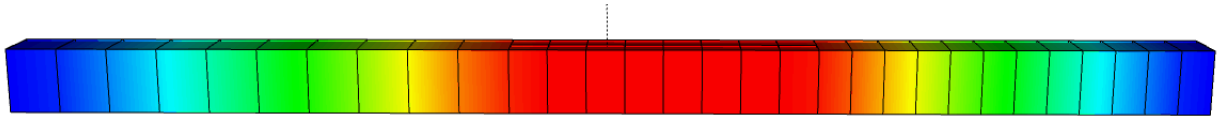
SAND2014-4794C

Model Parameterization for Electrochemical Predictions of $LiFeS_2$ Batteries



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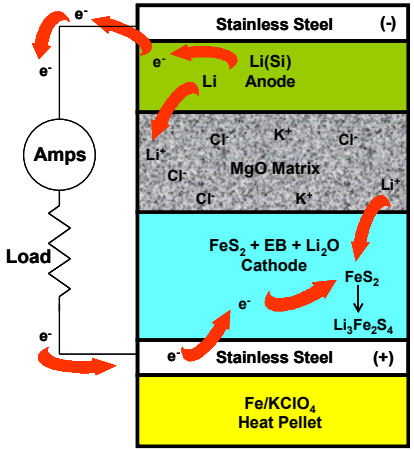
Sandia National Laboratories

Power Sources Conference
June 11, 2014



Schematic of thermal battery electrochemistry

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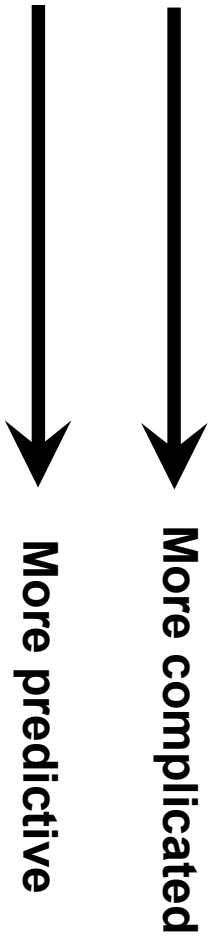
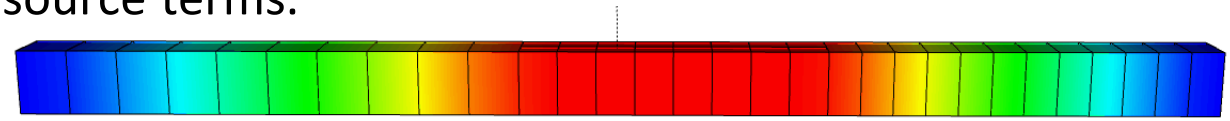
Electrochemical model options

- Purely empirical correlations—lack predictivity
- Highly simplified physics models—narrow predictivity
- Approaches based on fundamental conservation equations:
  - Simplification to analytical solutions.
    - Most educational.
    - Only address a fraction of the relevant issues.
    - Lack generality. Not scalable.
  - Numerical solutions with general properties.
    - Scalable. Arbitrary complexity.
    - Harder to build the general capability.
    - Best to identify properties in simpler environments.

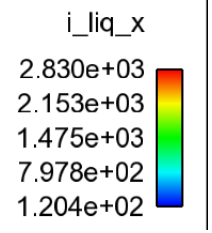


Electrochemical models implemented within Aria

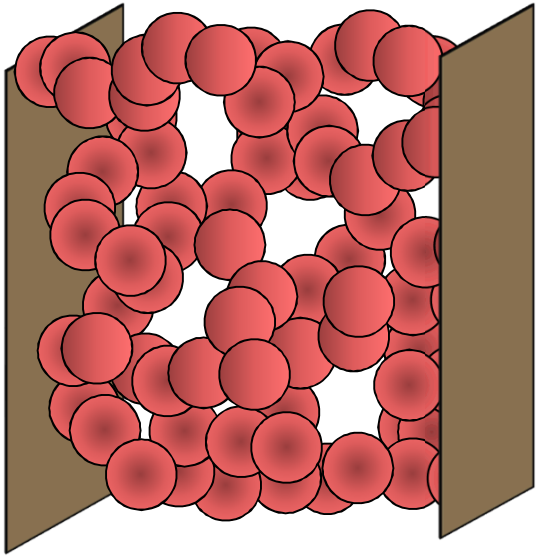
- Implementation in Aria allows 2D/3D, multiphysics capabilities, parallel implementation
- Within Aria, the electrode is discretized
  - Conservation equations are discretized so some losses determined from finite element solution.
  - Other losses are ‘subgrid’ so that they are computed using Electrode object reaction source terms.



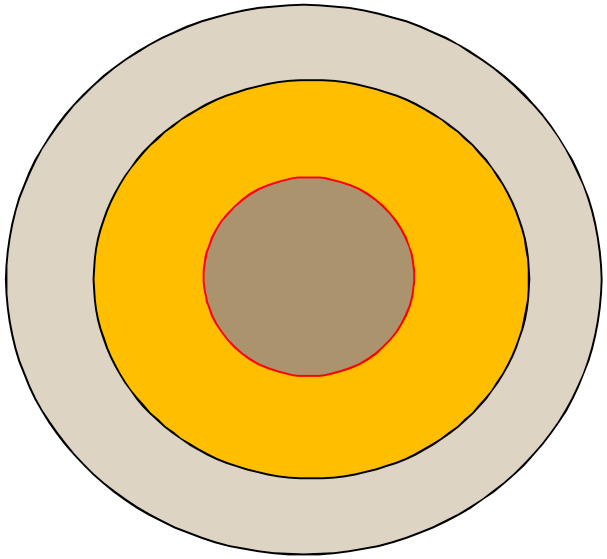
- Variable temperature simulations possible
  - Temperature table
  - Include energy equation (more work needed for source terms)



Electrode subgrid models



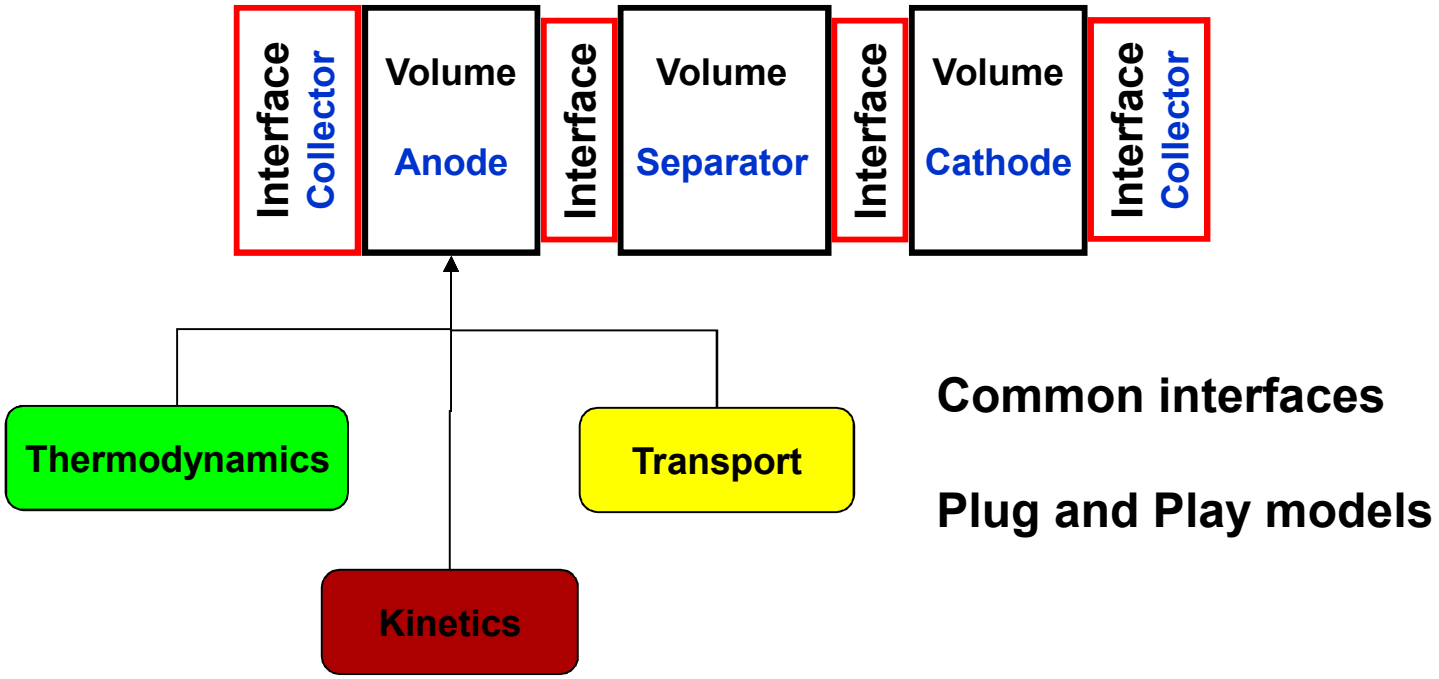
- Many electrode active material particles might exist in an Aria control volume.
- Active material (electrode)-electrolyte interface represented by subgrid Electrode model.



- Within electrode particles, multiple phases exist.
  - Shrinking core model.
- Interphase reaction rates.
- Solid-state diffusion.

Electrode model built on top of Cantera

- Active electrochemical material models built on top of Cantera.
- **Cantera**: open source framework for thermodynamics, transport, kinetics, etc.
  - Modularity allows specification of separate physics of each region.
  - Common interfaces: Exchange physics models to predict new material/configuration types.



A design consideration: Identifying potential losses limiting mission performance

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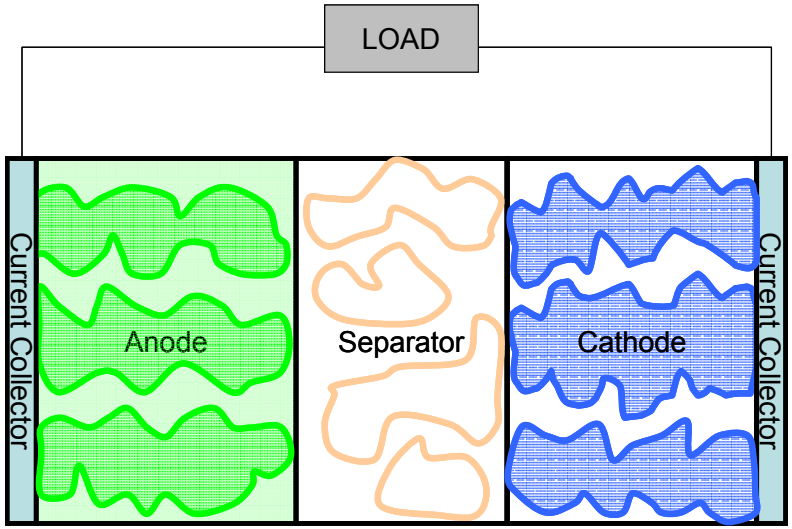
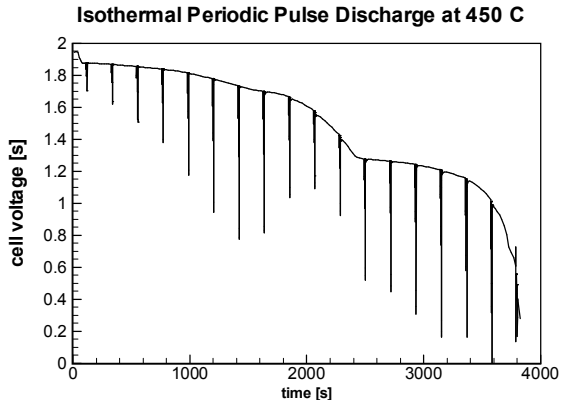
- Electrochemical performance is based on
  - Thermodynamic potential.
  - Potential losses (function of current).
    - Ohmic losses (solid & electrolyte).
    - Diffusive losses (solid & electrolyte).
    - Reaction overpotential losses.



- Objective is prediction of potential as a function of load and depth of discharge.



Thermodynamics: LiSi

Reaction

- Single species phases

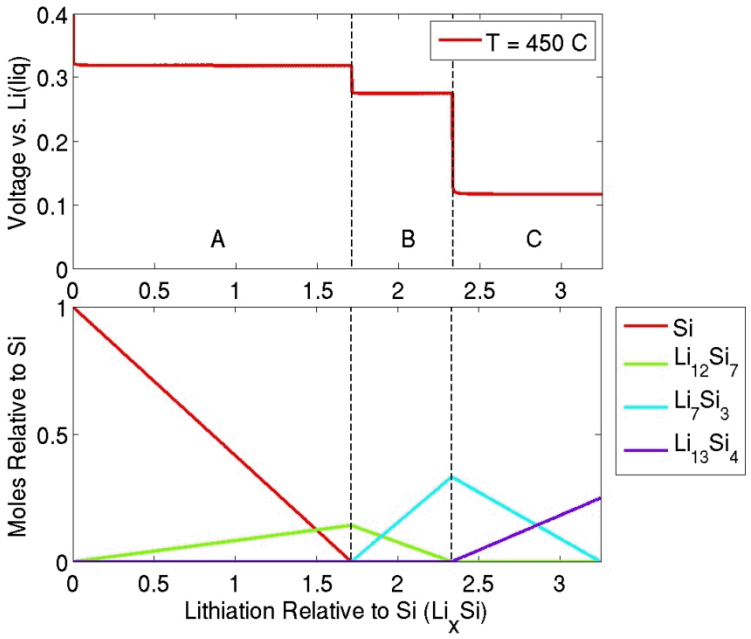
$$Si + Li(liq) \rightarrow Li_{12}Si_7$$

$$Li_{12}Si_7 + Li(liq) \rightarrow Li_7Si_3$$

$$Li_7Si_3 + Li(liq) \rightarrow Li_{13}Si_4$$

  - Free energies determined algebraically using voltage

Discharge Regimes

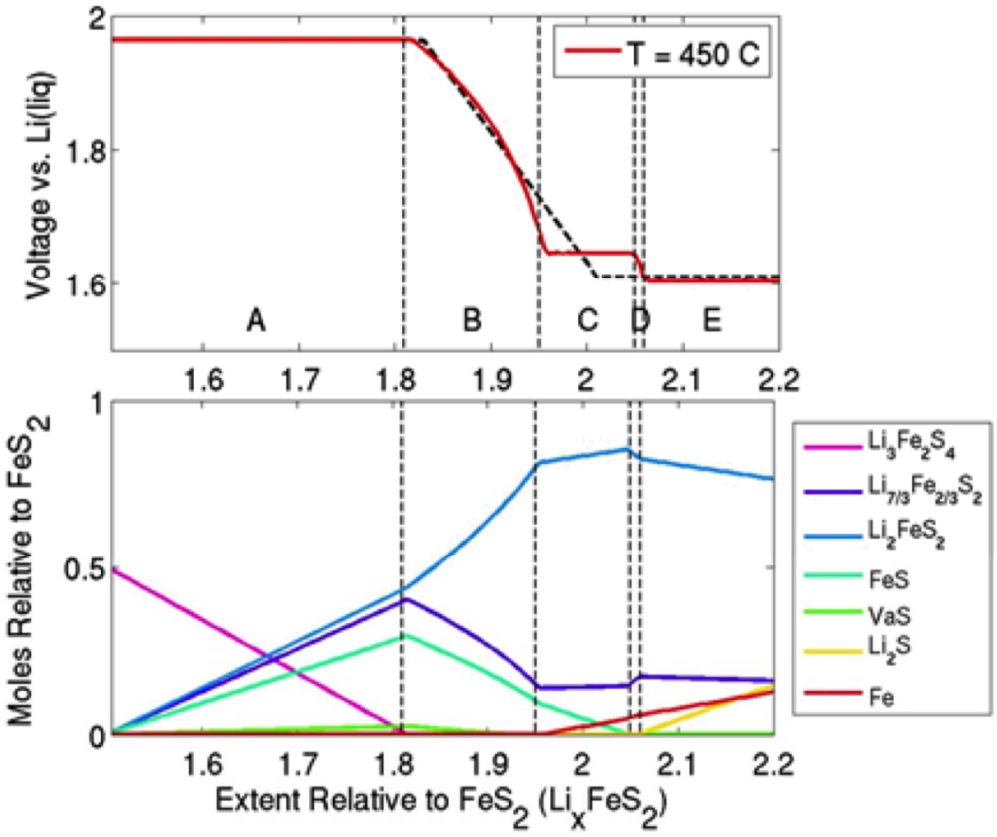


Li_xFeS_2 Thermodynamic Models

Four plateaus

$$FeS_2 \rightleftharpoons Li_3Fe_2S_4 \rightleftharpoons Li_{2+x}Fe_{1-x}S_2 + Fe_{1-x}S \rightleftharpoons Li_2FeS_2 \rightleftharpoons Li_2S + Fe$$

- Multi-plateau model has 'correct' thermodynamic treatment
  - Margules model for solutions: $Li_{2+y}Fe_{1-y}S_2$ and $Fe_{1-x}S$
- Newman Model: linear voltage fit over four regions
  - (No REAL thermodynamic phases)



Interphase kinetics

- Arrhenius rate coefficients

$$q_a = A_a \exp\left(-\frac{E_a}{RT}\right)\tilde{a}_a\tilde{a}_b \exp\left[\frac{\alpha F\eta}{RT}\right] \qquad \eta = \Phi_a - \Phi_c - U$$

$$q_c = A_c \exp\left(-\frac{E_c}{RT}\right)\tilde{a}_c \exp\left[-\frac{(1-\alpha)F\eta}{RT}\right]$$

- Exchange current density formulation

$$\omega_f - \omega_r = i_0\left\{\exp\left[-(1-\alpha)\frac{F\eta}{RT}\right] - \exp\left[\alpha\frac{F\eta}{RT}\right]\right\}$$

$$i_0 = k_f \exp\left[(1-\alpha)\frac{\Delta G^0}{RT}\right]\left(a_{\mathrm{Li}^+}a_{\mathrm{e}^-}\right)^{\alpha}\left(a_{\mathrm{Li}}\right)^{1-\alpha} = \left(k_f a_{\mathrm{Li}^+}a_{\mathrm{e}^-}\right)^{\alpha}\left(k_b a_{\mathrm{Li}}\right)^{1-\alpha}$$

$$k_f = A^0 \exp\left(\frac{\Delta S_f^{\ddagger}}{R}\right)\exp\left(-\frac{\Delta H_f^{\ddagger}}{RT}\right), \quad k_b = A^0 \exp\left(\frac{\Delta S_b^{\ddagger}}{R}\right)\exp\left(-\frac{\Delta H_b^{\ddagger}}{RT}\right)$$

Electrolyte transport

- Stefan-Maxwell transport for molten LiKCl salts: $X_k \nabla \mu_k = \tau^2 RT \sum_j \frac{X_k X_j}{D_{kj}} \left(\mathbf{V}_j - \mathbf{V}_k \right)$
  - Margules treatment of salt thermodynamics.

- Stefan-Maxwell interaction parameters determined from
  - Salt conductivity: / .
  - Self diffusivity, *D.*
  - Internal cation mobilities, *ε.*

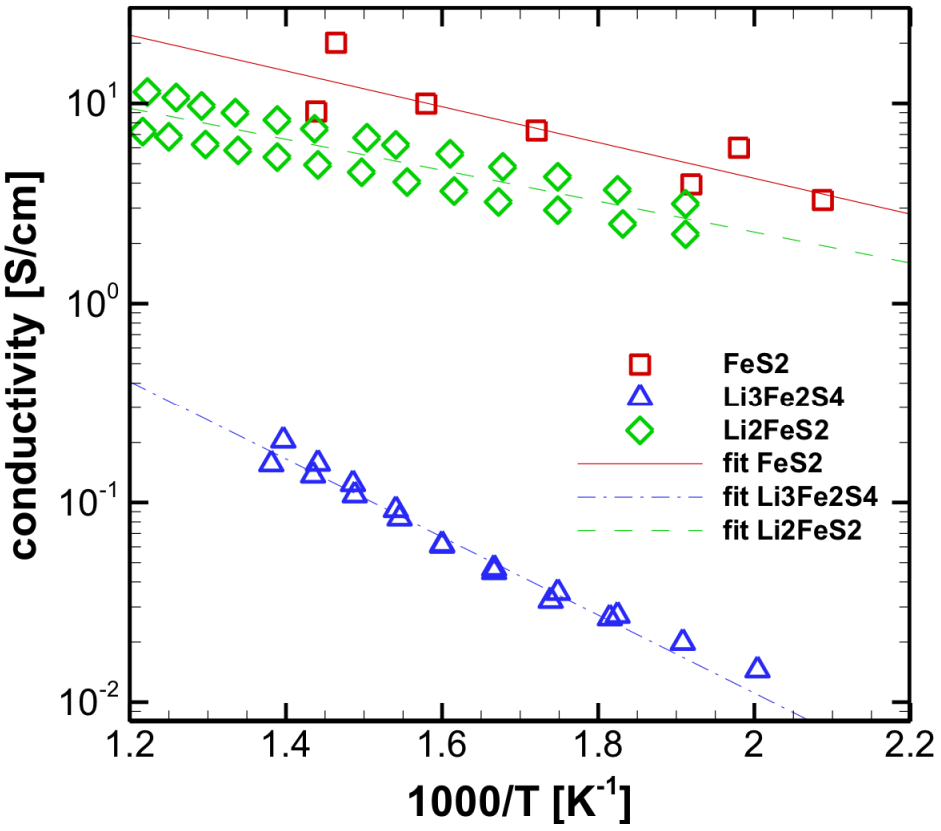
$$\frac{1}{D_{\mathrm{Li^+K^+}}} = \frac{2\left(1-\varepsilon X_{\mathrm{LiCl}}\right)\left(1+\varepsilon X_{\mathrm{KCl}}\right)}{\mathcal{D}} - \frac{2C_T F^2}{\kappa RT}$$

$$\frac{1}{D_{\mathrm{Li^+Cl^-}}} = \frac{-2\varepsilon X_{\mathrm{KCl}}\left(1-\varepsilon X_{\mathrm{LiCl}}\right)}{\mathcal{D}} + \frac{2C_T F^2}{\kappa RT}$$

$$\frac{1}{D_{\mathrm{K^+Cl^-}}} = \frac{2\varepsilon X_{\mathrm{LiCl}}\left(1+\varepsilon X_{\mathrm{KCl}}\right)}{\mathcal{D}} + \frac{2C_T F^2}{\kappa RT}$$

Solid-phase conduction

- Metal conduction in anode is probably fast
- Cathode conductivities are on par with electrolyte (1-2 S/cm).
  - Likely measurable effect on potential drop.
  - Variable, composition-dependent conductivities not yet implemented.



Electrode models

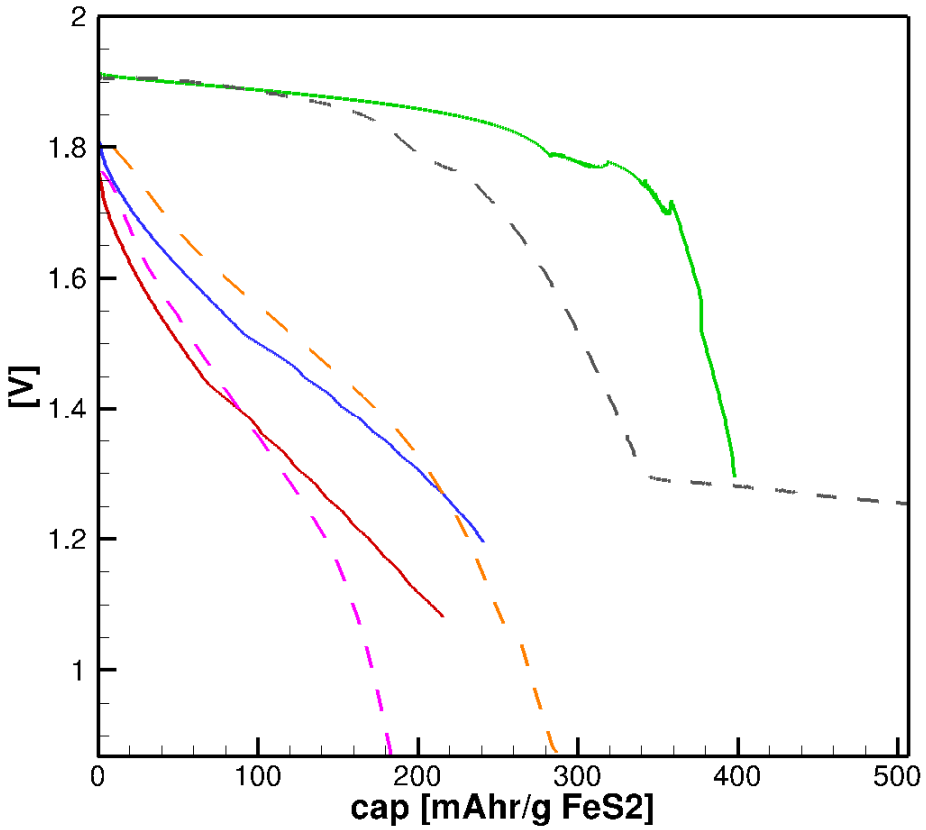
- Infinite capacity:
  - No change in electrode composition with discharge.
  - Ohmic and initial overpotential losses plus electrolyte concentration overpotential losses.
- Multi-plateau:
  - Each plateau has finite capacity.
  - Multiple plateaus can react simultaneously.
  - Reacting surface area assumed to vary with internal surface area.
  - Solid state diffusion not currently accessible through GUI.
- Newman Reaction Extent (FeS_2 cathode only)
  - Voltage fit based on Bernardi and Newman evaluation of Argonne data. Not 'real' thermodynamics.
  - Solid state diffusion models implemented.
  - More robust than multi-plateau for FeS_2 cath
- Finite capacity
  - Like multi-plateau but with only first phase change per electrode.

Recommended for anode

Recommended for cathode

Demonstration case

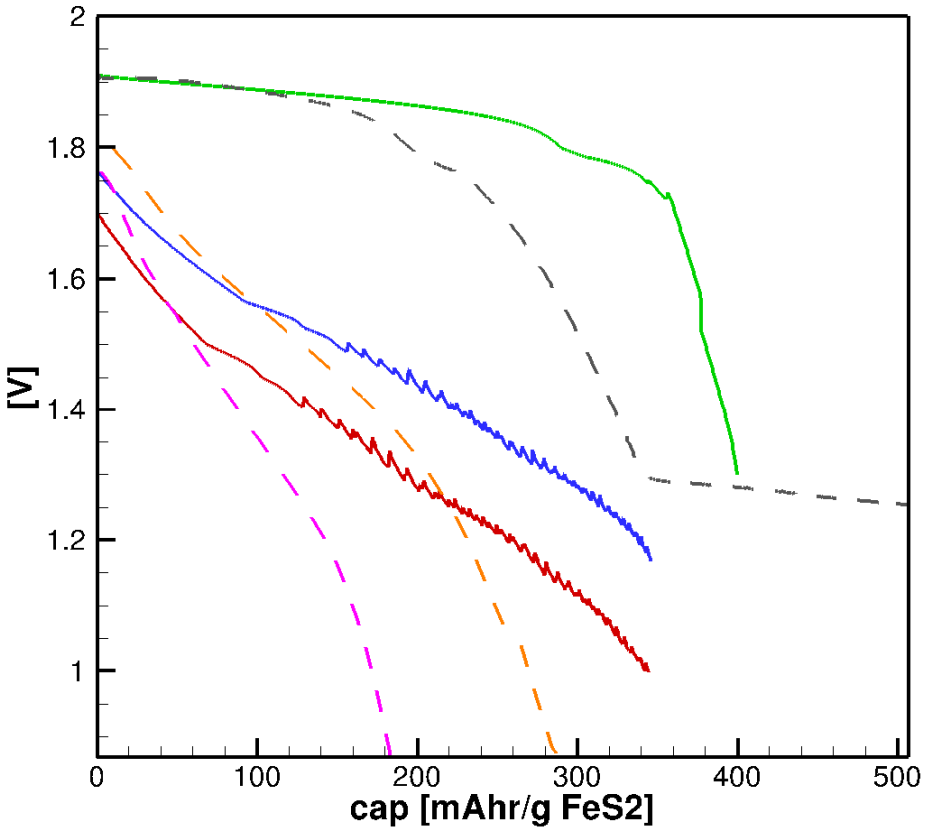
- Isothermal (500 C), constant current single-cell measurements.
- Multiplateau anode and Newman reaction extent cathode models.
- Looking here at base load and two high loads.
- Measurements: dashed line
- Predictions: solid line



Inner surface rate limiting on cathode

Demonstration case

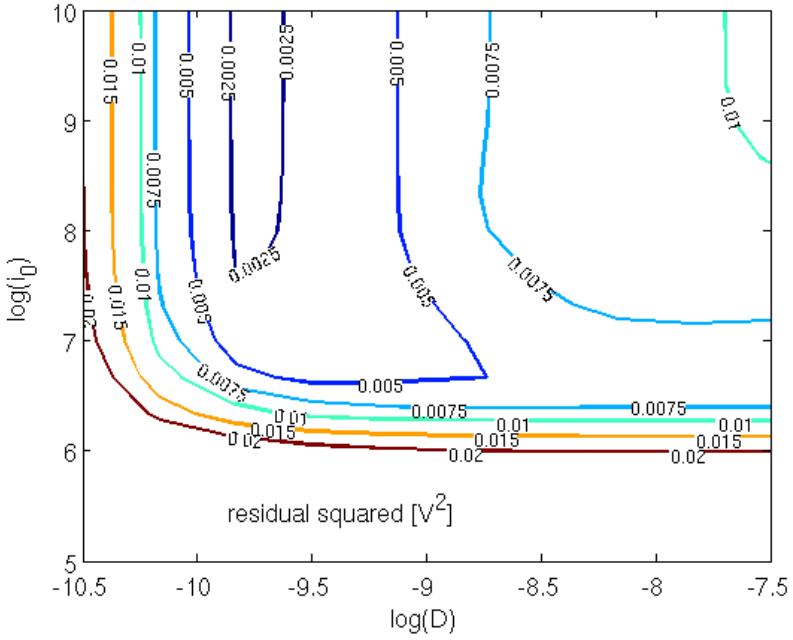
- Isothermal (500 C), constant current single-cell measurements.
- Multiplateau anode and Newman reaction extent cathode models.
- Looking here at base load and two high loads
- Measurements: dashed line
- Predictions: solid line

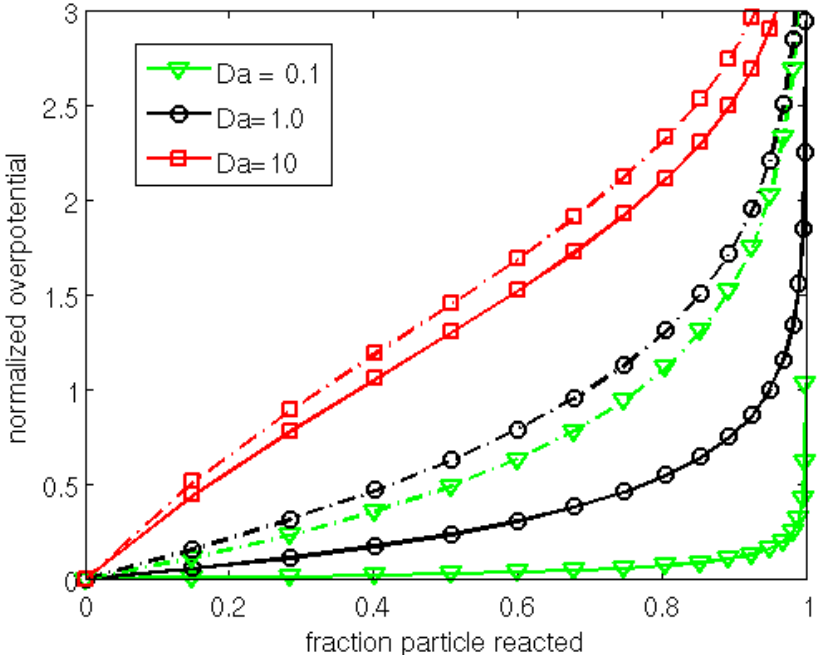


Outer surface rate limiting on cathode

Calibrating interphase reaction rates and solid state diffusion coefficients

- Interphase reaction rates and solid state diffusion coefficients are basically unknown.
- Use least squares calibration to get best fit, but there is long curved valley in state space that gives similar fits.

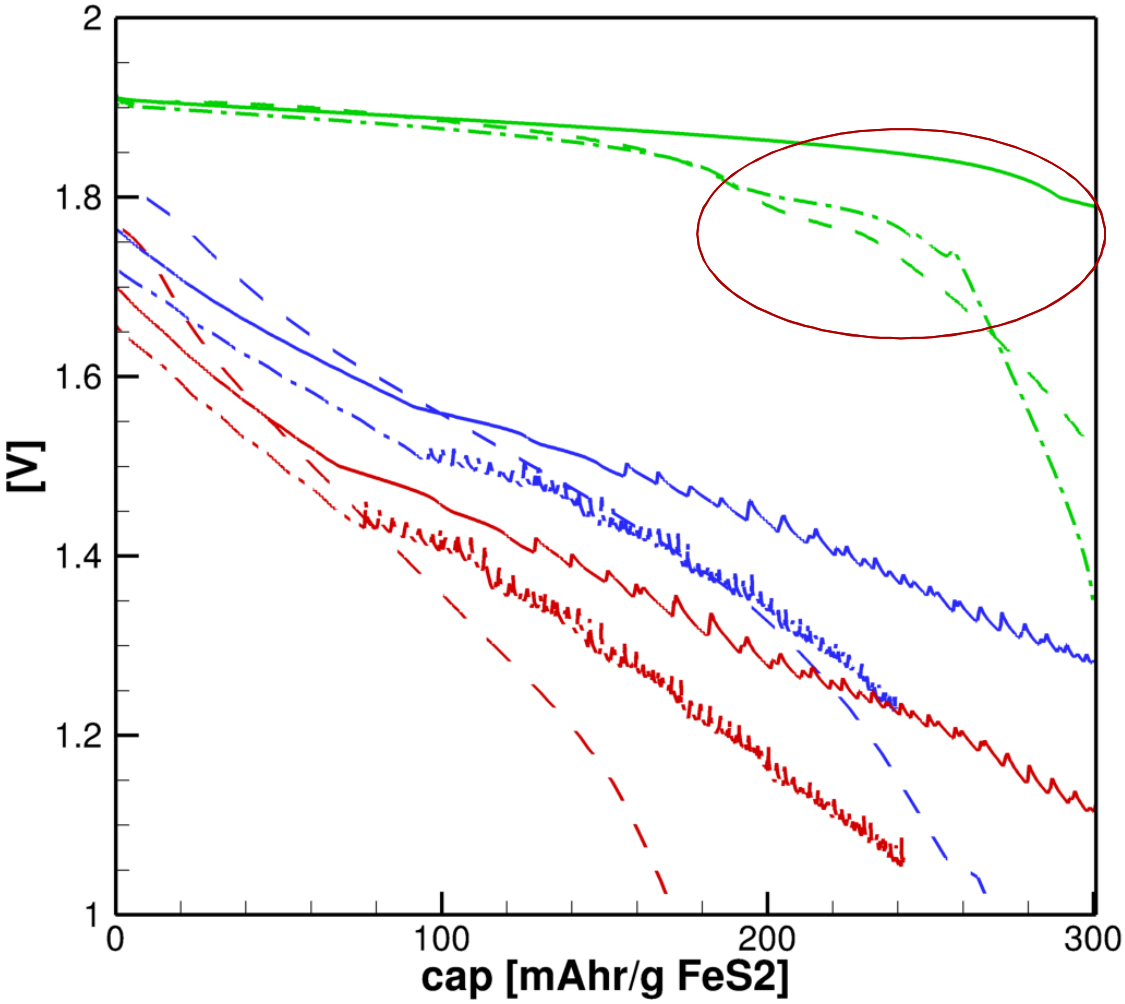




Predictions with self-discharge

- Self discharge is known to occur at elevated temperatures.
- Self discharge simulated by converting reactive materials to products.

- Dashed lines: measurements.
- Solid lines: no self discharge.
- Dash-dot: mimic self discharge (0.5 mole e^- per FeS_2).

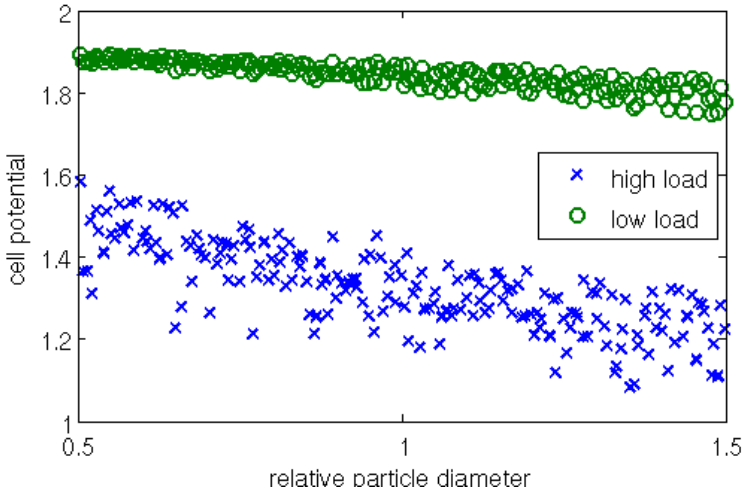


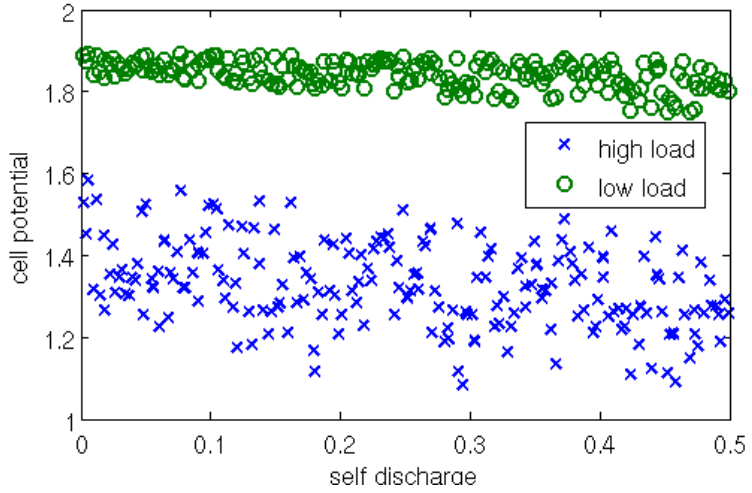
Outer surface rate limiting on cathode

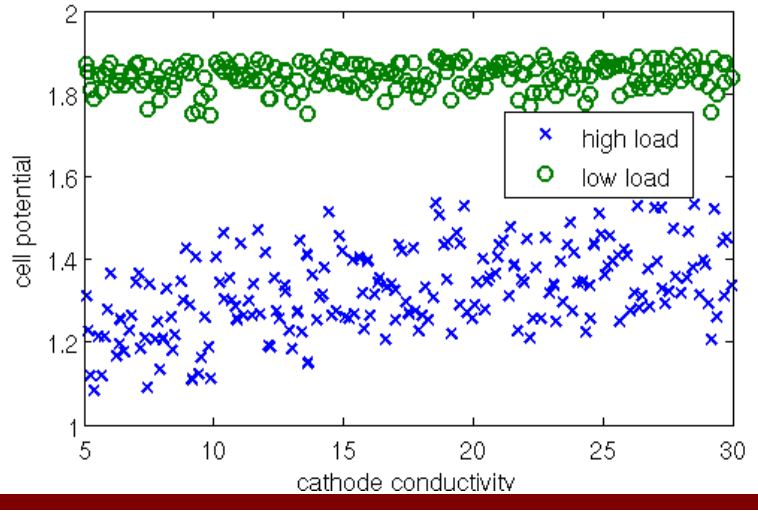
Quantifying prediction uncertainty through parameter uncertainties

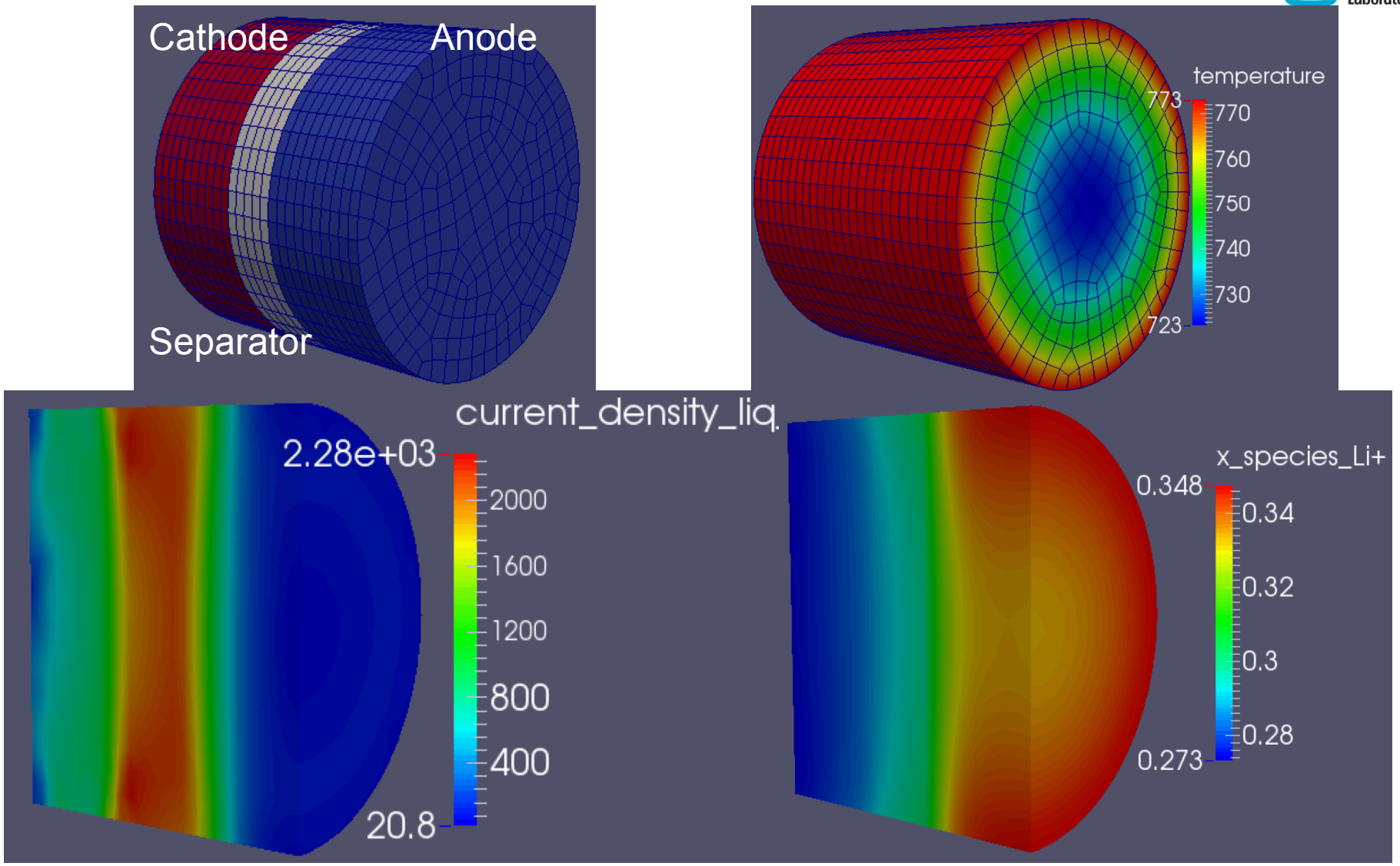
- Uncertain parameter values lead to prediction uncertainties.
- Quantify uncertainties by Latin-hypercube sampling.
- Correlation coefficients parameters and predictions

	Side reaction (e^- loss)	*Cathode particle diameter*	*Cathode conductivity*
Low load	-0.46	-0.84	0.11
High load	-0.38	-0.76	0.49

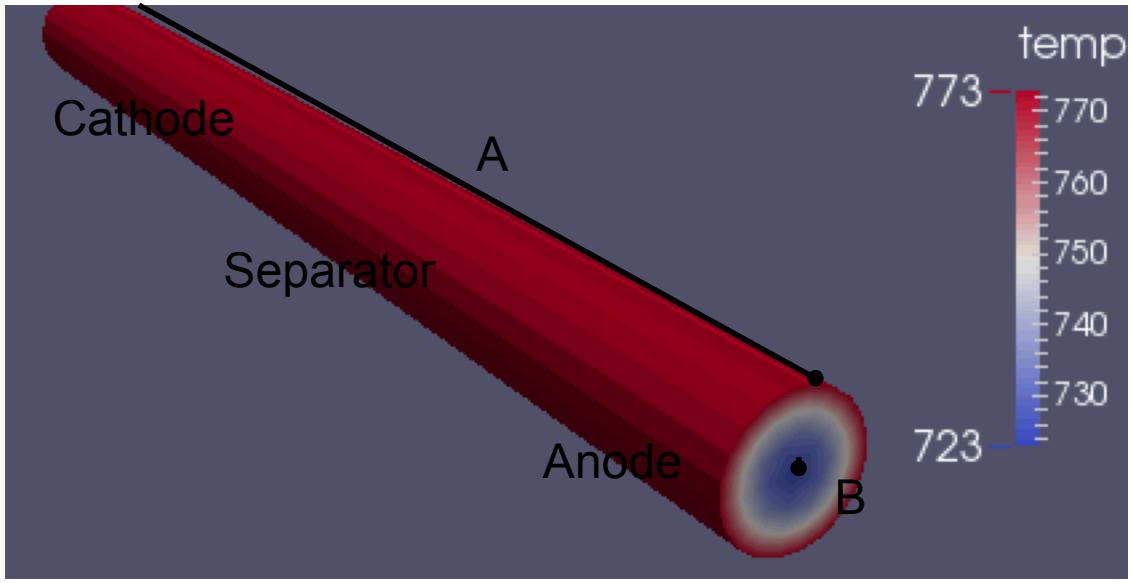


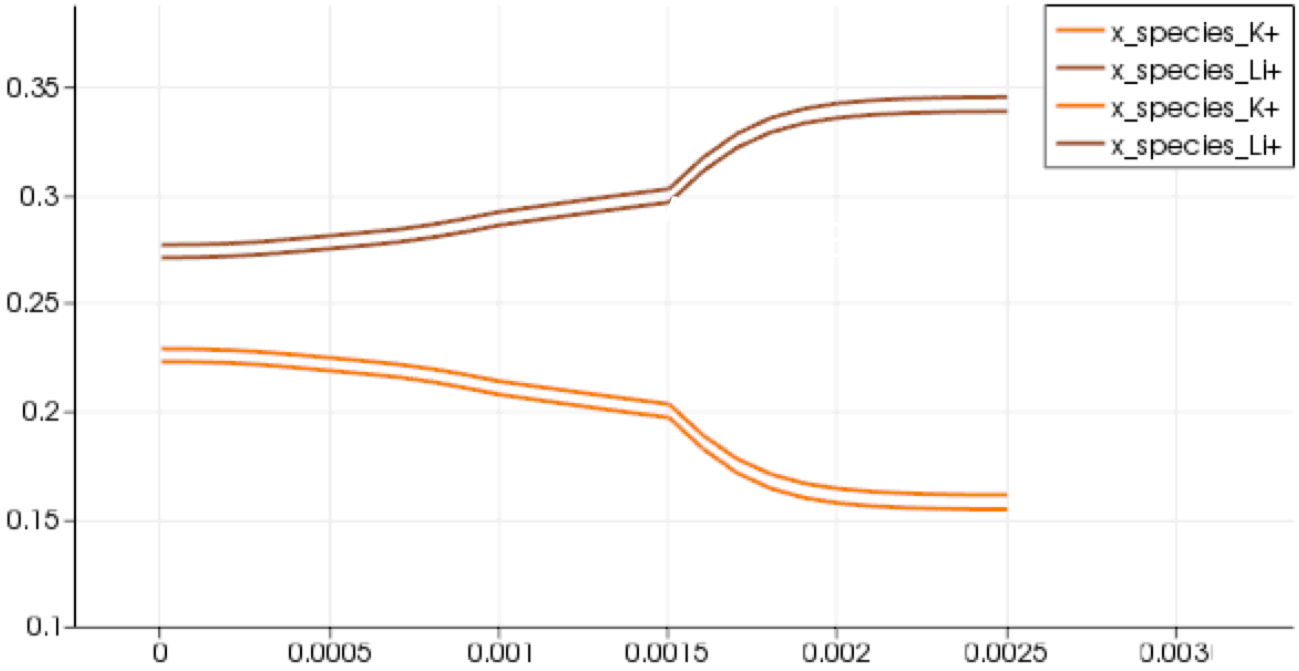






Simulations by Adrian Kopacz, Sandia National Laboratories





Simulations by Adrian Kopacz, Sandia National Laboratories

Summary

- Electrochemical model formulated from basic conservation equations.
  - Numerical approach allows incorporation of additional physics.
  - Numerous chemistry/physics sub-models usually validated in simpler configurations.
  - Simulations provide insight into hard-to-observe phenomena.
- Thermodynamic potential, transport and kinetic potential losses integrated to give predictions for LiSi/LiKCl/FeS_2 system.
- Predictions reasonable except for difficulties matching diffusive losses simultaneous with self-discharge losses.
- Some issues remain with possible added physics (self discharge, robust multi-plateau cathode, better treatment of diffusion, heat source terms)

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Thank you

Questions?

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