Continuum modeling as a guide to developing new battery materials

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VTO Merit Review

June 11, 2015

Project ID # ES234

Overview

Timeline

- Project start date: October 2013
- Project end date: September 2017
- Percent complete: 37%

Barriers

- Barriers addressed
  - Low power capability
  - Low energy
  - Low calendar/cycle life

Budget

- $430k/year
  - 0.1 FTE Staff Scientist
  - 1.5 FTE Postdoc

Partners

- Vince Battaglia
- Gao Liu
- Phil Ross
- Nitash Balsara
- CD Adapco
- Lawrencium computing cluster
- Advanced Light Source

Relevance

Objectives:

- Develop a mathematical model to guide the design of binders for silicon anodes.
  - Focus on impact of binder/silicon properties on degradation
  - Ensure that mechanical properties are measured accurately in the right environment

- Reduce the impedance of ceramic separators for use in Li-metal systems
  - Quantify the impedance and understand the nature of the problem

- Guide the development of controlled dissolution/precipitation in the sulfur cathode
  - Focus on the precipitation and film formation process

- Develop methodology to understand microstructure effects using direct numerical simulations
  - Combine x-ray tomography with 3D microstructure simulations

Milestones

- Incorporate material property values and behavior measured for binders saturated with electrolyte into simulations of silicon anode (March 2014)

  Completed

- Determine possible reasons for dynamic nature of polarization loss in liquid/ceramic interface (e.g., interfacial vs. bulk) (June 2014)

  Completed

- Quantify the impact of the interfacial polarization loss in ceramics by estimating the energy density of a Li-S cell (Sept 2014)

  Completed

- Develop a model of a Li-S cell using concentration solution framework (Dec 2014)

  Completed

- **Go/no-go**: Develop custom Li-S cell with small (~200um) catholyte layer incorporating ceramic separator (March 2015)

  Completed/ Go

- Use custom cell for experimental data for model comparison (June 2015)

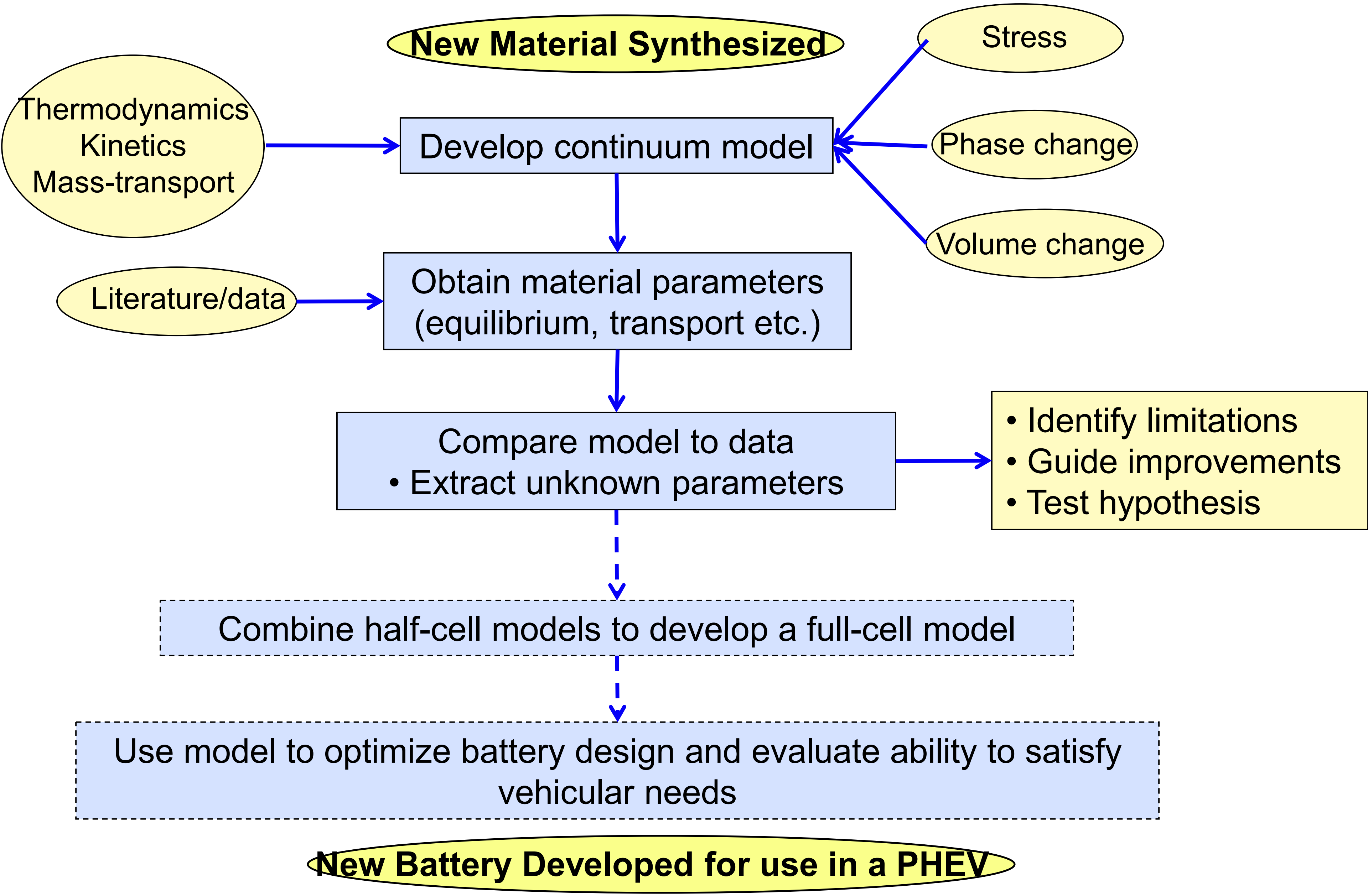
  In Progress

- Compare microscale and macroscale simulation results and experimental data to determine the importance of microstructural detail (Sept 2015)

  In Progress

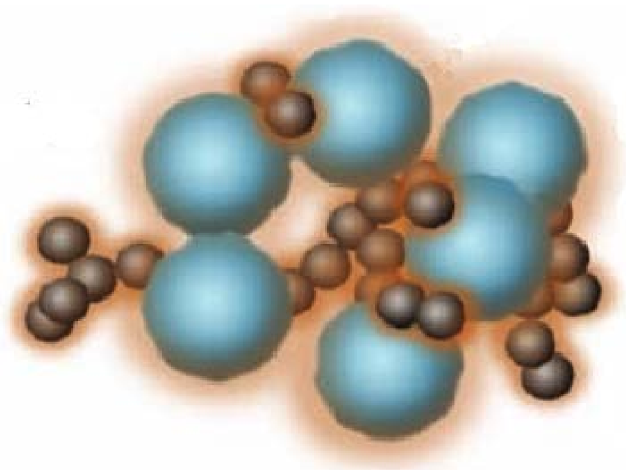
Sept 2013 | Sept 2014 | Sept 2015

Approach

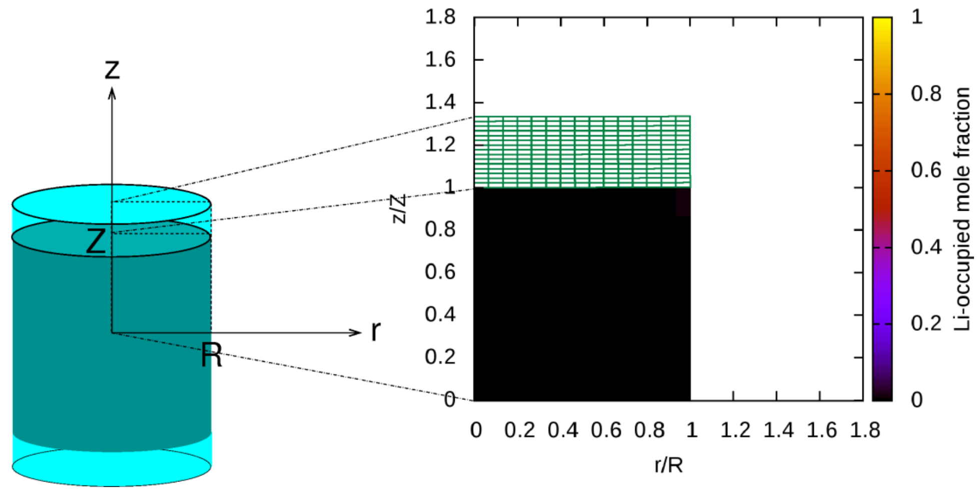


New Material Synthesized
Thermodynamics
Kinetics
Mass-transport
Develop continuum model
Stress
Phase change
Volume change
Literature/data
Obtain material parameters (equilibrium, transport etc.)
Compare model to data
• Extract unknown parameters
• Identify limitations
• Guide improvements
• Test hypothesis
Combine half-cell models to develop a full-cell model
Use model to optimize battery design and evaluate ability to satisfy vehicular needs
New Battery Developed for use in a PHEV

Technical Accomplishments- Silicon anodes

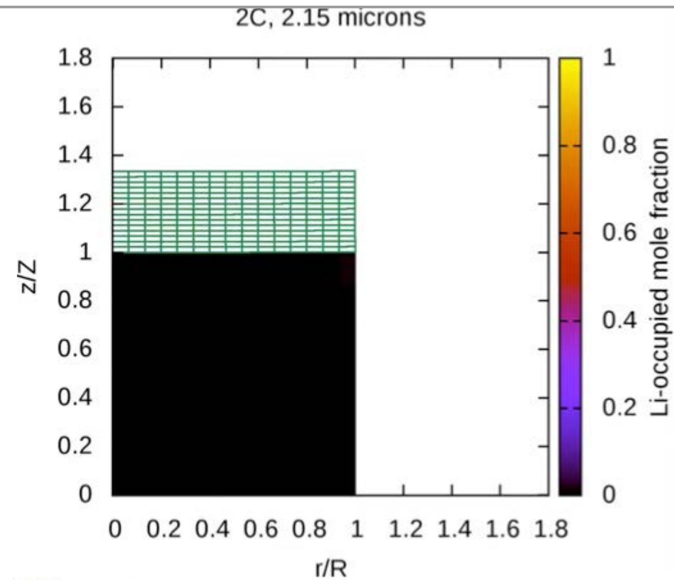


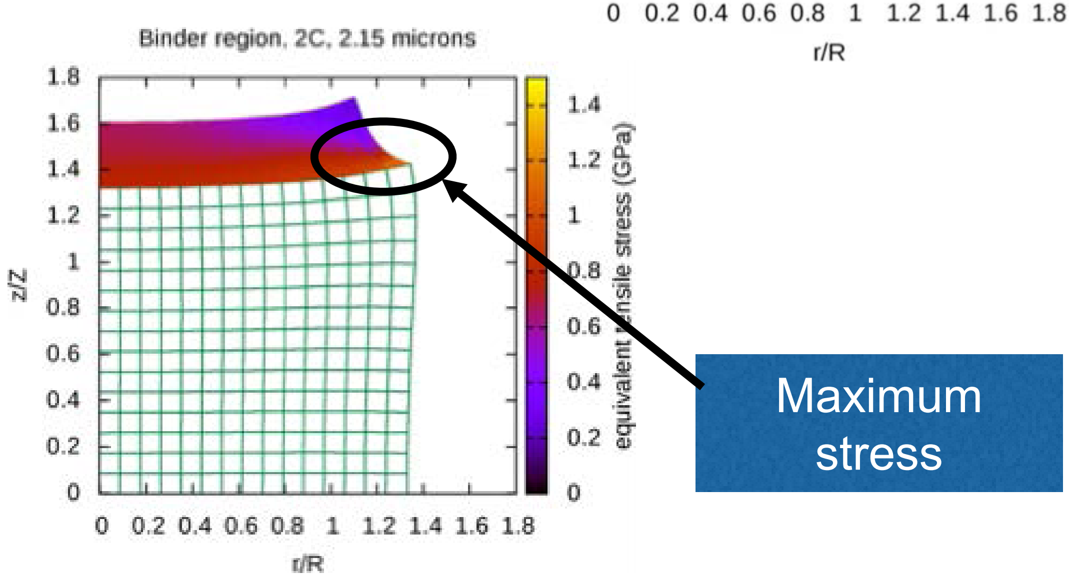
G. Liu, et al., Adv. Mater. 2011, 23, 4679-4683

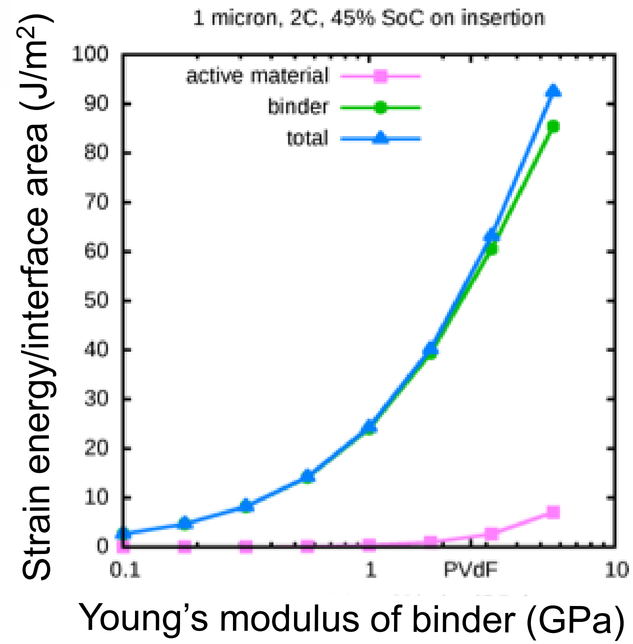


- Represent binder attached to part of expanding particle
- Cylindrical particle (R=Z), amorphous silicon
- Attached “PVdF” binder layers (3:1 volume ratio)
- Two spatial dimensions

Guiding materials development

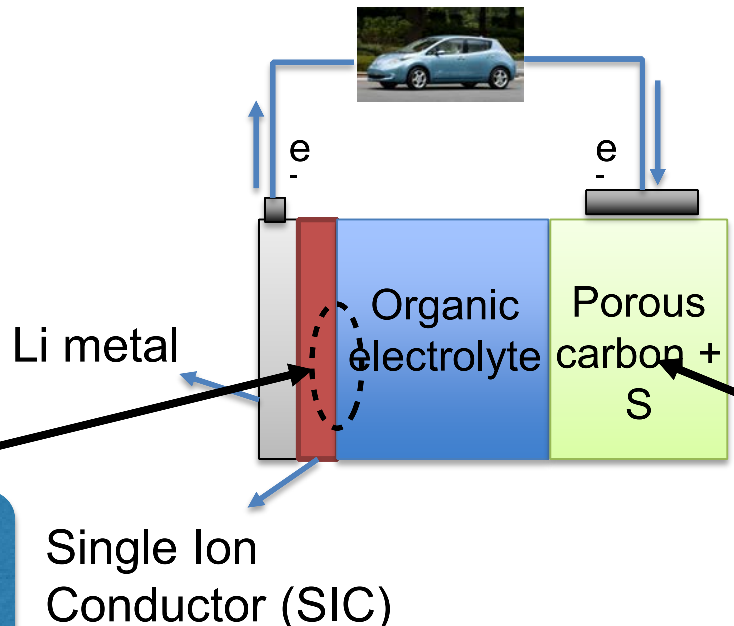






Model allows exploration of impact of size, binder properties, and binder-Si adhesion energy on cracking and de-lamination

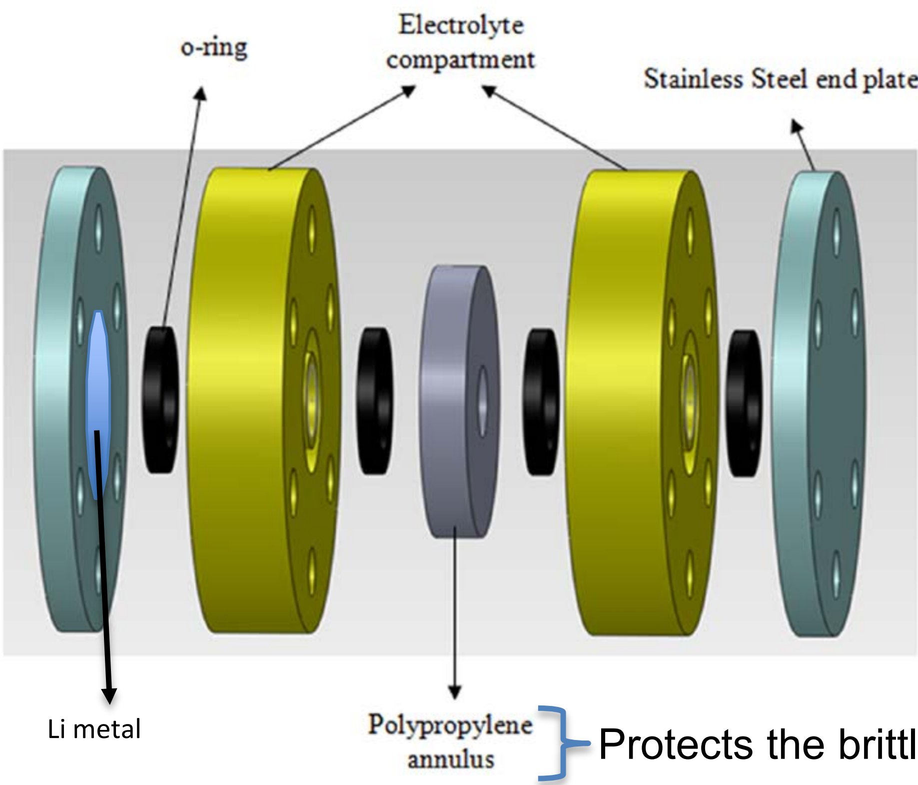
Lithium-sulfur: Next-generation storage device?



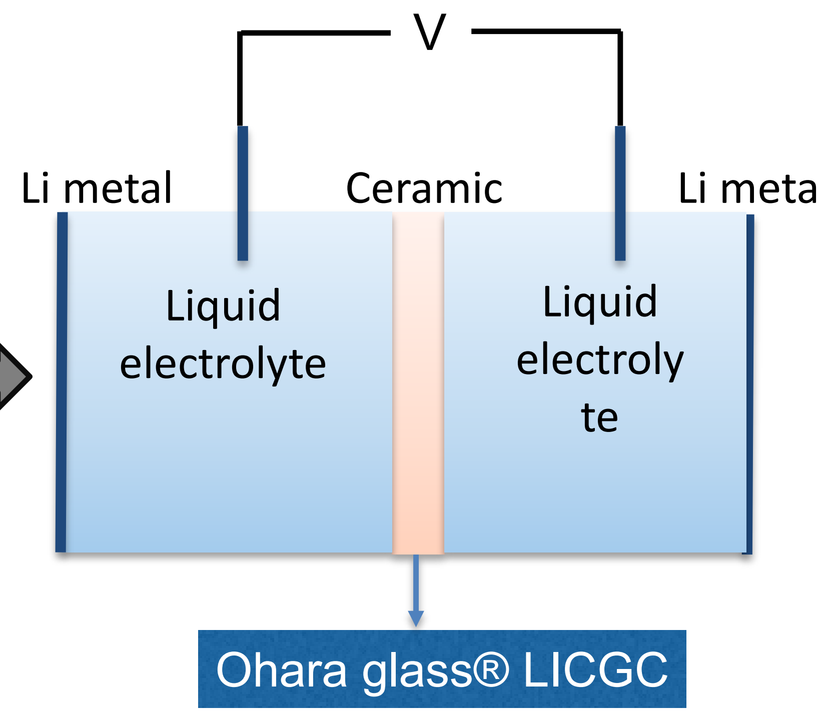
Quantify resistance at the interface

Develop a model that captures the precipitation reaction

Extracting interfacial resistance

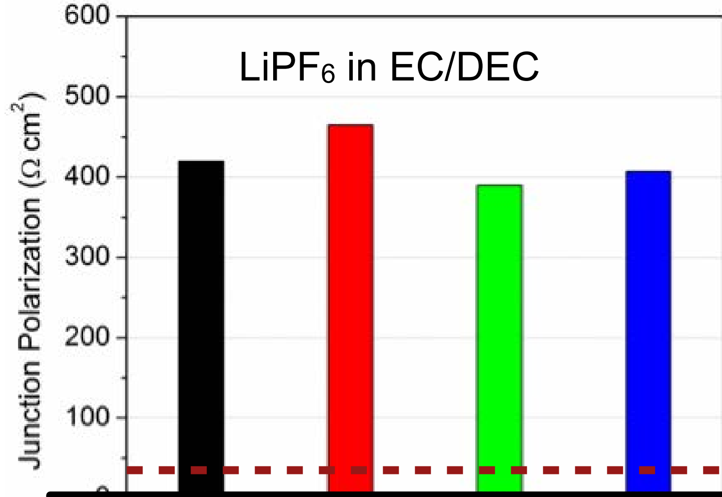


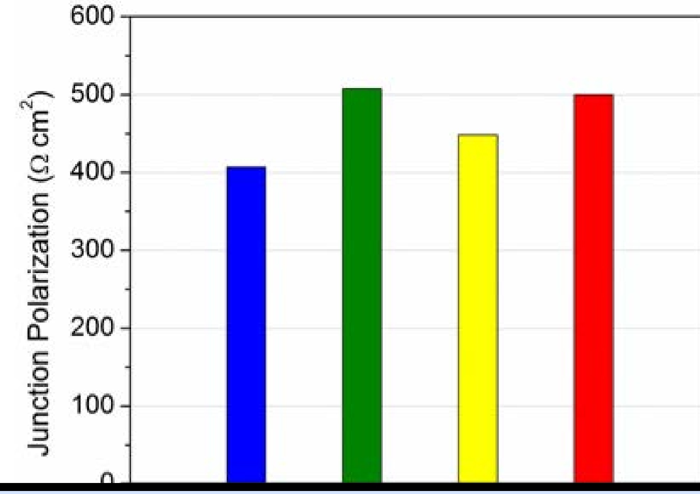
Protects the brittle SIC from o-ring



- Ohara glass® LICGC (Li_2O-Al_2O_3 -SiO_2 –P_2O_5 -TiO_2 -GeO_2)used as Single Ion Conductor - commercially obtained from Ohara Corporation, JP
- Developed a technique that allows for measuring the interface resistance while correcting for changes in the liquid phase

Interfacial impedance is large

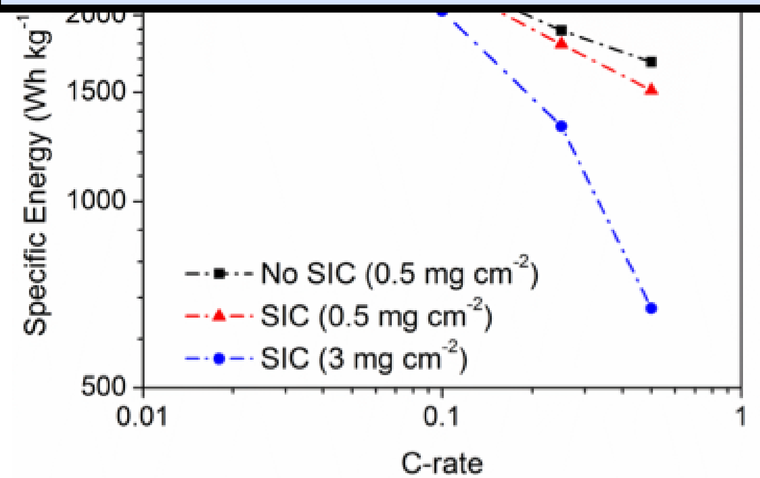




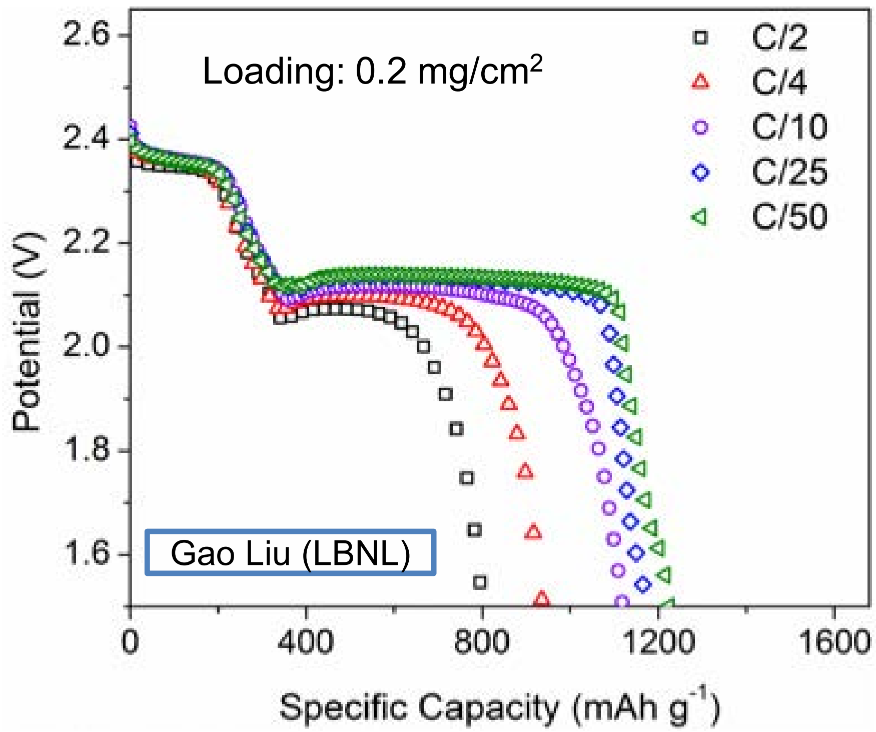
Exchange current density, i_0=0.57 A/m^2

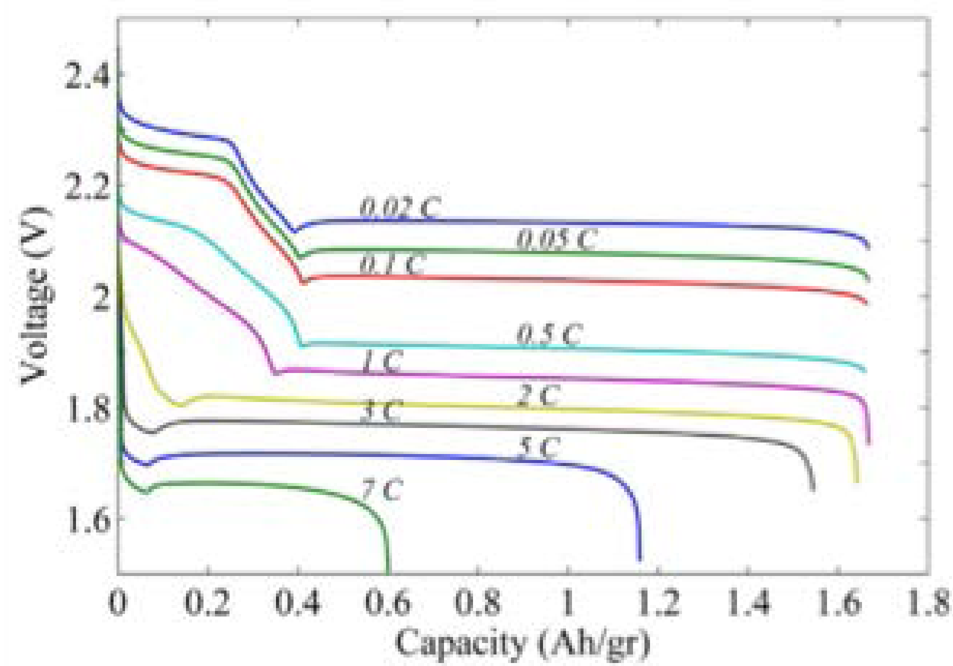
Exchange current density of typical Li-ion cathodes=0.6 A/m^2

Cause of polarization: Lack of area for ion transfer?



Models have not been able to capture the physics

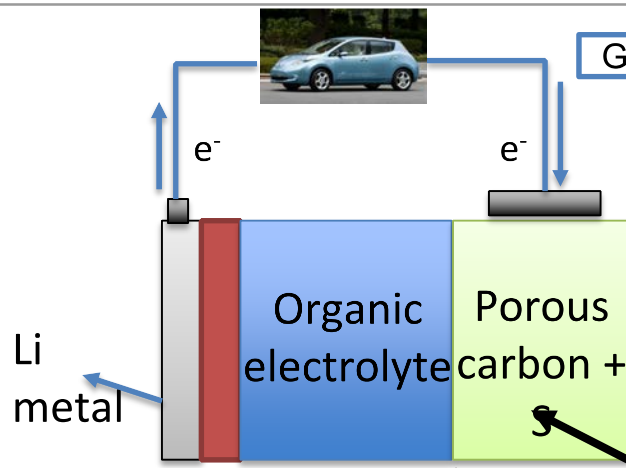




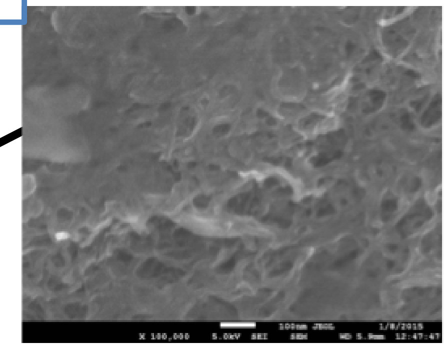
M. Ghaznavi; P. Chen, *J. Power Sources*, **2014**, *257*, 394.

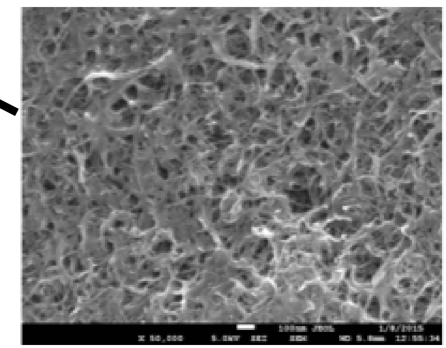
Rate effects not captured correctly in previous models

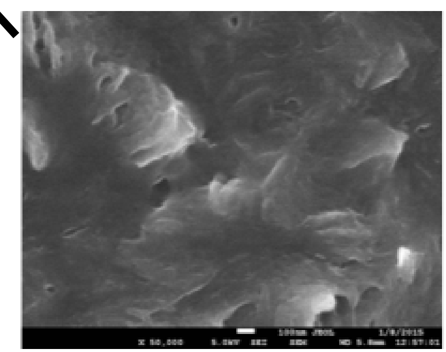
Models have not been able to capture the physics

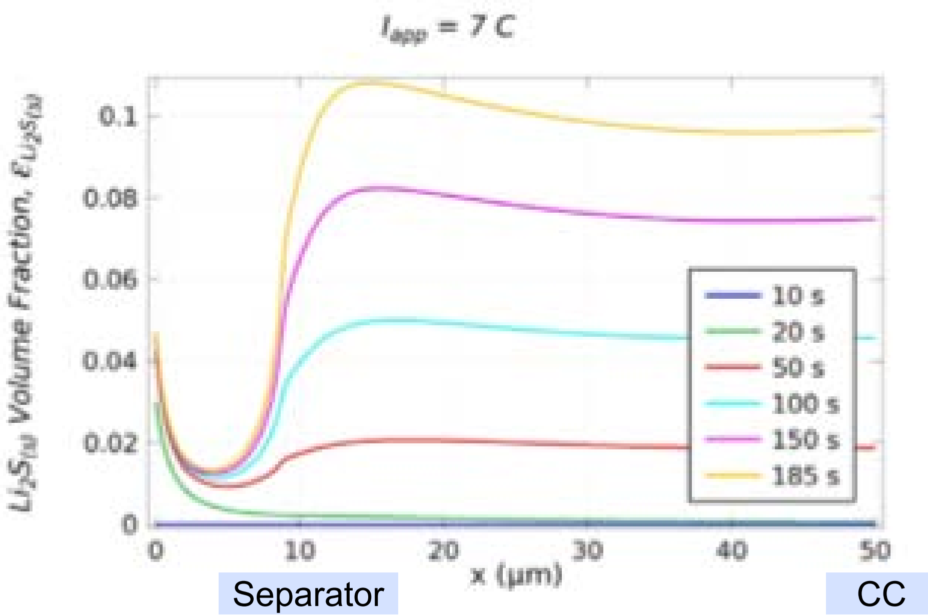


Gao Liu (LBNL)









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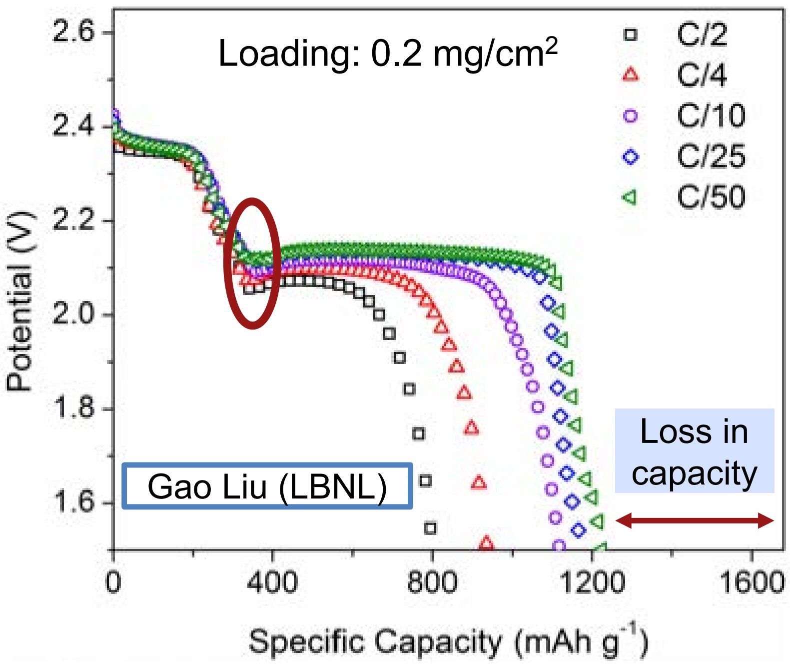
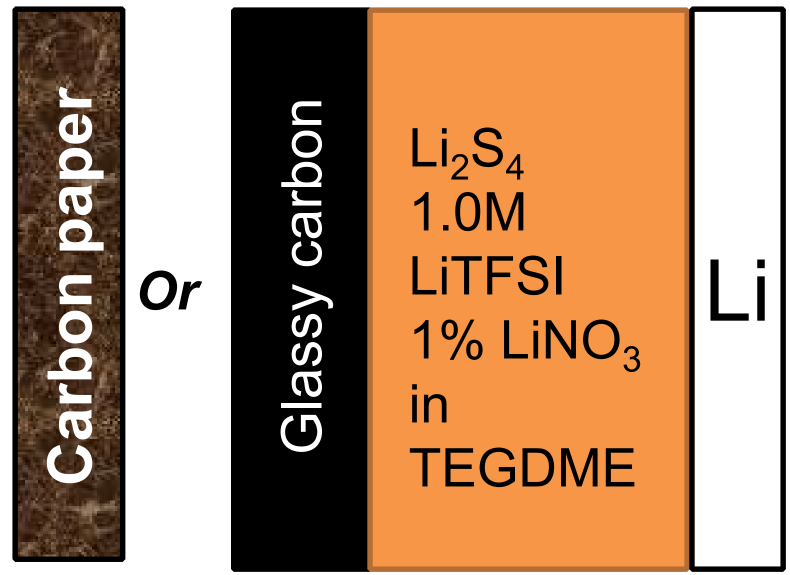
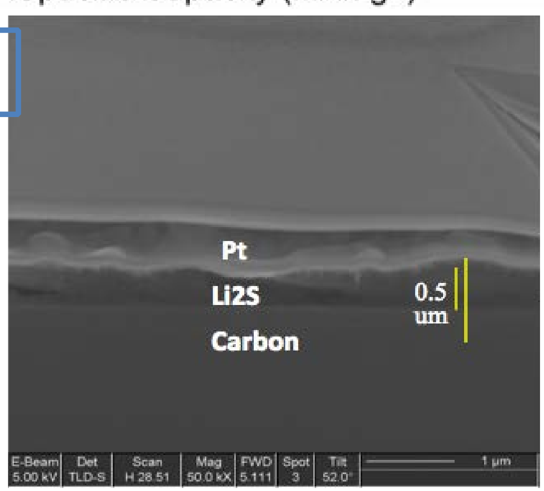
SEM consistent with: *J. Electrochem. Soc*, **2003**, *150*, A800.

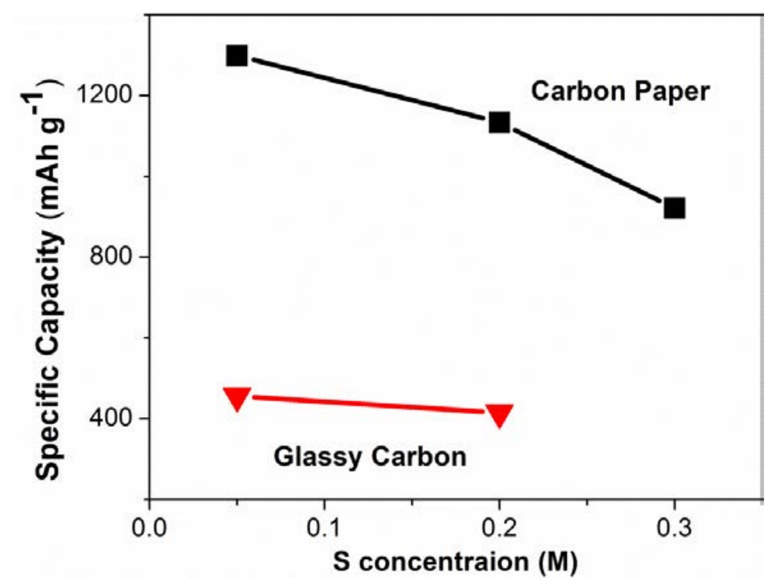
Understanding performance limitations in the sulfur cathode





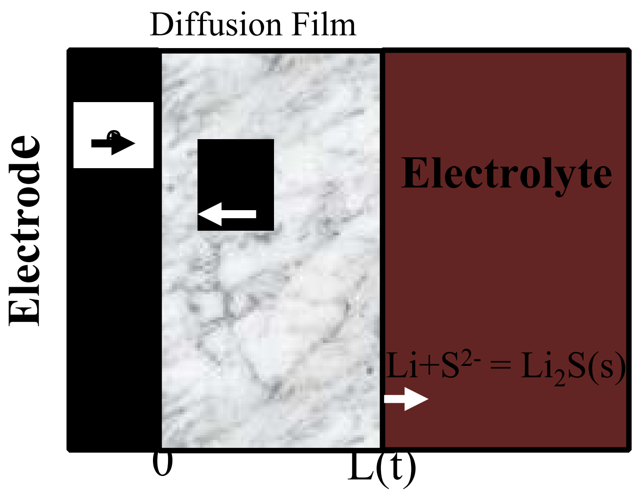
Alpesh Shukla(LBNL)





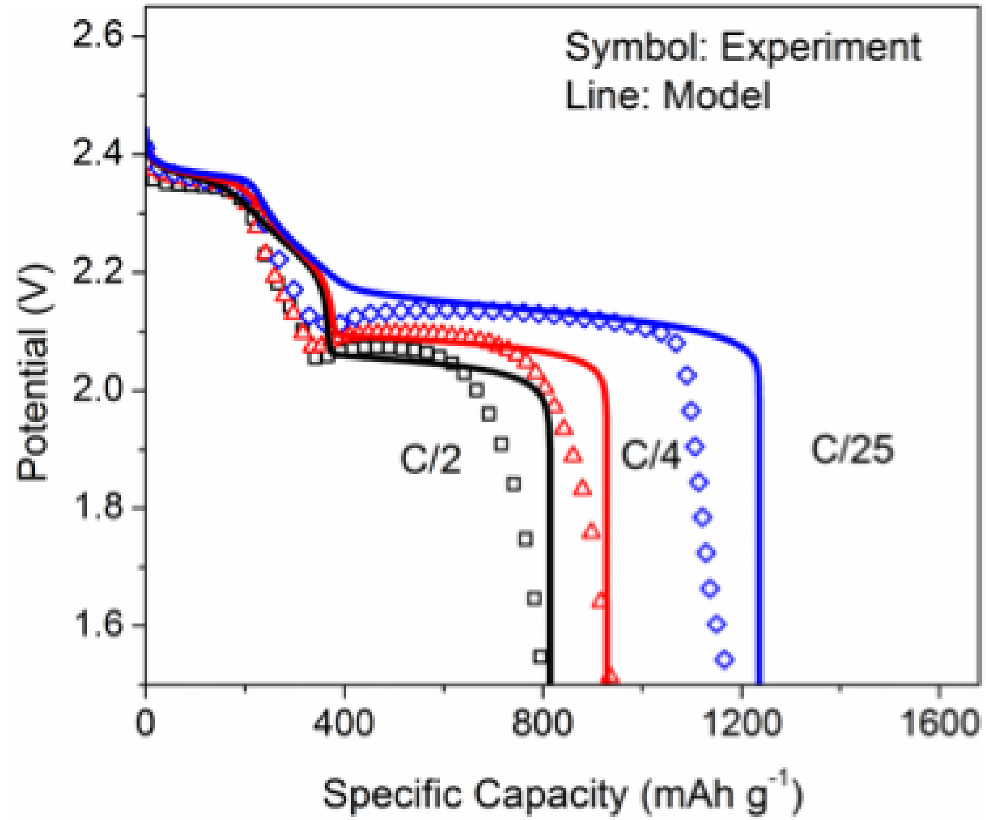
Deposited Li_2S layer plays an important role

A model to describe film growth and transport



$$\frac{\partial C_i}{\partial t} = D_{eff}\left(\frac{\partial^2 C_i}{\partial x^2}\right)$$

$$\frac{\partial L(t)}{\partial t} = r_{Li_2S}\tilde{v}_{Li_2S}$$

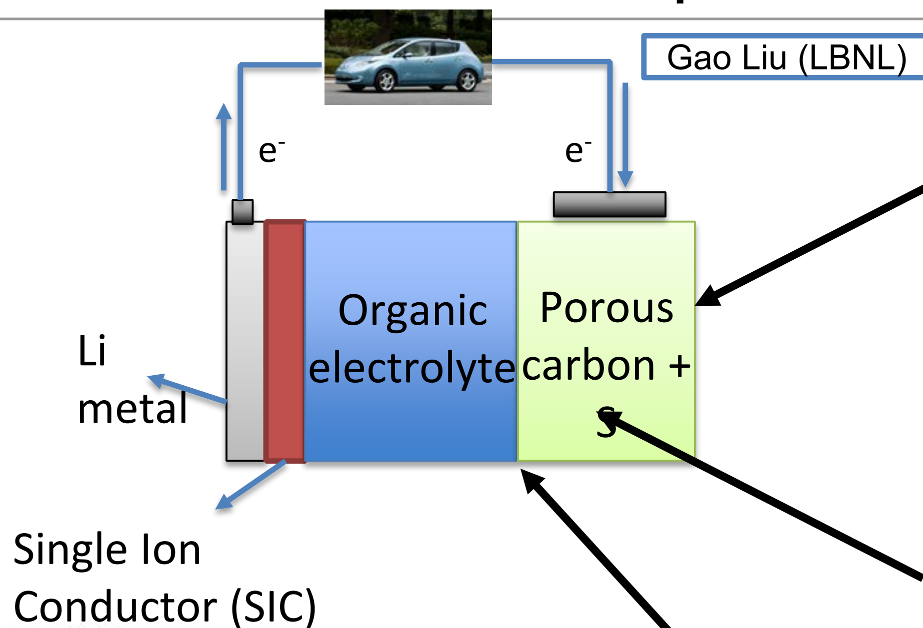


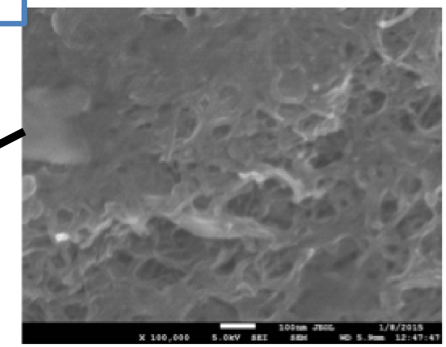
Diffusion and growth model used to describe film resistance.
Need: More data to correlate growth with C-rate

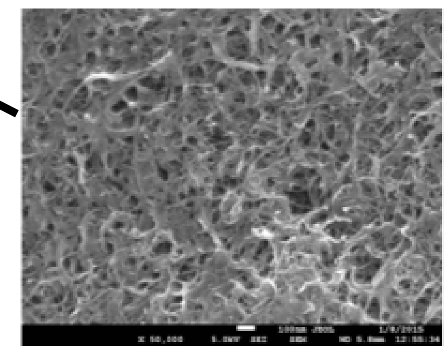
We have also developed a porous electrode model.

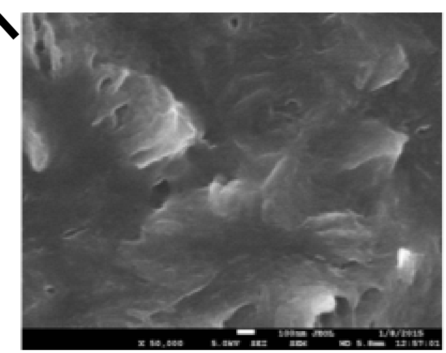
Film model is being incorporated into the porous electrode model

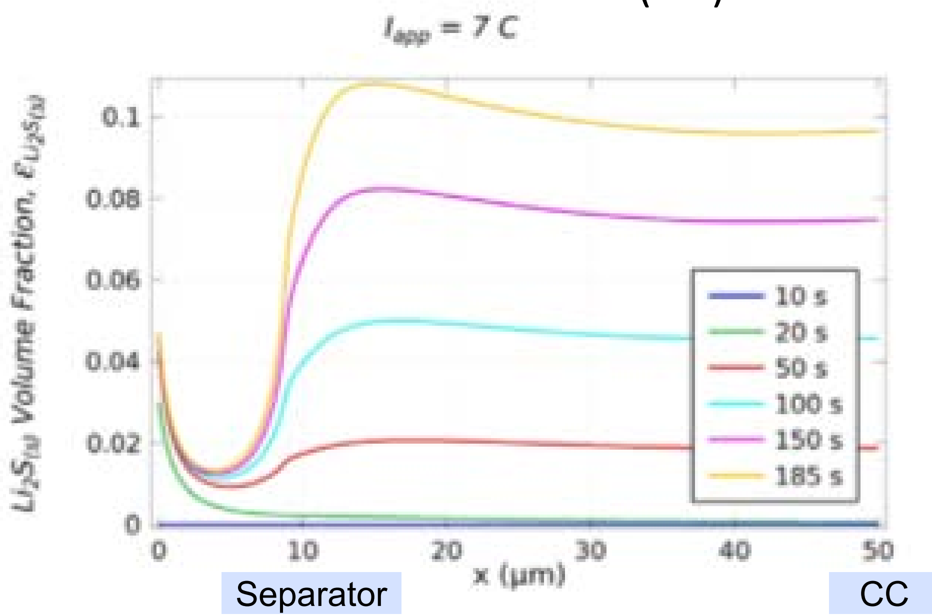
Models have not been able to capture the physics











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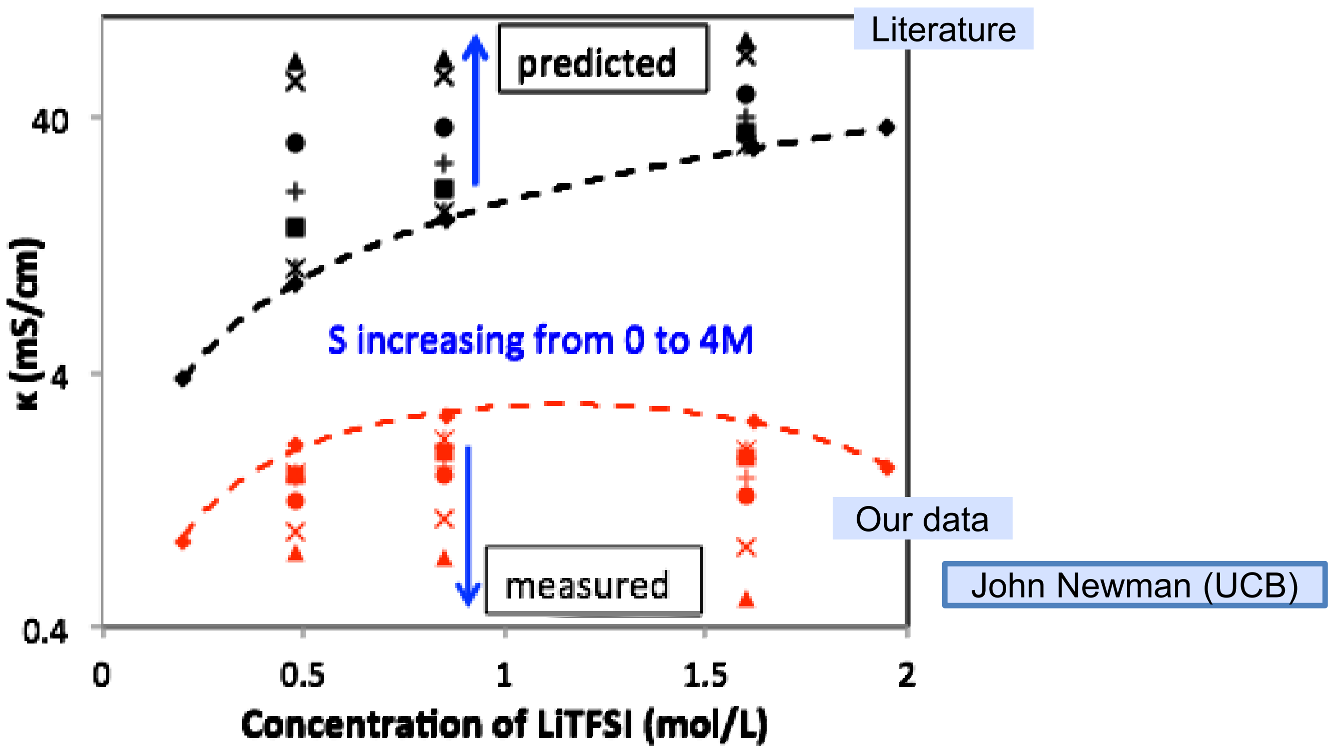
Technical Accomplishments: Transport data highlights problems with previous models

- Models based on dilute solution theory

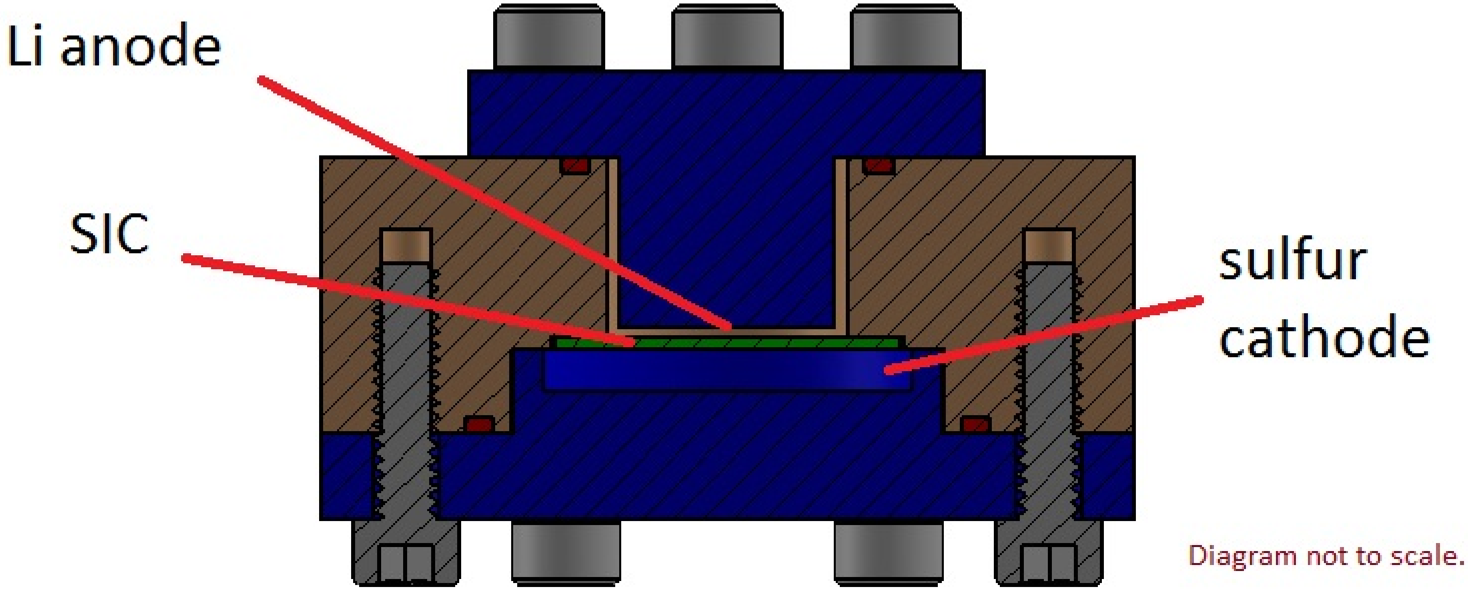
$$\kappa = \frac{F^2}{RT}\sum_i z_i^2 D_i c_i$$



We are measuring other transport properties.

Cell design for “protected” Li cell

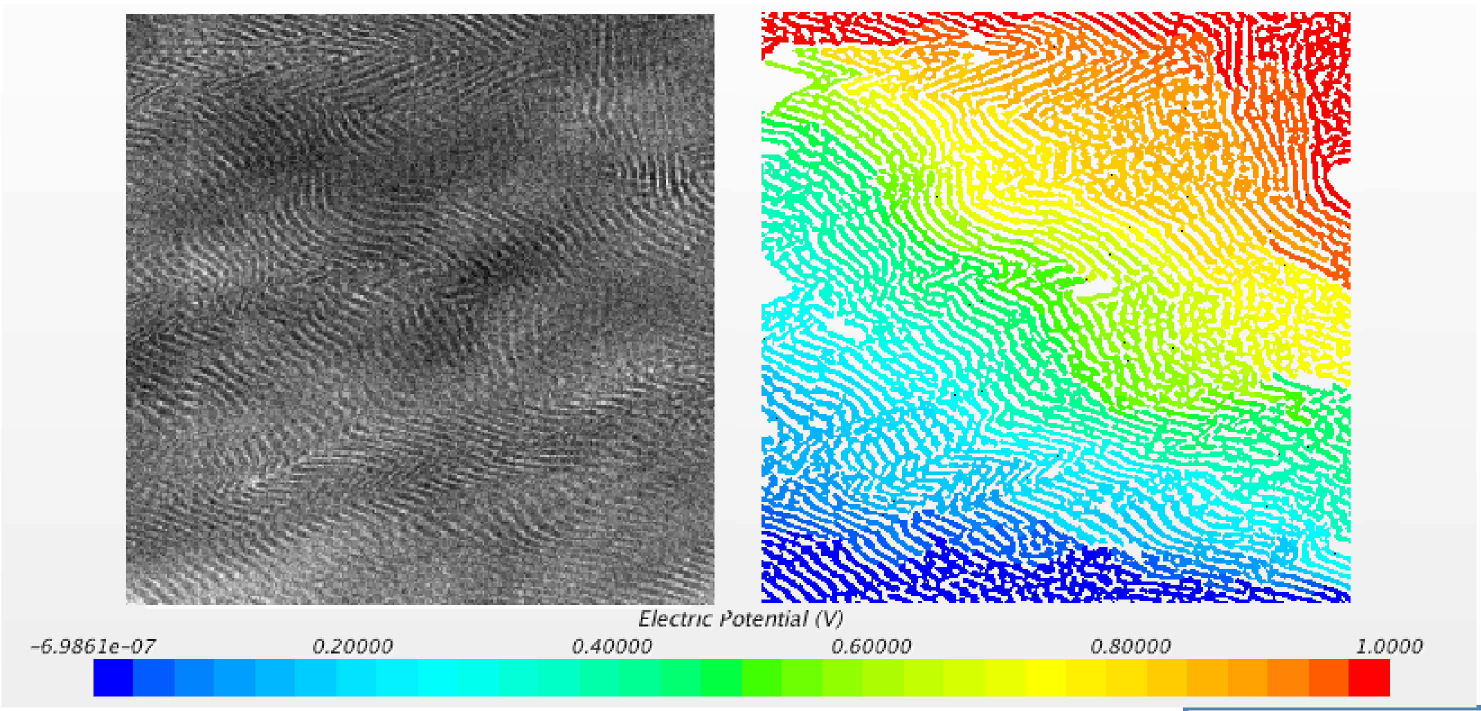
- Protects fragile SIC
- Allows for separate anolyte and catholyte
- Catholyte volume < 200 μL, distance between SIC and cathode surfaces < 125 μm
  - Allows exploration of low electrolyte/sulfur ratio regime



Example of microstructure simulation: Block copolymer

- Traditional macro-homogeneous models (*i.e.,* Newman model) use average parameters
  - Porosity, tortuosity, surface area per volume

Nitash Balsara (LBNL)



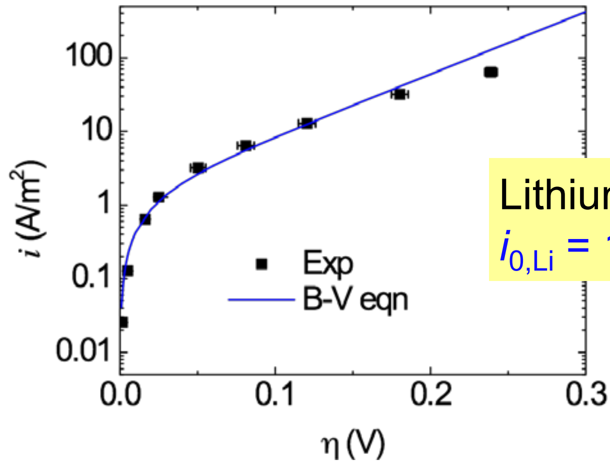
Simulations at Lawrencium cluster (LBNL)

Microstructure simulations capture details not captured in macro-homogeneous models

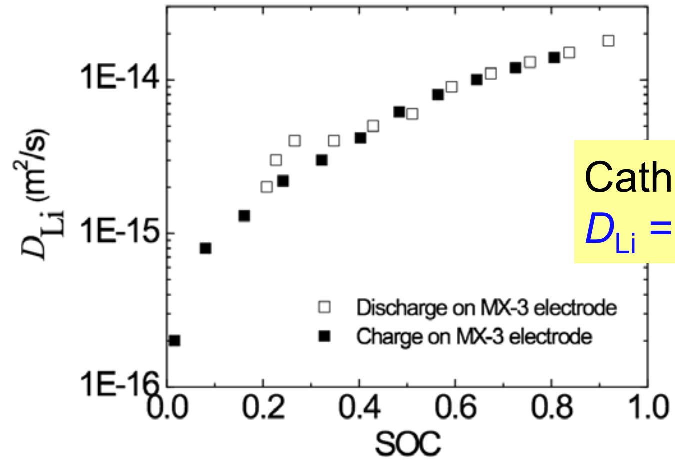
Present focus: NCM cathode/Li metal anode

We know a lot of parameters for this cell

Vince Battaglia,
Gao Liu (LBNL)

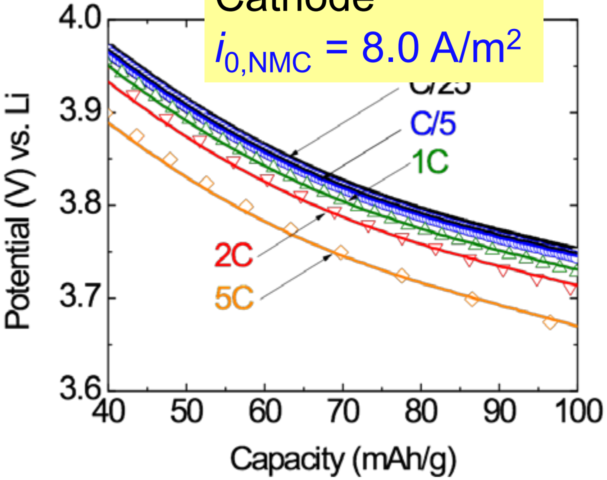


Lithium metal
$i_{0,Li}$ = 1.2 A/m^2



Cathode:
D_{Li} = f(SOC)

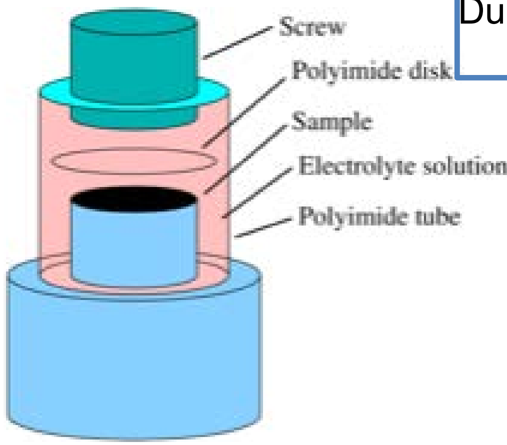
Cathode
$i_{0,NMC}$ = 8.0 A/m^2



- Reasonably consistent electrolyte transport properties, especially at low concentrations
- Wealth of cell data (different loading, thickness, electrolyte concentration)
- Collaboration with CD-Adapco for a microstructure model

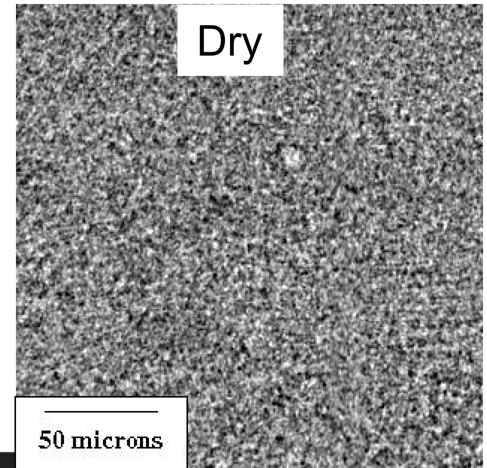
With good microstructure data, we are ready for full simulations

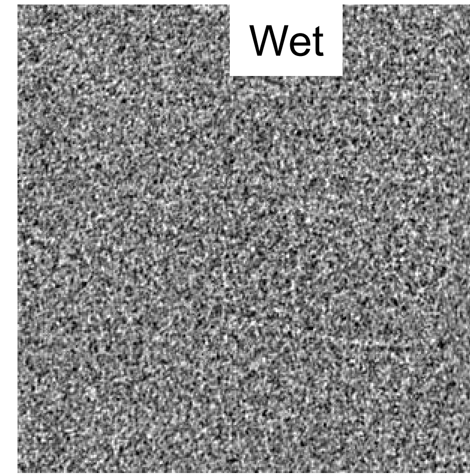
X-ray tomography to obtain microstructure



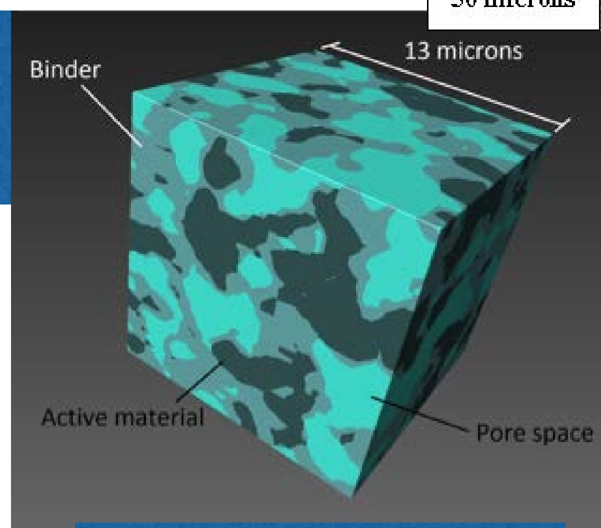
Dula Parkinson (ALS)

Cell for wet, compressed tomography





Effect of wetting



3D reconstruction

Wetting and compression both matter in resolving microstructure

Responses to Previous Year Reviewers' Comments

This project was not reviewed last year

Collaboration and Coordination

- CD-Adapco
  - 3D microstructure software
- DOE User Facilities (Outside VT Program)
  - Advanced Light Source
  - Lawrencium computing cluster
- Within VT Program
  - Nitash Balsara
  - Vince Battaglia
  - Gao Liu
  - Phil Ross

Remaining Challenges and Barriers

- Li-S system:
  - Experiments to date are on low sulfur/electrolyte (S/E) ratio.
  - Failure modes at high S/E need to be captured in model (kinetics of deposition, pore clogging etc.)
- Microstructure model:
  - Need to resolve the microstructure under real conditions (wet and under compression)
  - Does a microstructure model provide better predictions compared to macro-homogeneous models?

Proposed Future Work

- Li-S system: Provide guidance on preventing shuttles and controlling dissolution/precipitation
  - Extract properties at high S/E ratio
  - Compare data at high S/E ratio to mathematical model
- Microstructure models: Understand effect of microstructure on the ability of continuum models to predict performance
  - Understand impact of wetting and compression
  - Compare macro-homogeneous simulations to microstructure simulations
  - Beamtime at SLAC to obtain data with finer resolution

Summary

- Model developed for Silicon-binder composite anode
  - model allows design of binders to minimize mechanical damage
- Single-ion conducting ceramics suffer from large impedance issues
  - Appears to be invariant with electrolyte, and surface of the single-ion conductor
- Mathematical models for sulfur cathodes do not predict experimental features, even qualitatively.
  - Deposition of insulating Li_2S layer plays a large role in controlling end-of-discharge of the sulfur cathode
  - Right properties needed especially at high S/E ratio
- Microstructure models may allow better predictions compared to the macro-homegeneous approach
  - Resolving microstructure requires taking into consideration compression and wetting.