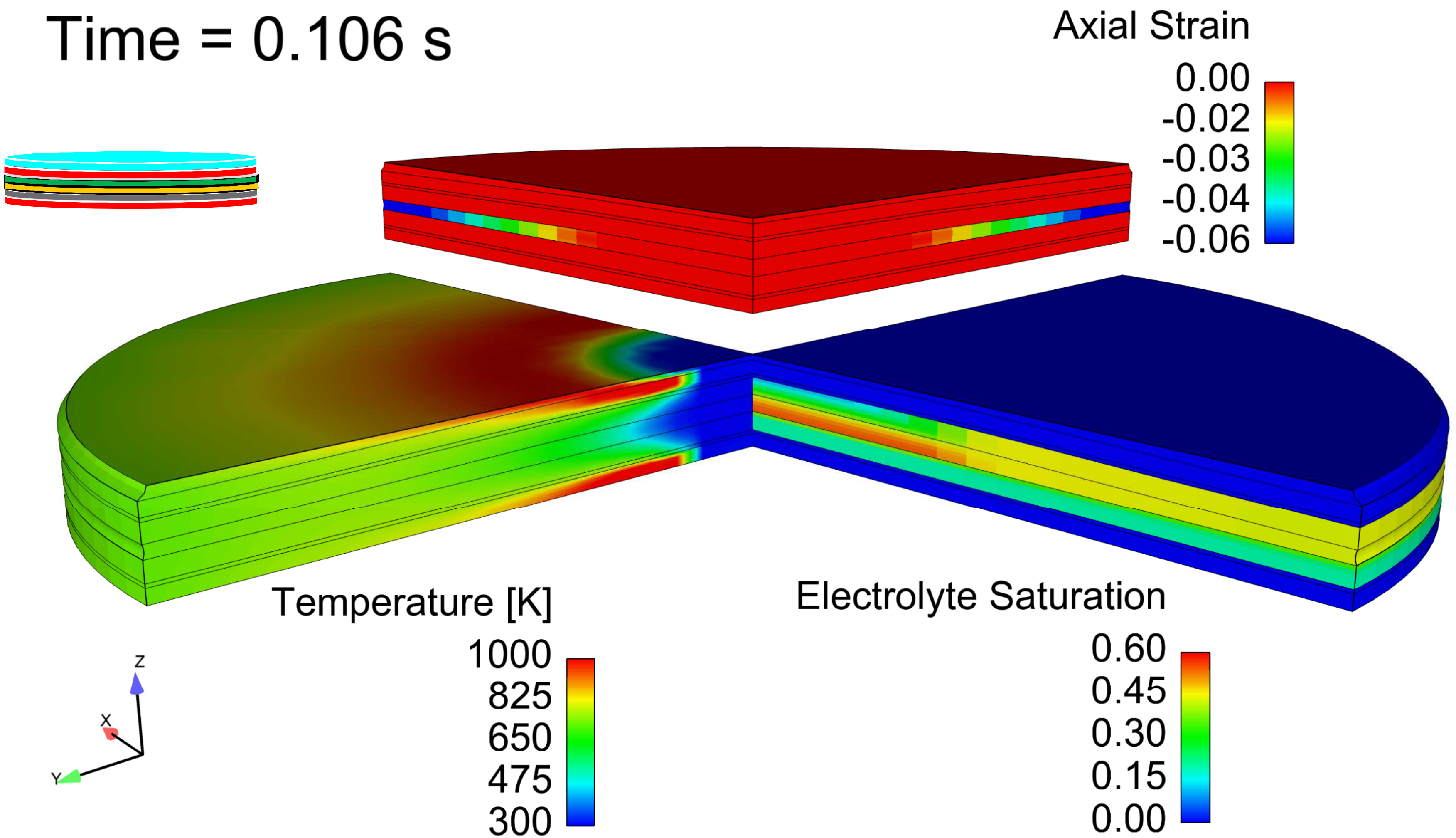
Predict the transient temperature, height, final porosity, electrolyte distribution and internal resistance of the single cell

All are critical to battery performance!

# Coupled physics single cell demonstration

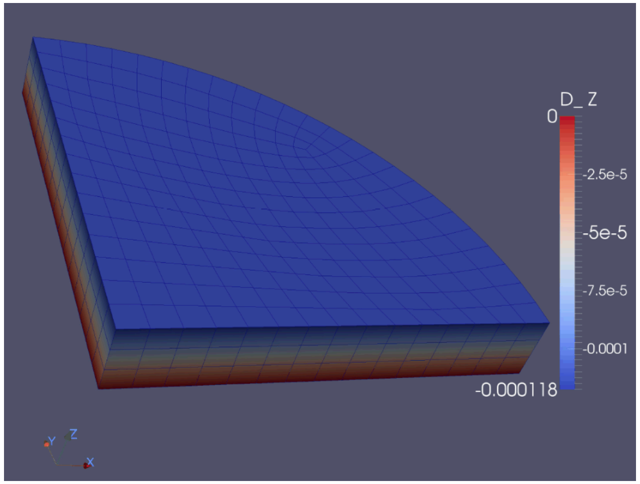


# Coupled physics single cell demonstration

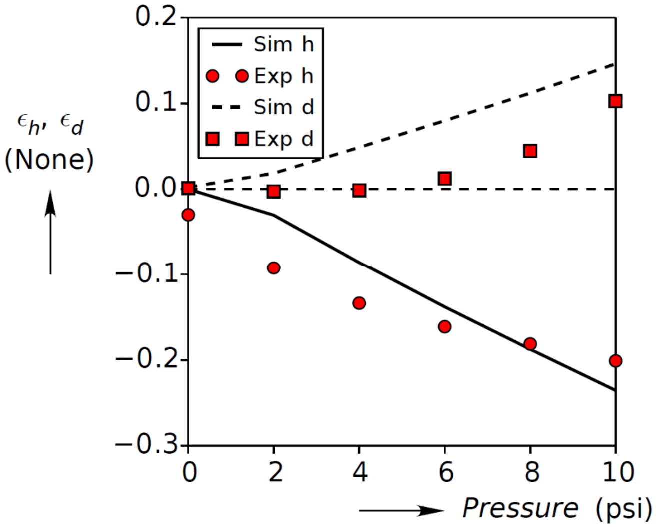


# Calibrating the mechanical properties

- Mechanical model parameters calibrated to experiments of C. Roberts
  - Single separator loaded between two metal platens
  - Constant axial stress applied
  - Temperature ramped up to above melting temperature
  - Axial displacement measured as a function of applied stress
- Simulation includes fully-coupled thermo-poro-mechanical physics




Snapshot of one of the demonstration simulations, showing the axial displacement




Plot of model calibration compared to experimental data

# Two-phase porous flow model

- Electrolyte and gas form two immiscible phases upon melting

$$\frac{\partial(\rho_w \phi S_w)}{\partial t} = \underline{\nabla} \cdot \left( \rho_w \frac{k_{rw}}{\mu_w} \underline{\underline{K}} \cdot (\underline{\nabla} p_w - \rho_w \underline{g}) \right) + Q_w$$

$$\frac{\partial(\rho_n \phi S_n)}{\partial t} = \underline{\nabla} \cdot \left( \rho_n \frac{k_{rn}}{\mu_n} \underline{\underline{K}} \cdot (\underline{\nabla} p_n - \rho_n \underline{g}) \right) + Q_n$$

- Saturation and capillary pressure related to DOFs (wetting and non-wetting pressures) through model relations

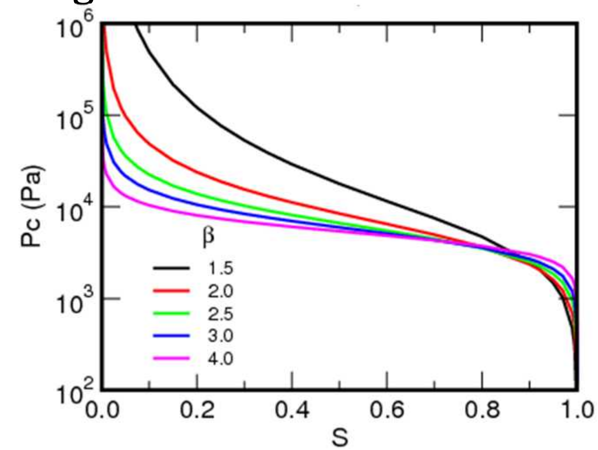
$$S = S(p_c); \quad p_c = p_n - p_w$$

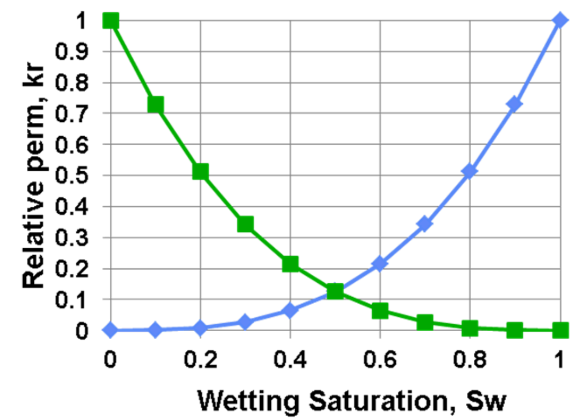
- Coupling to other physics important!
  - Required:

$$\phi = \phi(\underline{d}); \quad \mu_i = \mu_i(T)$$

  - Optional?:

$$S_i = S_i(p_c, \underline{d}); \quad \underline{\underline{K}} = \underline{\underline{K}}(\underline{d})$$



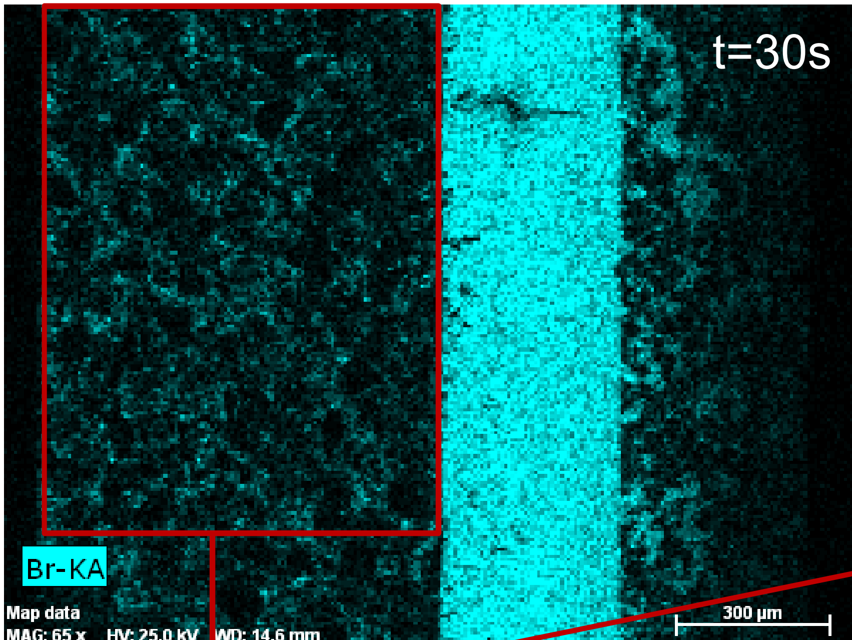

Capillary pressure (top) and relative permeability (bottom) depend on wetting phase saturation and electrode pore structure

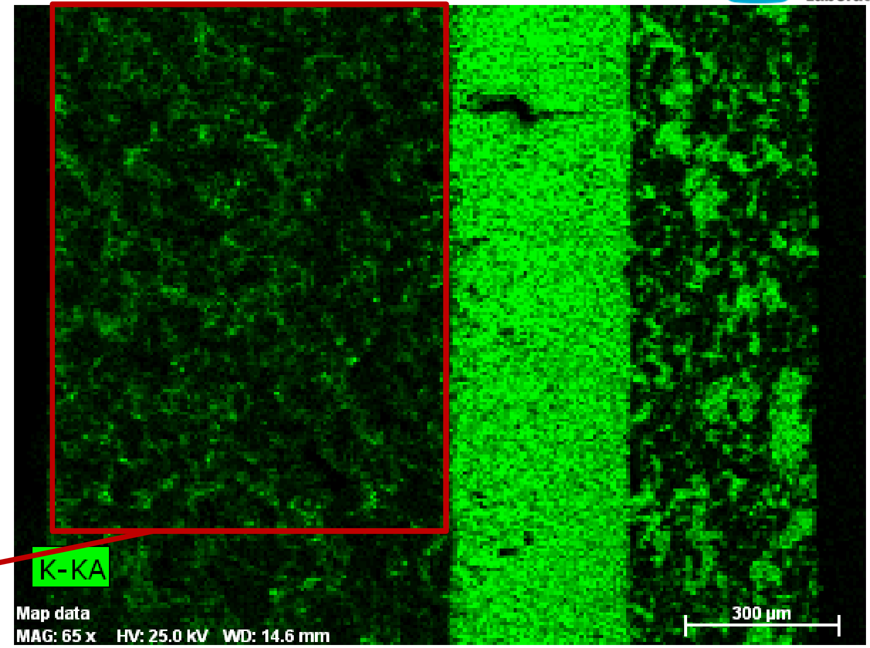
# Estimating porous flow properties

| Material Prop | Separator | Anode | Cathode | Reference & Notes |
|---|---|---|---|---|
| Permeability (mD) | 2000 | 2000 | 0.4 | No reliable data. Separator and anode estimated from Bauer (SNL memo, 2011) experiments on unconsolidated powders; Cathode reduction based on Bromine diffusion study. |
| Porosity | 0.807 | 0.25 | 0.25 | Volumetrics based on manufacturing process specs (S. Roberts, tech. notes) |
| Relative permeability | | | | Cubic functions of phase saturations |
| Capillary pressure | | | | Van Genuchten model $p_c = p_{c0}\left(s^{-1/\lambda} - 1\right)^{1/\beta}$ |
| Entry pressure (kPa) | 15 | 15 | 15 | Estimated from $p_c = \sigma\cos\theta / r$. Surface tension, $\sigma = 0.138$ N/m$^2$ (Mondy, 2012); entry pore radius estimated from PSD in Mondy (2012) & Waldrip SNL presentation; contact angle from Waldrip SNL presentation; Estimated 8 < $Pc_{entry}$ < 16 kPa. |
| Initial electrolyte saturations | 0.695 | 0.05 | 0.2 | Volumetrics based on manufacturing process specs (S. Roberts, tech. notes) |

| Fluid Properties | | Reference & Notes |
|---|---|---|
| **Liquid phase (Electrolyte)** | | |
| Density (kg/m3) | 1650 | Mondy (snl memo 1/2012) |
| Viscosity (Pa-s) | 0.003 | Mondy (snl memo 1/2012; based on Janz et al.; 1975; Leuth et al., SNL memo) |
| **Gas phase (Air at 600 K)** | | |

# Permeability Estimation from Structure



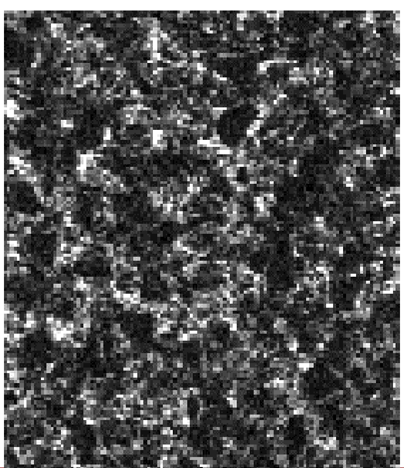



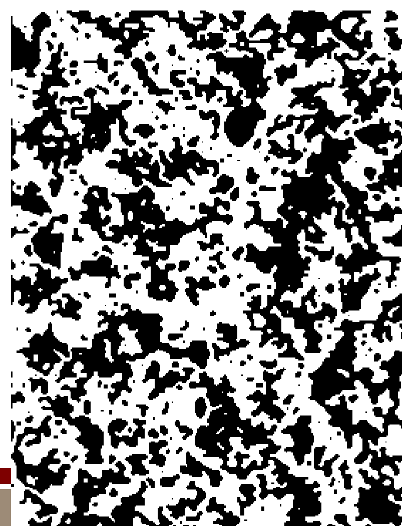

Combine Br & K images

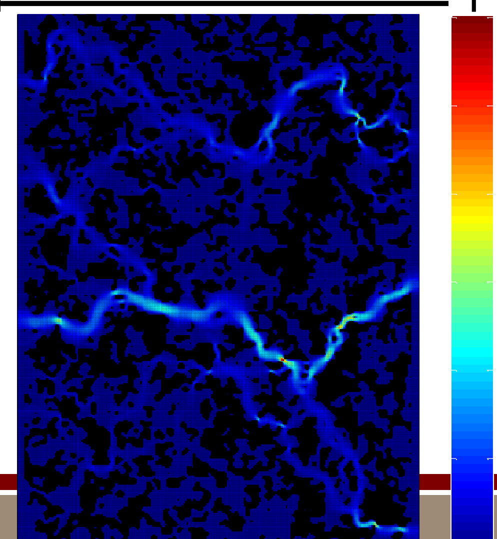
Segmentation (white-void)

Lattice Boltzmann 2D simulation

Flow








High

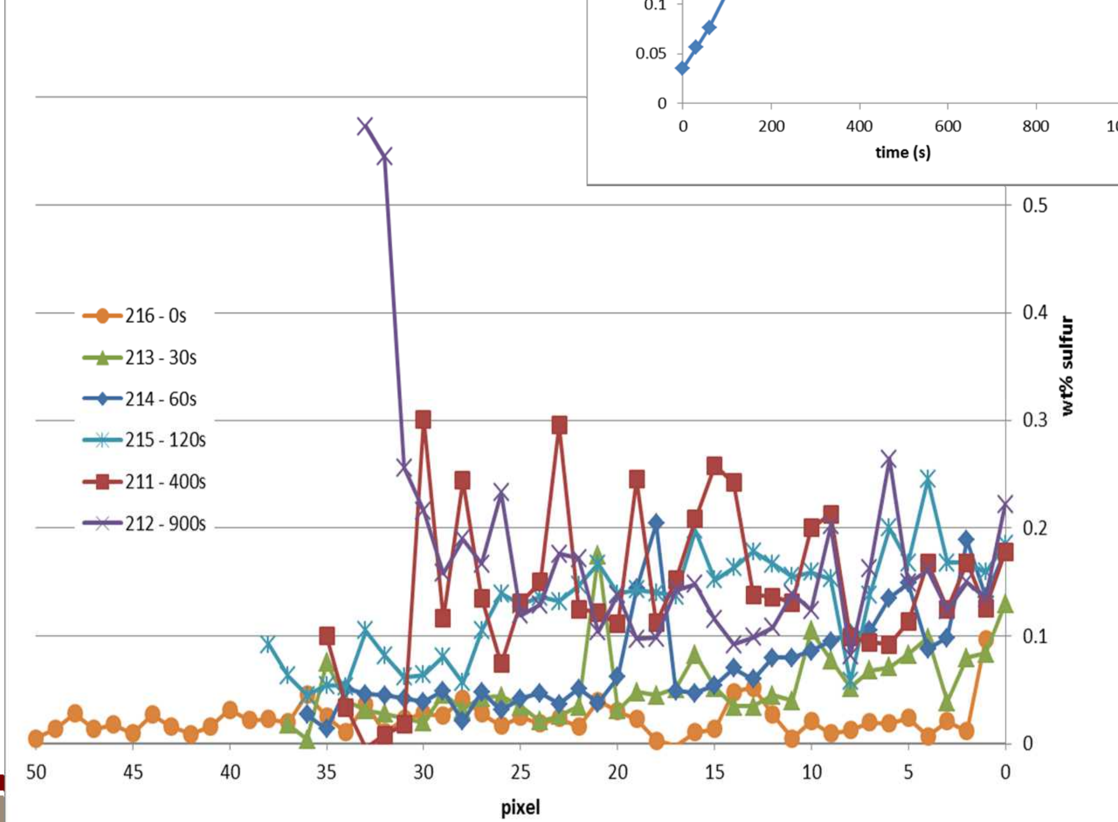
permeability
1.23E-12 m$^2$

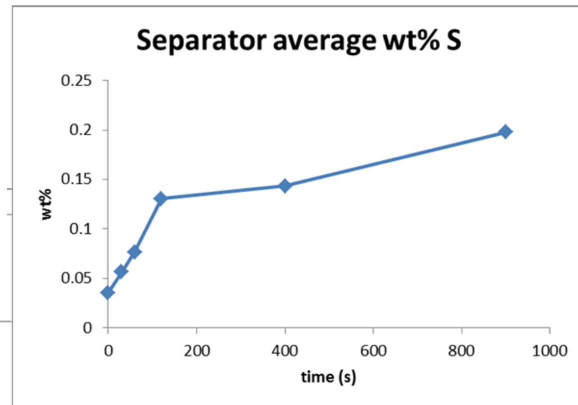
Low

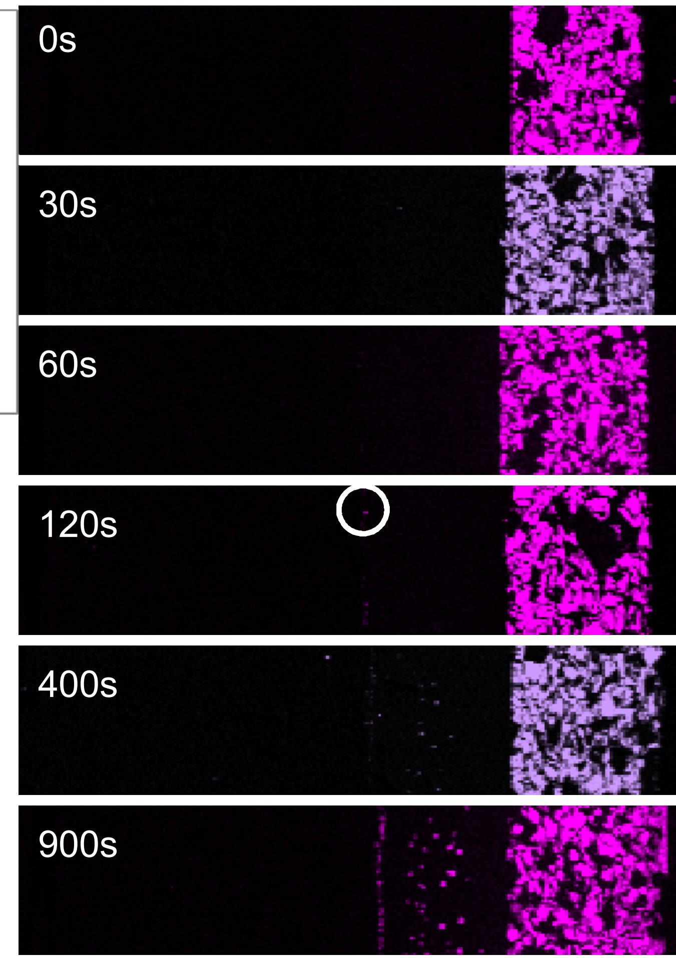
# Sulfur in the separator

- See small but consistent rise in sulfur concentration to ~0.15wt%
- Saturation of separator occurs when $Li_2S$ inclusions begin to appear

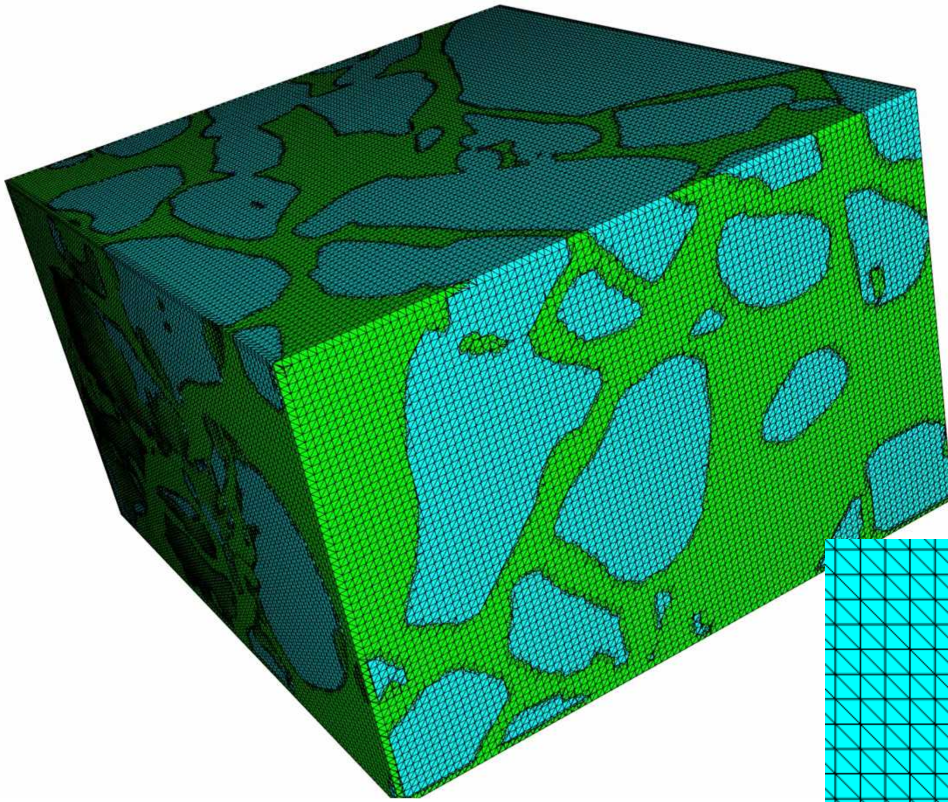
Sulfur concentration in separator from the edge of the cathode

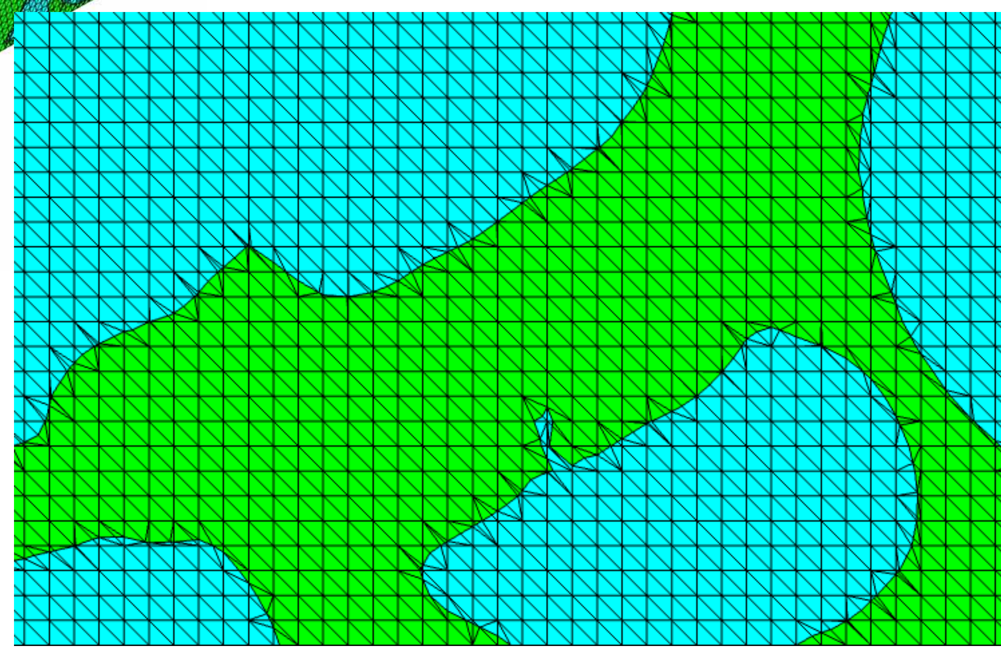


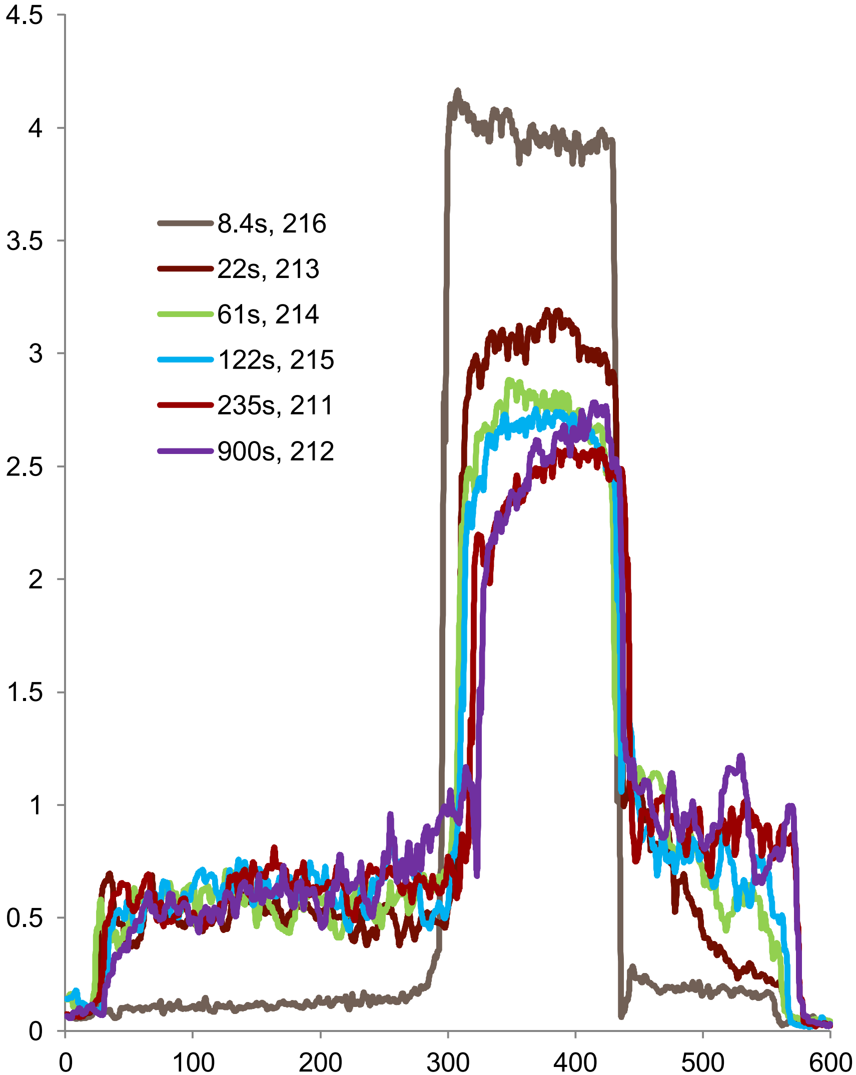



# Representation of microstructure

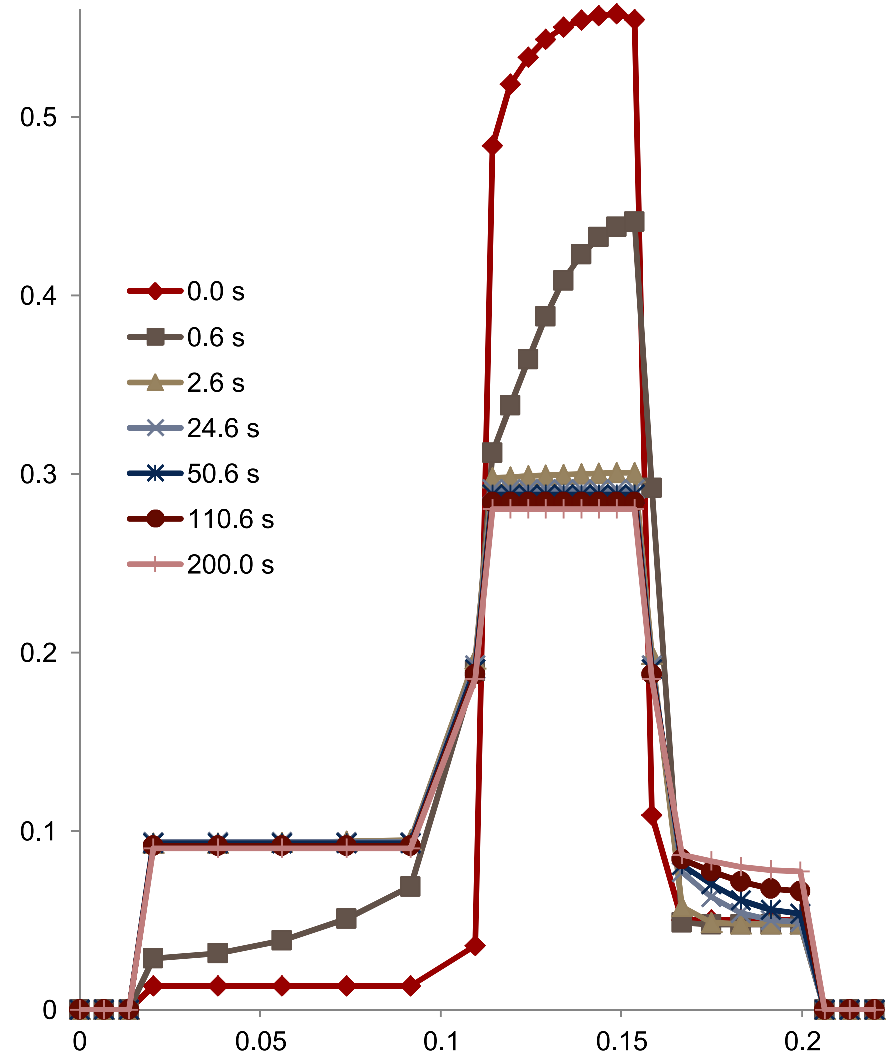




# Qualitative comparison to migration study




Experiments (SEM/EDS)




Simulations