Modeling Li^+ Ion Battery Electrode Properties

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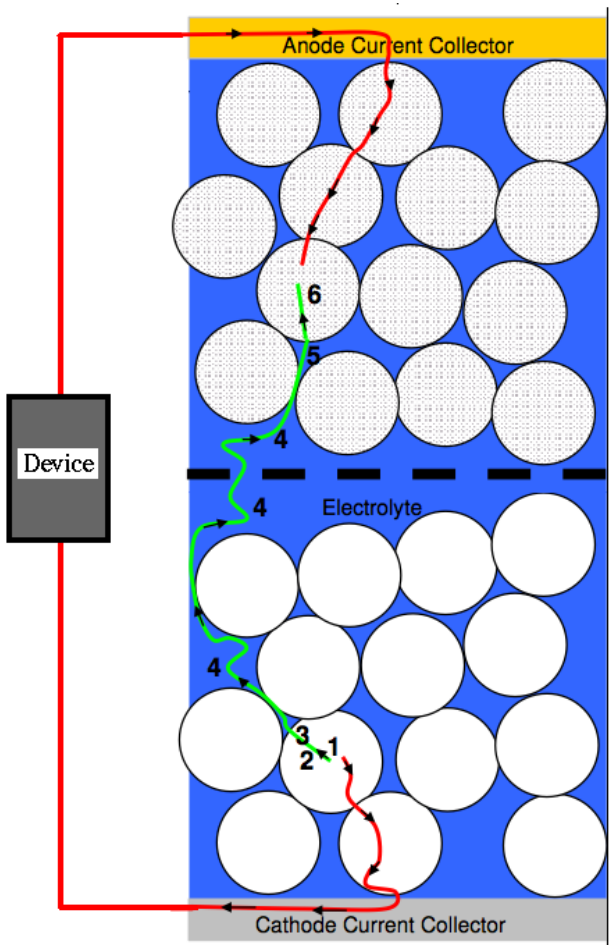
Outline

The Big Picture



The Little Picture

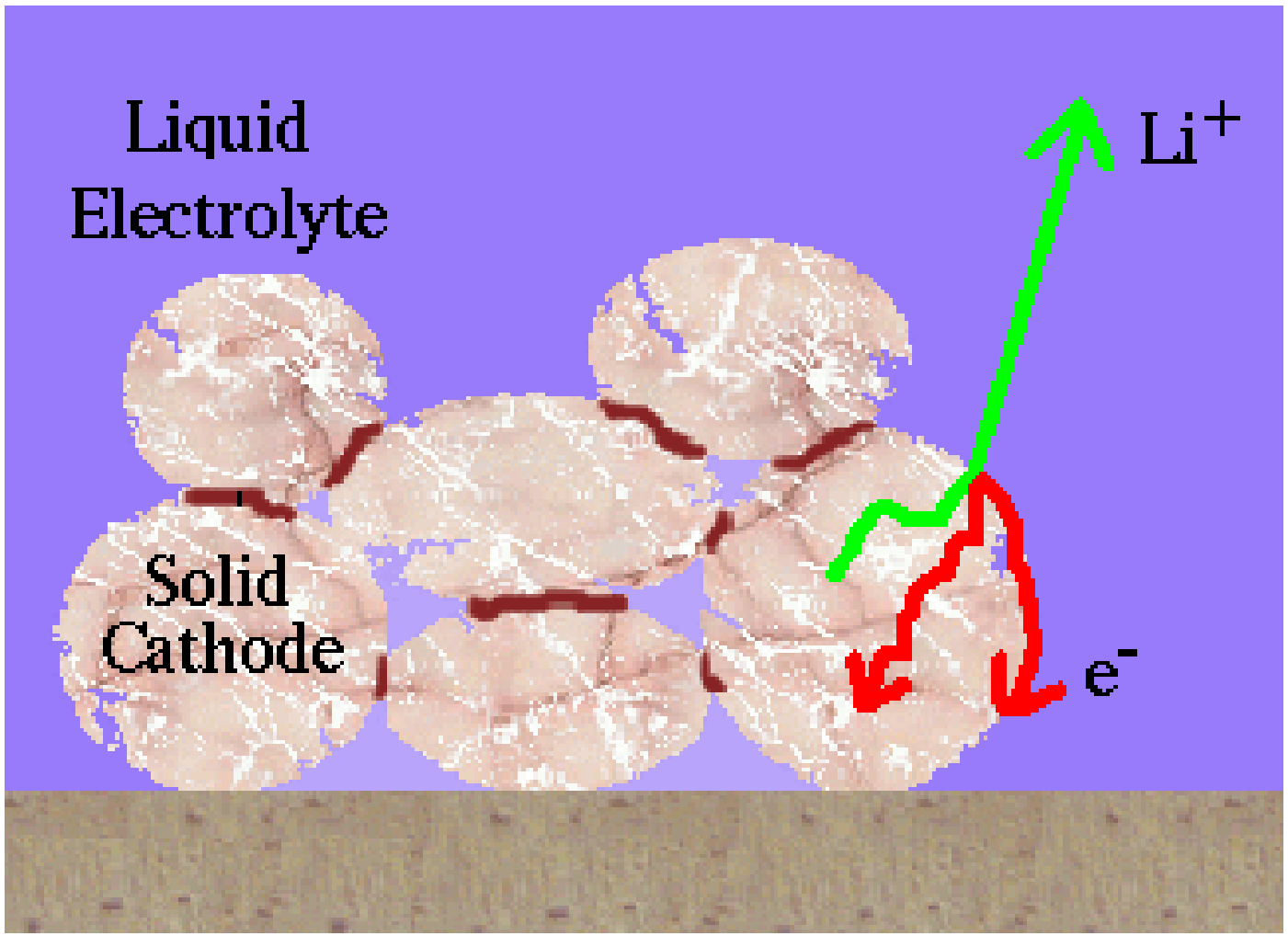


Figure: Cathode schematic.

The *Really* Little Picture

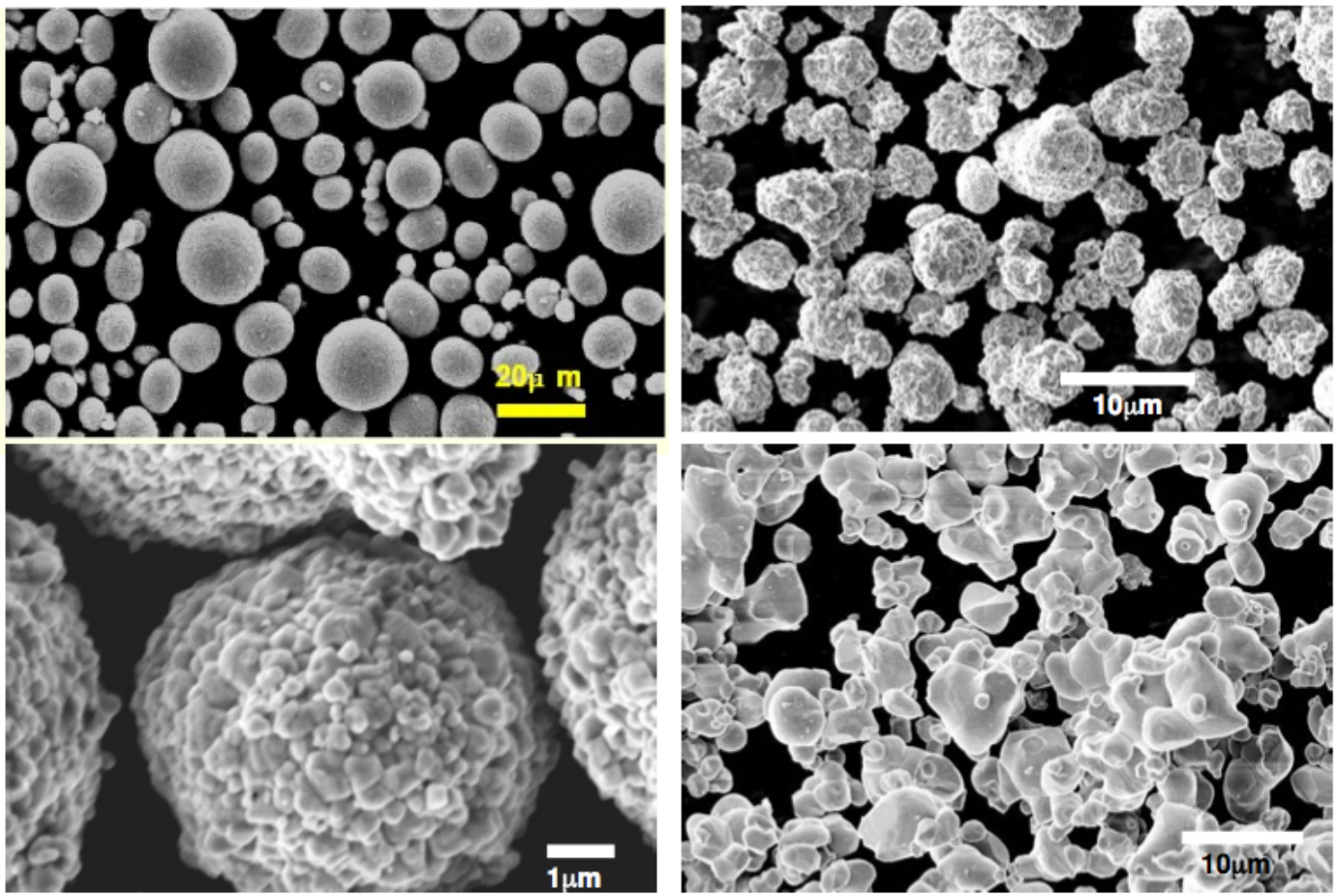


Figure: Cathode particles with different geometric properties.

Project Goals

TIAX would benefit from algorithms, methods, models, scaling relations, or frameworks to analyze the effect of different particle characteristics on electrode properties.

Conservation Laws

Conservation of concentrations:

$$\frac{\partial c_1}{\partial t} + \nabla \cdot q_1 = 0$$
$$\frac{\partial c_2}{\partial t} + \nabla \cdot q_2 = 0$$
$$c_1 = c_2$$

where $c_1 = [Li^+]$ and $c_2 = [PF_6^-]$, and the flux is given by:

$$q_1 = -D_1(\nabla c_1 + \frac{F}{RT} c_1 \nabla \Phi_e)$$
$$q_2 = -D_2(\nabla c_2 - \frac{F}{RT} c_2 \nabla \Phi_e)$$

Butler-Volmer Kinetics

At the electrolyte/solid interface, reaction rate R:

$$R = q_1 \cdot \hat{n}|_{\partial\Omega} = -q_s \cdot \hat{n}|_{\partial\Omega} =$$

$$k_1 c_s \exp\left(\frac{F}{2RT}(\phi_s - \phi_e - u(c_s))\right) - k_2 c \exp\left(-\frac{F}{2RT}(\phi_s - \phi_e - u(c_s))\right)$$

This is the reaction governing the departure of Li^+ ions from the solid into the electrolyte.

Dimensionless Equations

Dimensionless conservation:

$$\frac{\partial \bar{c}}{\partial \bar{t}} + \frac{\alpha}{\lambda}\bar{\nabla}\cdot\left[-\bar{\nabla}\bar{c} - \lambda\bar{c}\bar{\nabla}\bar{\phi}_e\right] = 0$$

$$\frac{\partial \bar{c}}{\partial \bar{t}} + \frac{D_2\alpha}{\lambda}\bar{\nabla}\cdot\left[-\bar{\nabla}\bar{c} + \lambda\bar{c}\bar{\nabla}\bar{\phi}_e\right] = 0$$

where α/λ dimensionless diffusivity of Li^+

$$\lambda = \frac{F\phi_0}{RT} >> 1$$

Dimensionless Butler-Volmer reaction:

$$R = \frac{k_1\bar{c}_s}{\lambda}\exp\left(\frac{\lambda}{2}(\bar{\phi}_s - \bar{\phi}_e - \bar{u}(\bar{c}_s))\right) - \frac{k_2\bar{c}}{\lambda}\exp\left(-\frac{\lambda}{2}(\bar{\phi}_s - \bar{\phi}_e - \bar{u}(\bar{c}_s))\right)$$

Electrode Equations

c_s: Concentration of Li in solid electrode particles.

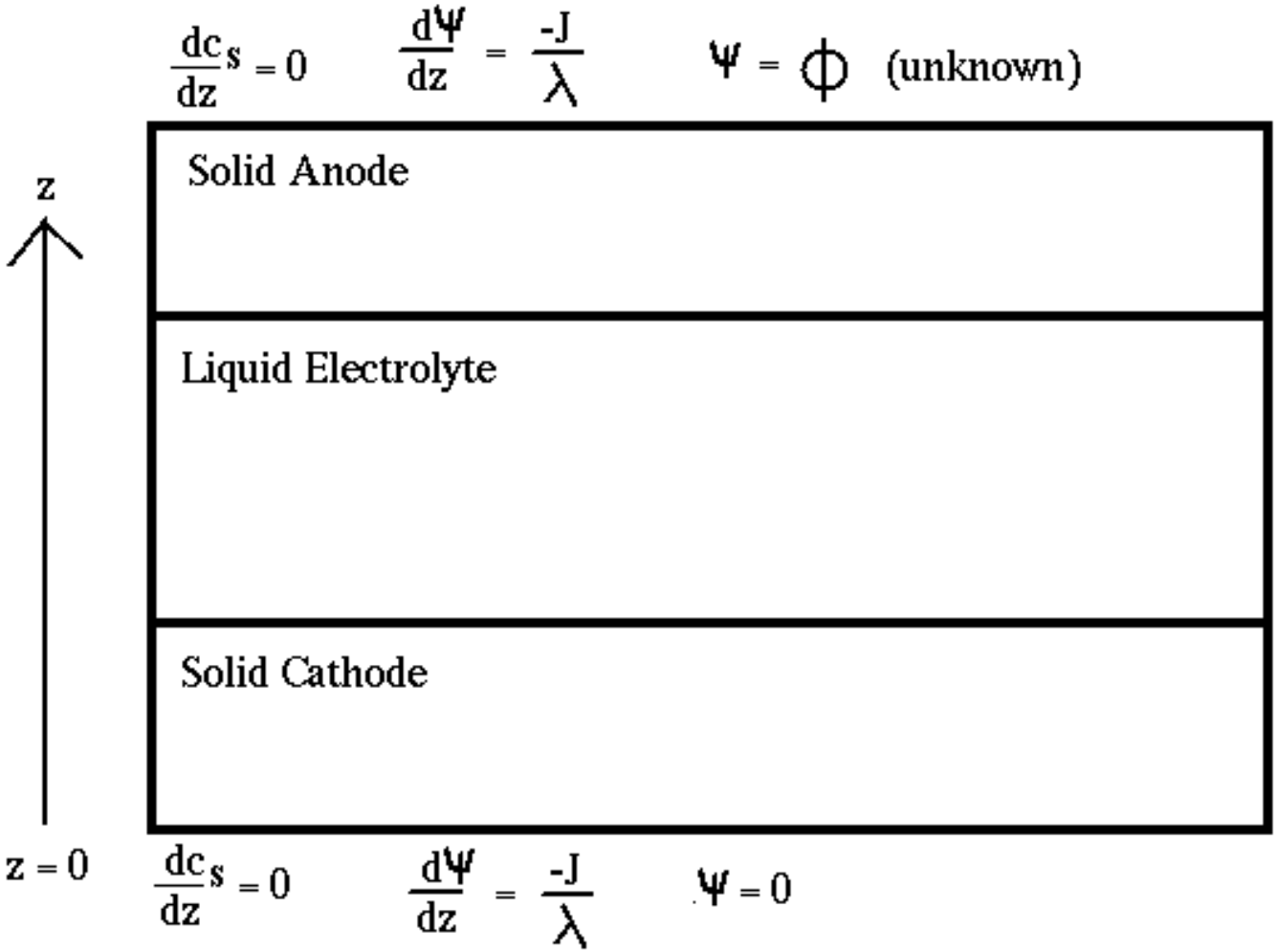
Diffusion equation for c_s coupled to Laplace's equation $\nabla^2\psi = 0$ for potential in particles.

Various conditions on interface relating

ψ, c_s in electrode particles,
ϕ, c in electrolyte

to reaction rate R.

Model Problem



Nondimensional Equations

$$\chi \sim O(1), \qquad \Sigma \sim O(1)$$
$$\lambda \sim O(100), \qquad \frac{\alpha}{\lambda} = O(1), \qquad \beta = O(1)$$

Electrolyte

$$\frac{\partial c}{\partial t} = \frac{\alpha}{\lambda}\left(\frac{1+D_2}{D_2}\right)\nabla^2 c$$
$$\nabla(c\nabla\phi) = -\frac{1}{\lambda}\left(\frac{1-D_2}{1+D_2}\right)\nabla^2 c$$

Electrode

$$\frac{\partial c_s}{\partial t} = \beta\nabla^2 c_s$$
$$\nabla^2\psi = 0$$

Nondimensional Equations

Boundary Conditions

$$c\frac{\partial \phi}{\partial n}|_{\partial\Omega} = -\frac{R}{2}, \qquad \frac{\partial c}{\partial n}|_{\partial\Omega} = -\frac{\lambda R}{2}$$
$$\frac{\partial \psi}{\partial n}|_{\partial\Omega} = \frac{R}{\Sigma}, \qquad \frac{\partial c_s}{\partial n}|_{\partial\Omega} = -\frac{R}{\chi}$$

$$R = \frac{k_1 \bar{c}_s}{\lambda}\exp\left(\frac{\lambda}{2}(\bar{\phi}_s - \bar{\phi}_e - \bar{u}(\bar{c}_s))\right) - \frac{k_2 \bar{c}}{\lambda}\exp\left(-\frac{\lambda}{2}(\bar{\phi}_s - \bar{\phi}_e - \bar{u}(\bar{c}_s))\right)$$

Expanding in powers of $1/\lambda$

Since $1/\lambda << 1$, expand dependent variables as:

$$c(z,t) = c_0(z,t) + \frac{1}{\lambda}c_1(z,t) + \cdots$$

$$c_s(z,t) = c_{s0}(z,t) + \frac{1}{\lambda}c_{s1}(z,t) + \cdots$$

$$\phi(z,t) = \phi_0(t) + \frac{1}{\lambda}\phi_1(z,t) + \cdots$$

$$\Phi(z,t) = \Phi_0(t) + \frac{1}{\lambda}\Phi_1(z,t) + \cdots$$

etc.

Qualitative Results

- At $O(1)$ we find Φ_0 determined by Butler-Volman conditions is constant. By proceeding to $O(1/\lambda)$ can find evolution of Φ_1, the correction to the potential drop across electrode.
- Show timescale analysis would yield evolution of $\Phi_0(t/\lambda)$ over long times as $c_{s0}(t/\lambda)$.

Unsystematically averaged macroscale model

Some wild assumptions

- transport of ions occurs in spaces between spheres (which form a porous medium).
- spheres provide source of ions. Rate given by solving the microscale problem and is proportional to surface area per sphere and number of spheres per control-layer volume

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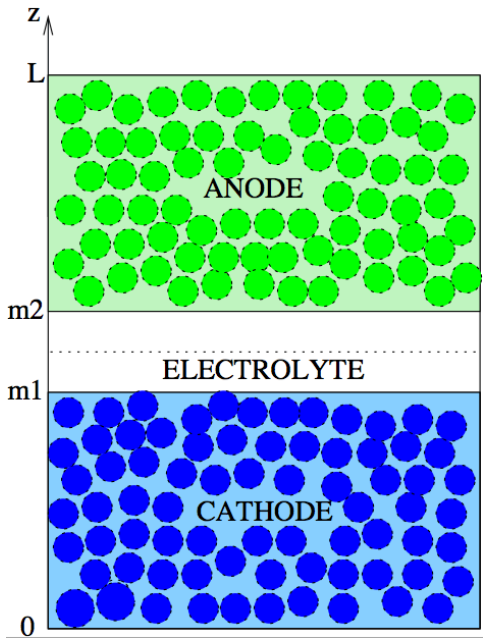

The Model

Notation:

- C is the concentration of lithium ions (also counterions) in the electrolyte at a certain height
- Φ is the electric field at a certain height
- C_s is the concentration of lithium atoms at a certain height
- θ is the liquid volume fraction $= 1 - 4/3\pi a^3 N/V$

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$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial z}\left(\lambda_1 \theta \frac{\partial C}{\partial z}\right) + \frac{2\pi a^2 N}{V} R \tag{1}$$

$$\frac{\partial}{\partial z}\left(-\lambda_2 \theta \frac{\partial C}{\partial z} - \lambda_3 \theta C \frac{\partial \Phi}{\partial z}\right) = \frac{4\pi a^2 N}{V} R \tag{2}$$

$$\frac{dC_s}{dt} = -\frac{4\pi a^2 N}{V} R \tag{3}$$

Initial conditions

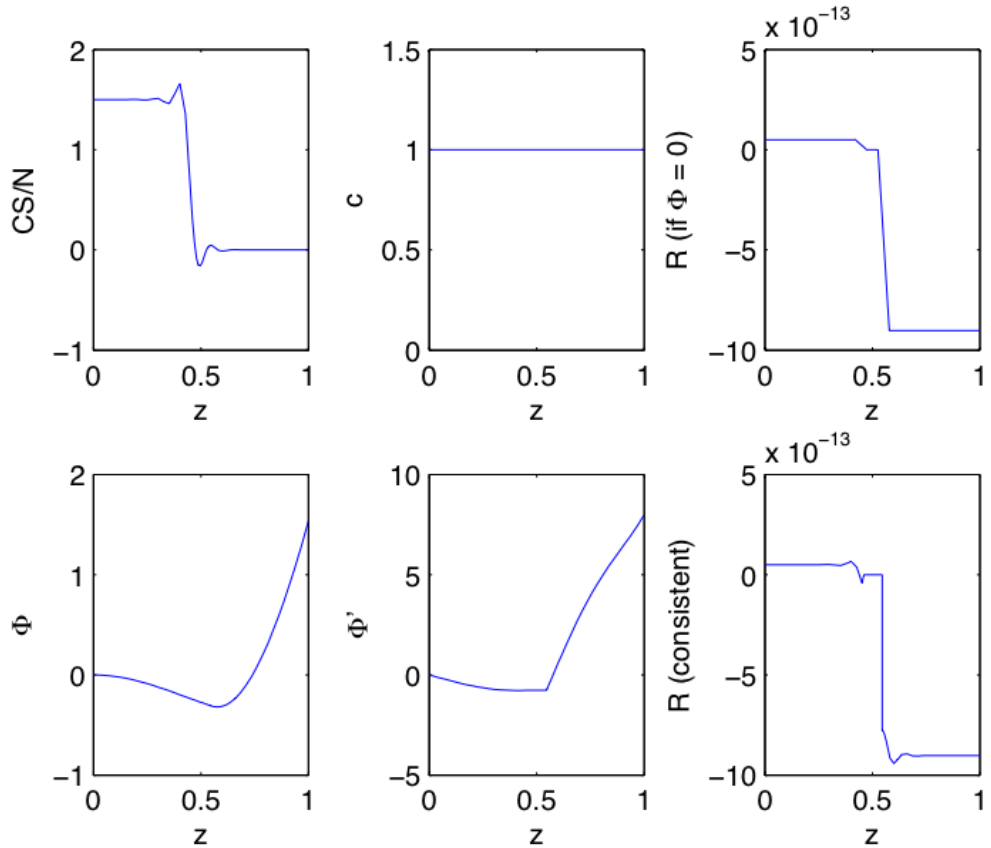
$$C_s = C^* H(m_1 - z), \qquad C = C_0, \tag{4}$$

Boundary conditions

$$\frac{\partial C}{\partial z} = 0, \qquad \Phi = 0, \qquad \frac{\partial \Phi}{\partial z} = -J \qquad \text{at} \qquad z = 0 \tag{5}$$

$$\frac{\partial C}{\partial z} = 0, \qquad \text{at} \qquad z = L \tag{6}$$

Numerical Solution of the Model



Flux stuff

Simple model says that

- reaction at surface has Butler-Volmer form
- particles small enough that diffusion ensures that c_s is constant in each sphere, i.e. C_s is constant at each level (NB - not what TIAX wants!).

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$$R = k_1 \frac{C_s}{N} e^{\Phi - U(C_s/N)} - k_2 C e^{-(\Phi - U(C_s/N))} \quad \text{cathode} \tag{7}$$

$$R = 0 \quad \text{in between} \tag{8}$$

$$R = -k_3 \frac{C_s}{N} e^{\Phi - V(C_s/N)} + k_4 C e^{-(\Phi - V(C_s/N))} \quad \text{anode} \tag{9}$$

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- Better plan: solve microscale problem and relate what's going on in each sphere to the reaction on the surface
- Can get c_s as an infinite sum of exponentials and will (probably) get Abel-esque equation for c_s on the surface.

What can we do with model?

- Vary surface area while keeping volume fraction constant.
- Vary volume fraction while keeping surface area constant.
- Consider populations of spheres - the surface area will become average surface area and formula for θ will change.

Nondimensional Steady-State Potential Equations

$$\text{PDE}: \quad \begin{cases} \triangle u_+ = 0 & x \in \Omega_e \\ \nabla \cdot (\epsilon \nabla u_s) = g & x \in \Omega_s \end{cases}$$

$$\text{BC}: \quad -\partial_n u_+ = \epsilon\, \partial_n u_s = i_0 \sinh(u_s - u_+) \quad x \in \Gamma$$

where

- u_s : Li atom potential in the solid particles
- u_+: Li ion potential in the electrolyte
- $\epsilon := \kappa_s / \kappa_+$

Bounds on Effective Cathode Conductivity

u : Homogenized Li potential throughout the cathode

- $$\nabla \cdot (\kappa \nabla u) = \theta_p g \qquad \forall\, x \in \text{Cathode}$$

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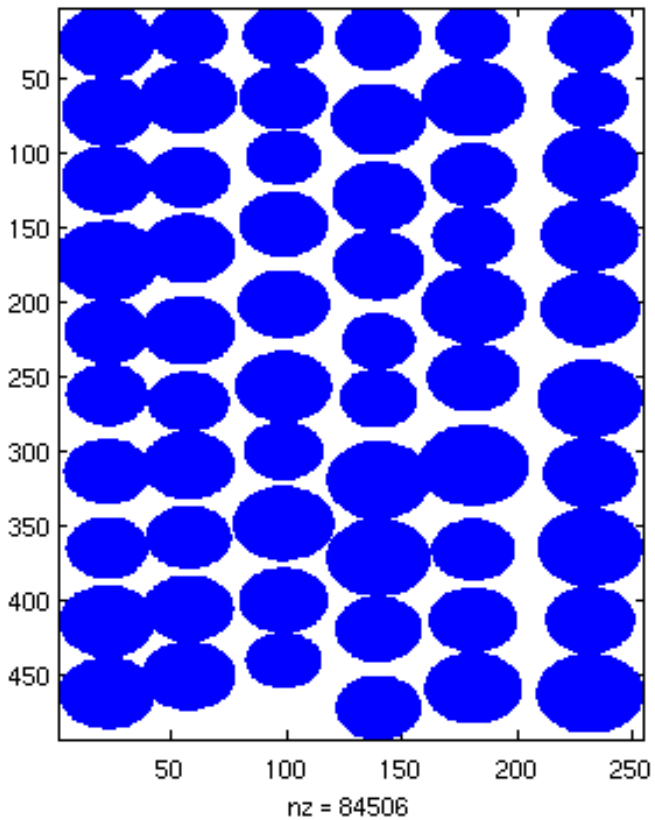
- $$1 - \left(\frac{1}{1 - m_0} + \frac{1}{\theta_p c} \right)^{-1} \leq \kappa$$

- $$\kappa \leq \left(\frac{1}{\epsilon} + \frac{\theta_e i_0 + \theta_p \lambda + \frac{2}{3}\epsilon}{i_0 \lambda + \frac{2}{3}\theta_e \lambda \epsilon + \frac{2}{3}\theta_p \epsilon i_0} \right)^{-1}$$

Kinetic Monte Carlo Method

Model of circular lithium metal oxide particles:



Initial battery setup allows for variable particle size and packing.

Kinetic Monte Carlo Method

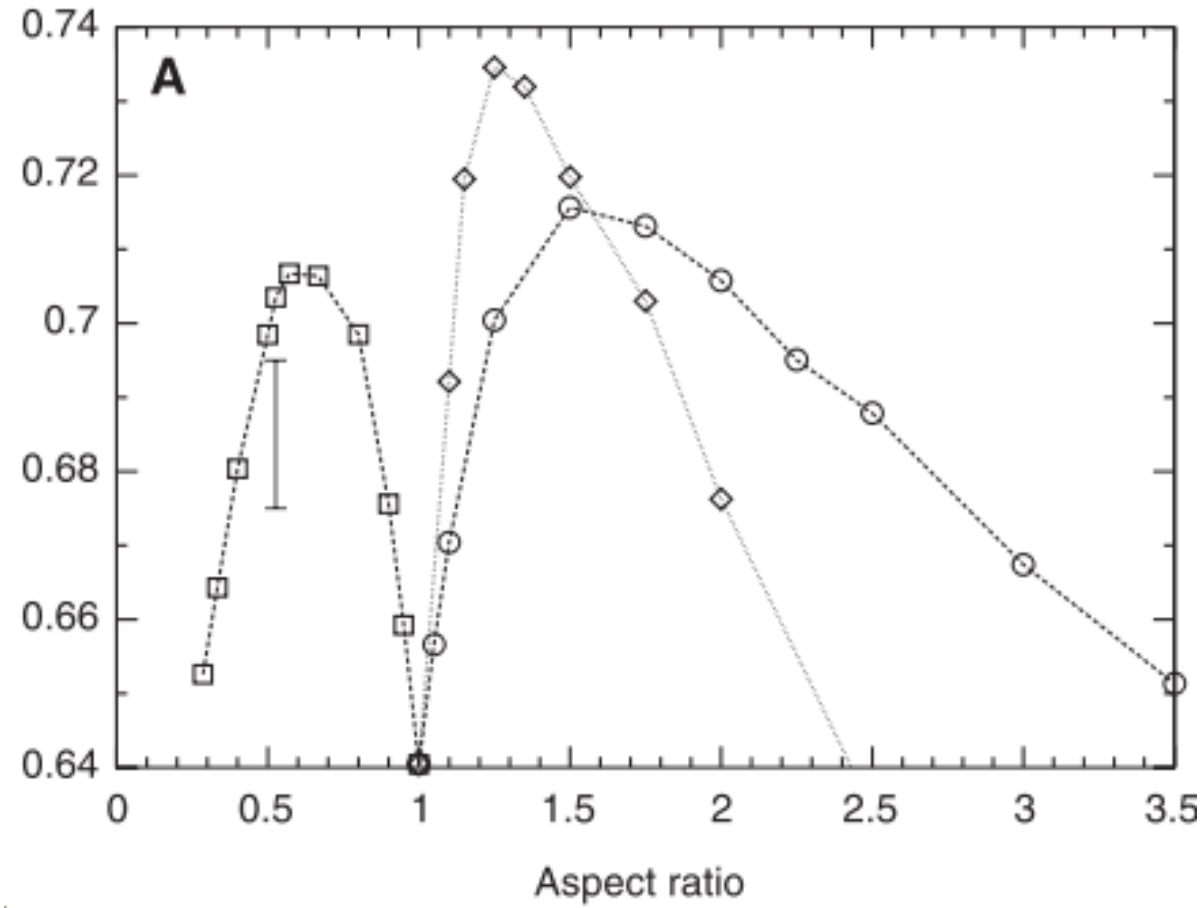
Based on KMC models of Schulze (2002, 2006) and Voter.

- Atoms in the solid hop with rates determined by the number of neighbors.
- Atoms hop out of the solid into electrolyte with specified rate.
- Lithium ions diffuse away in the electrolyte instantaneously.

Volume Fraction Results: Donev, Science 2004

- Ellipsoids with an aspect ratio close to M&M's candies can randomly pack more densely, up to $\phi = 0.68 - 0.71$.
- According to their experiments, the aspect ratio $\alpha \approx 1.3$ gives the best density $\phi \approx 0.735$ with no significant orientational ordering.
- Higher density related to the larger number of particle contacts required to mechanically stabilize the packing.

Volume Fraction



Conclusion

Made progress on several areas TIAX requested, including:

1. Developed thorough microscopic and macroscopic models.
2. Scaling relations.
3. Various numerical approaches.

Thank you

Questions?

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