Electrode Materials Design and Failure Prediction

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ES234

Overview

Timeline

- Project start date: October 2013
- Project end date: September 2016
- Percent complete: 87%

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 (Dula Parkinson)

Relevance

Objectives:

- Develop methodology to understand microstructure effects using direct numerical simulations
  - Combine x-ray microtomography with electrochemical simulations on 3D microstructural domains
  - Compare with optimized macroscale models
- Guide the development of controlled dissolution/precipitation in the sulfur cathode
  - Focus on the precipitation and film formation process

Milestones

- 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

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

Completed

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

Completed

- Replace parameters (porosity gradient and tortuosity) in macroscale NMC model with corresponding values or functions obtained from tomography data (Dec 2015)

Completed

- Measure the relationship of film growth to electrochemical response and develop a model to interpret the relationship (June 2016)

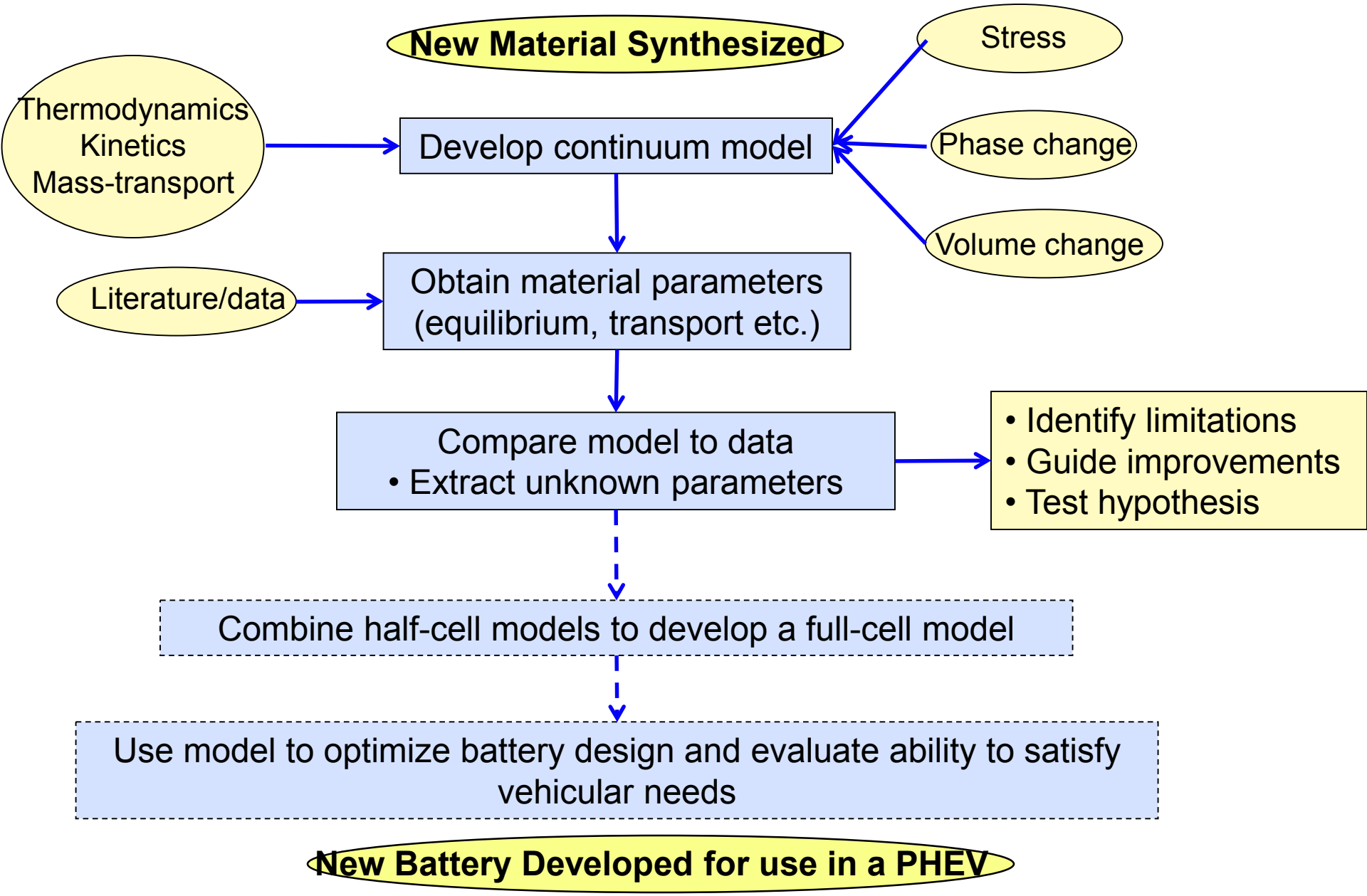
Completed

- **Go/no-go**: Measure transport properties of polysulfide solutions using electrochemical methods. If unsuccessful at obtaining concentration-dependent diffusion coefficient, use fixed diffusion coefficient value in upcoming simulations (Sept 2016)

In Progress

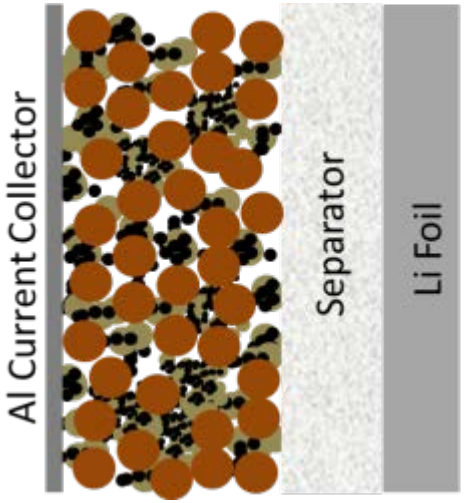
Sept 2014 Sept 2015 Sept 2016

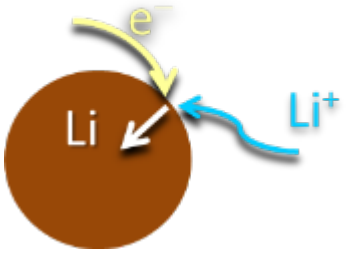
Approach

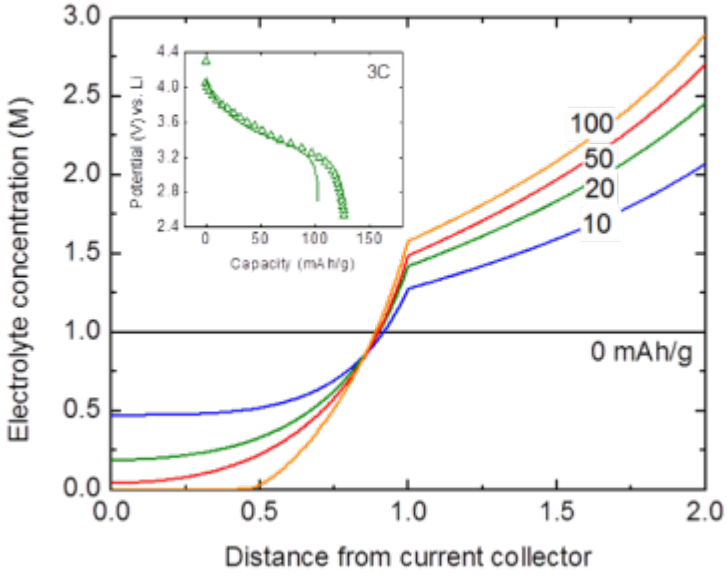

New Material Synthesized
Stress
Thermodynamics
Kinetics
Mass-transport
Develop continuum model
Phase change
Volume change
Literature/data
Obtain material parameters
(equilibrium, transport etc.)
Compare model to data
• Extract unknown parameters
• Identify limitations
• Guide improvements
• Test hypothesis
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-Model comparison

- Macroscale porous electrode model previously developed within this project, unknown parameters tuned to fit experimental data (Yanbao Fu and Vince Battaglia, LBNL)
- Macroscale model averages electrode geometry—how does loss of spatial detail affect predictions?

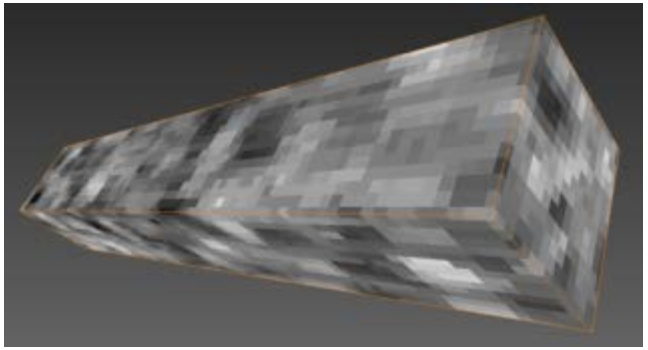


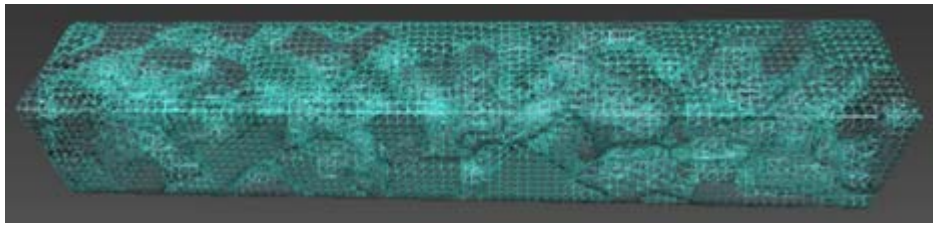


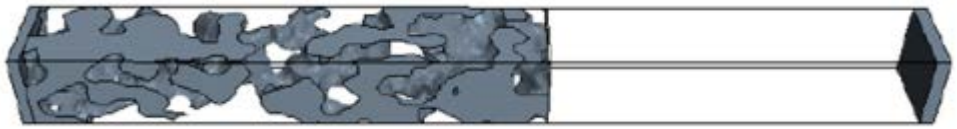


- Compare with microscale models on spatial domains constructed from electrode microstructure

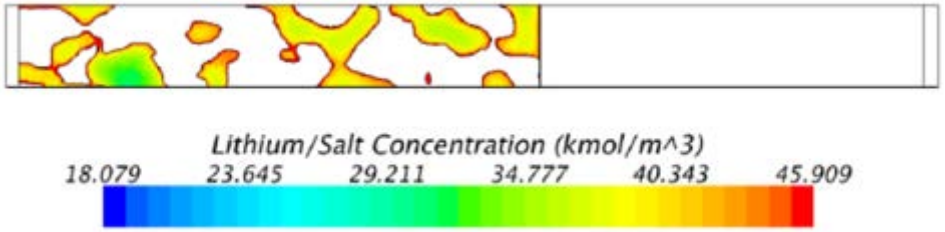
From electrodes to microscale simulation





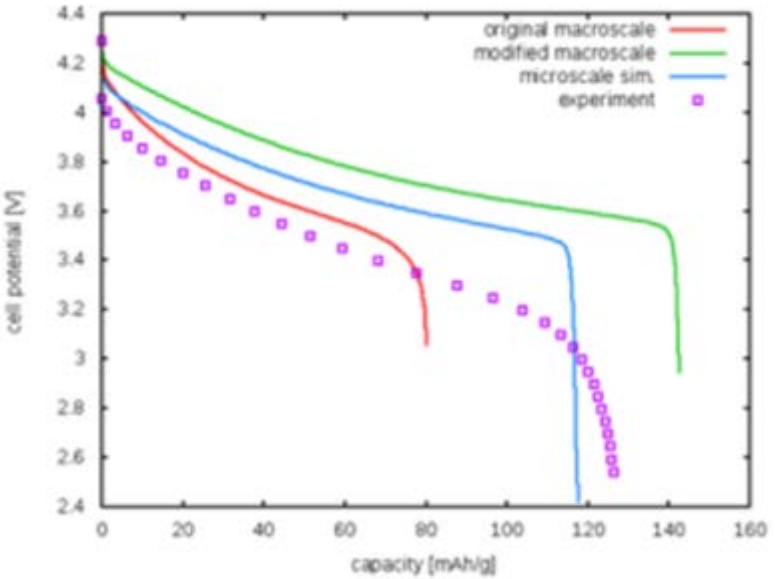


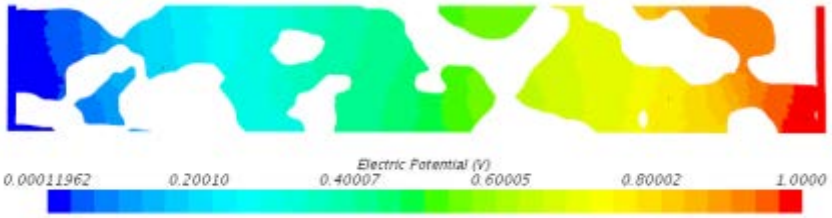
- Electrode microstructure obtained from X-ray microtomography (ALS beamline 8.3.2, Dula Parkinson)
- Electrode samples imaged while immersed in electrolyte solution
- Volume reconstructions transformed into meshed domains
  - Assignment of phase identities based on porosity used in macroscale simulations
  - Direct use of microstructure eliminates macroscale geometric parameters such as porosity, tortuosity, electrode thickness from equations
  - All other parameters taken from macroscale model
  - No fitting parameters in microscale model



Microscale and macroscale models

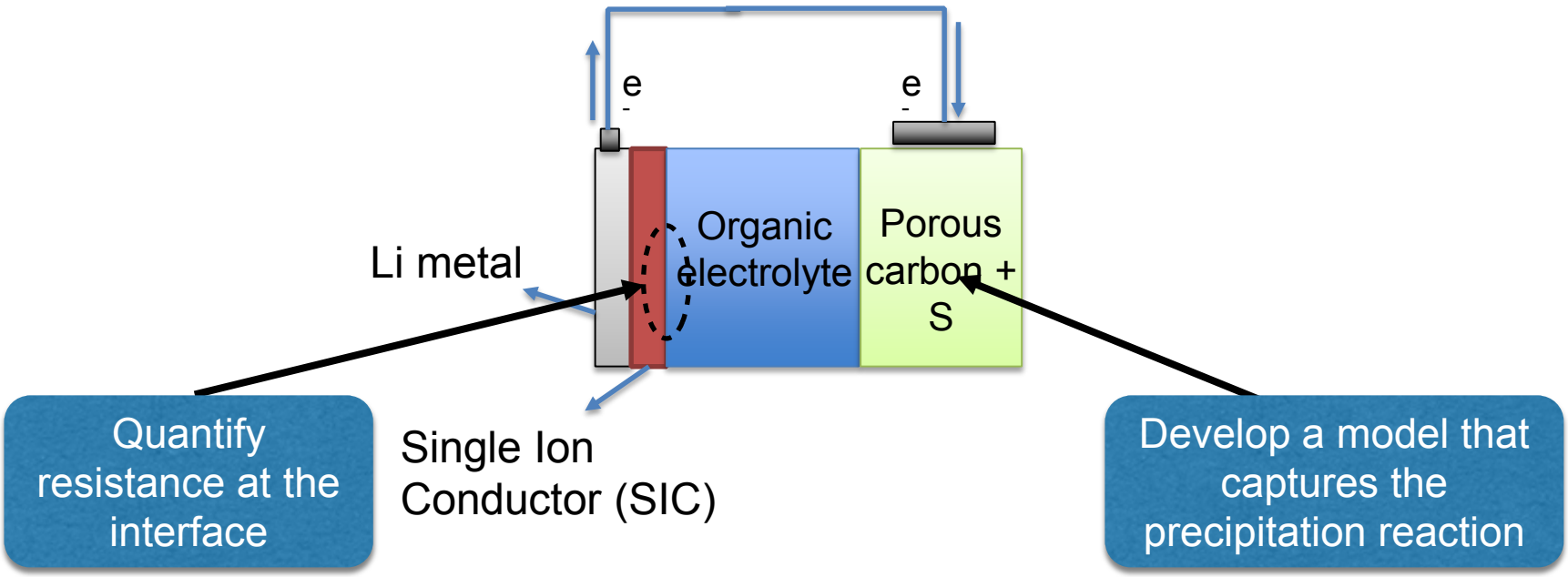
- Microscale and macroscale models show discrepancy
  - Spatial information distinguishes microscale and macroscale models
- Present discrepancy due primarily to limited microscale domain size
- Two macroscale model changes explored to reduce discrepancy
  - Steady-state diffusion problem solved in microscale pore network to obtain tortuosity
    - Replaces Bruggeman's relationship between porosity and tortuosity
  - Porosity gradient obtained by least-squares fit to porosity of individual voxel slices
    - Determined by thresholding and voxel counting



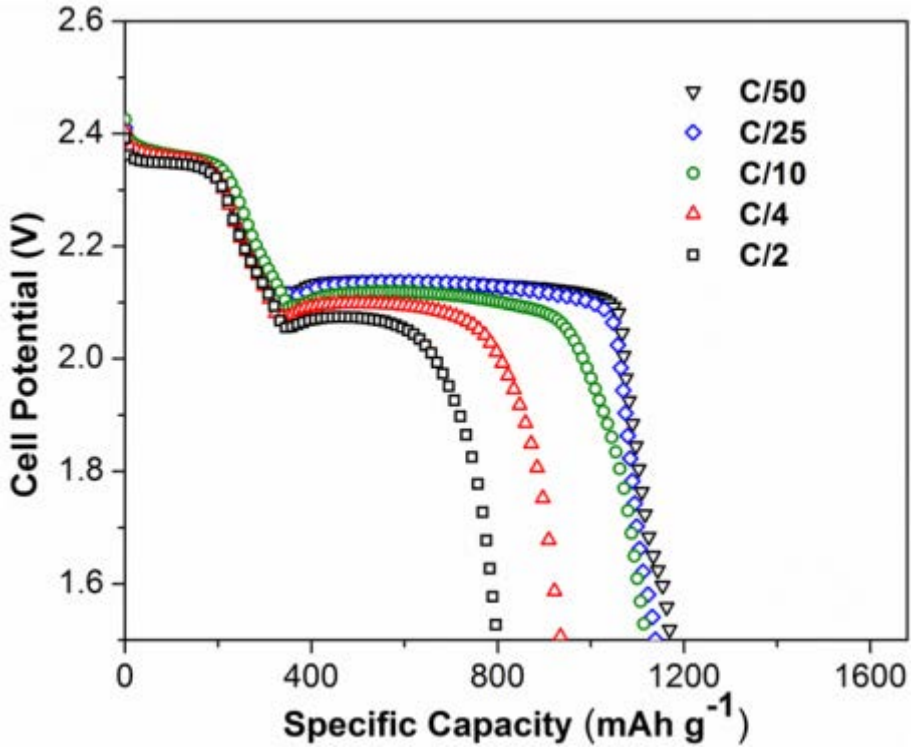


Larger microscale domains needed

Lithium-sulfur: Next-generation storage device?

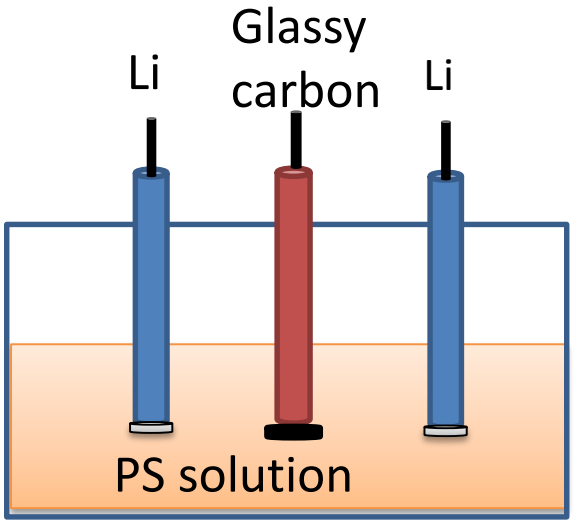


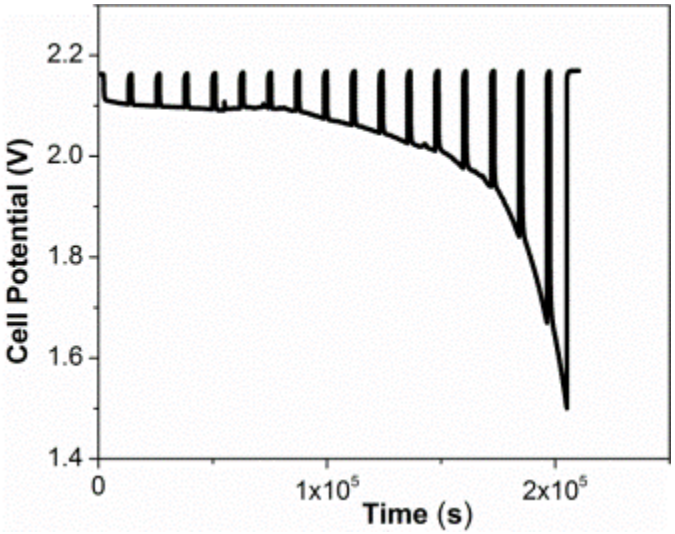
Rate performance of Li-S batteries

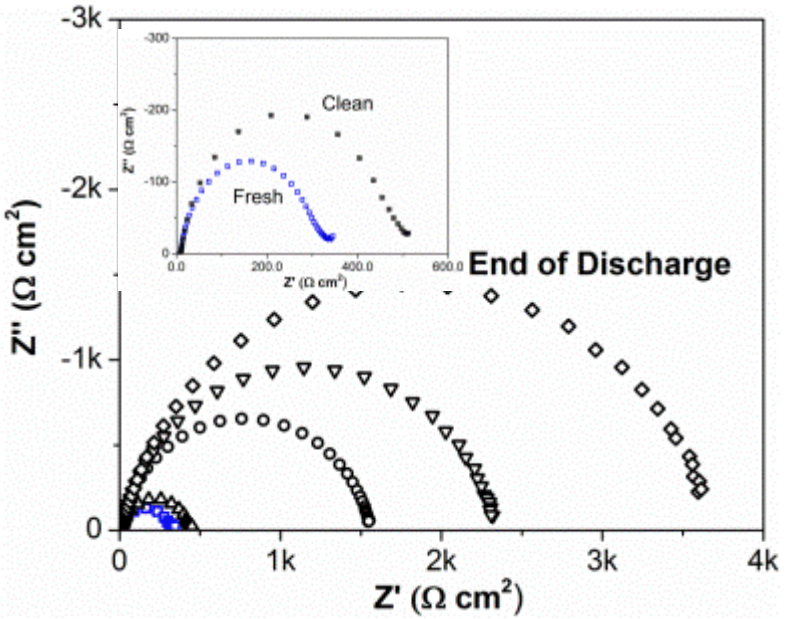


Difference in rate capacity largely due to second plateau

Identifying the resistance sources

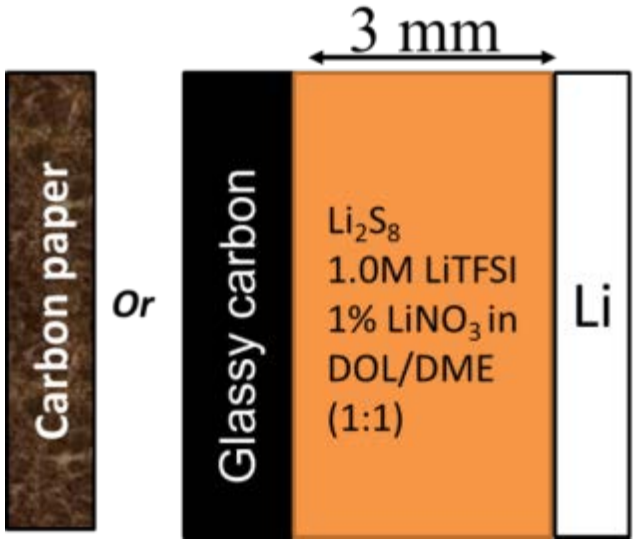


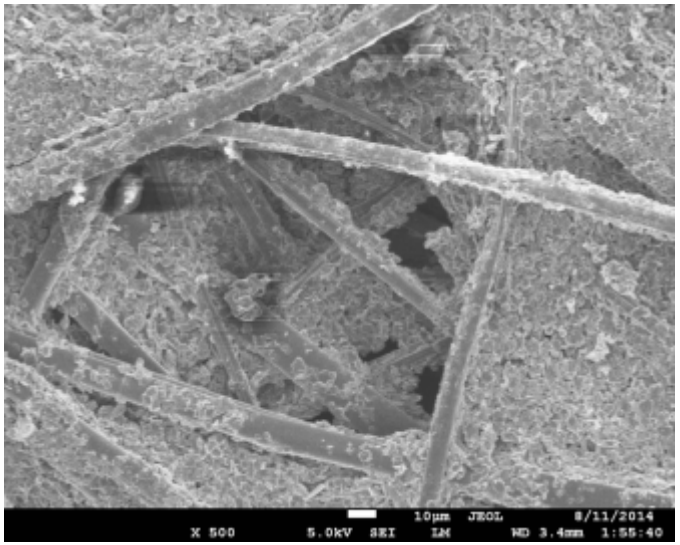


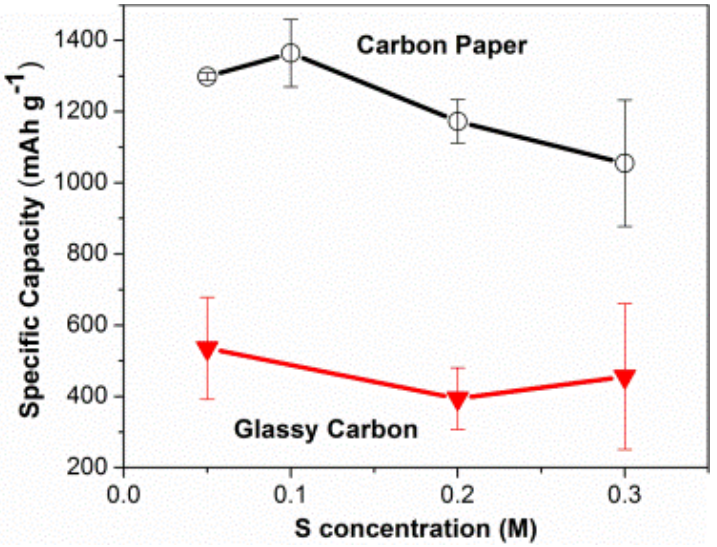


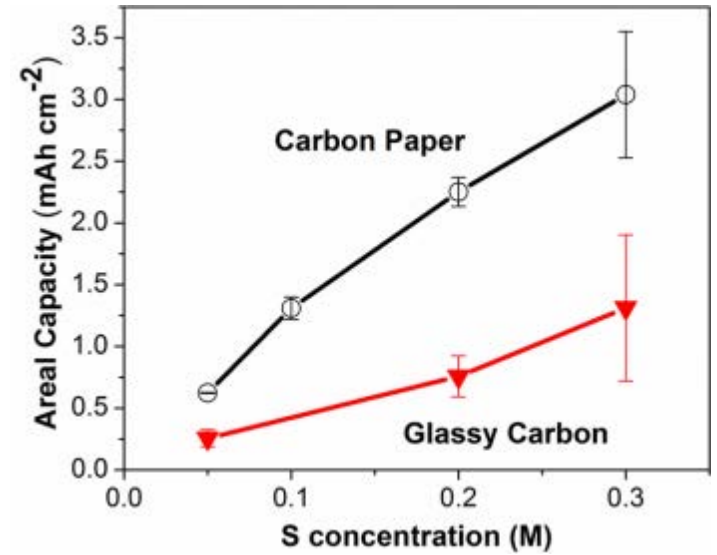
Deposited Li_2S layer increases resistance

Performance limitations in the sulfur cathode



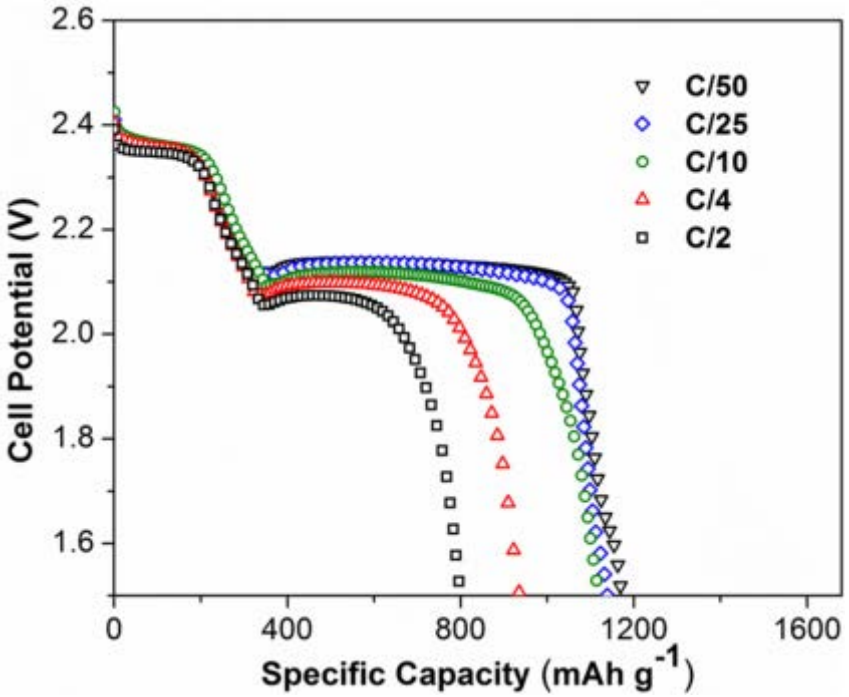


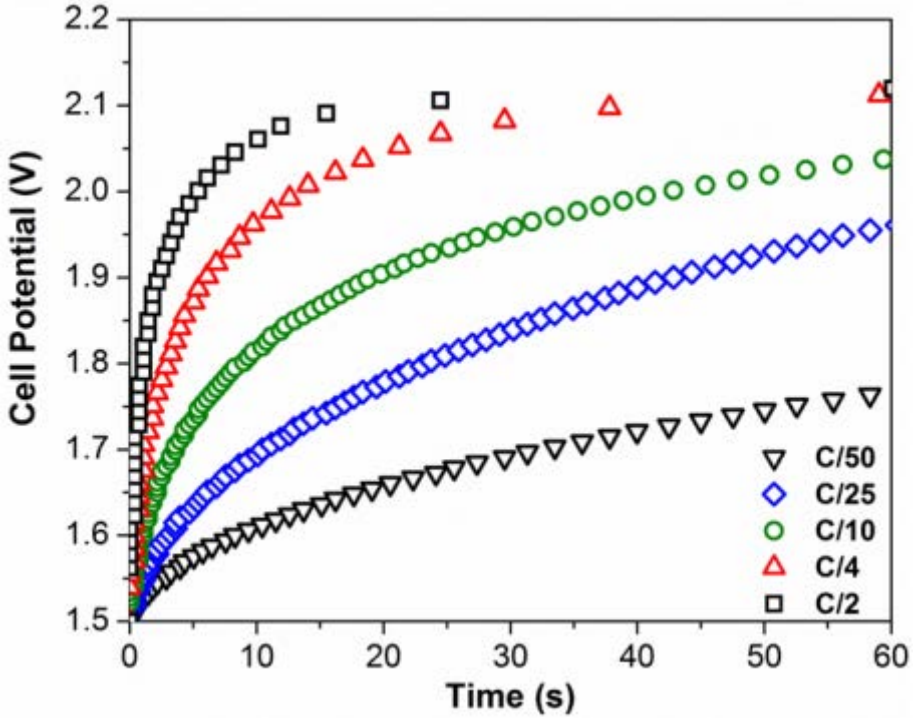




Deposited Li_2S layer plays an important role. Not a simple passivation process with critical layer thickness

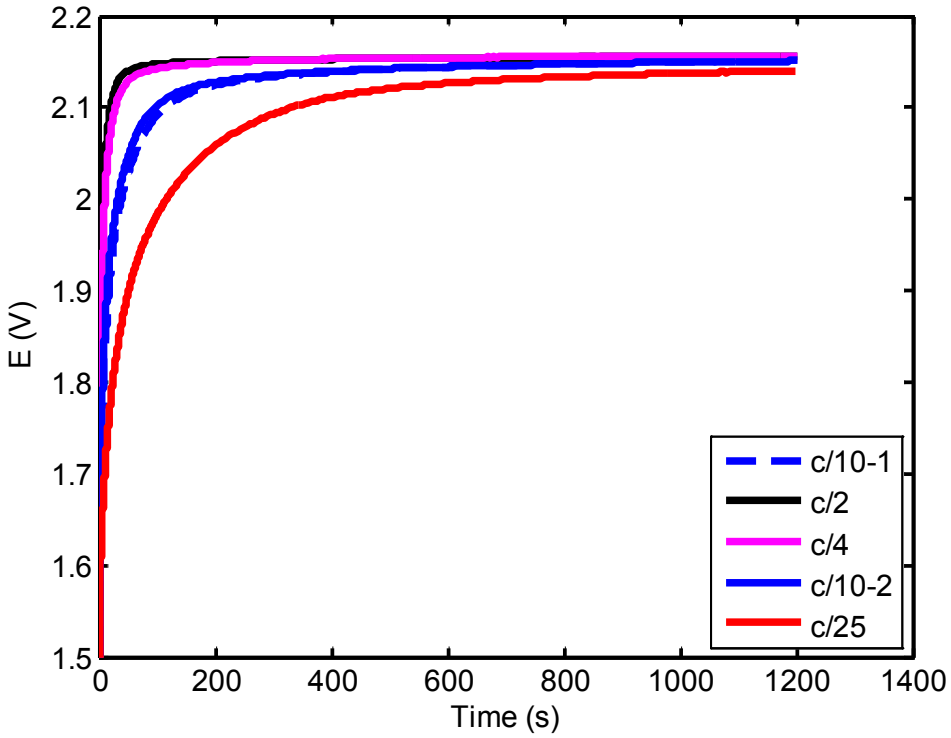
Relaxation behavior of Li-S cells





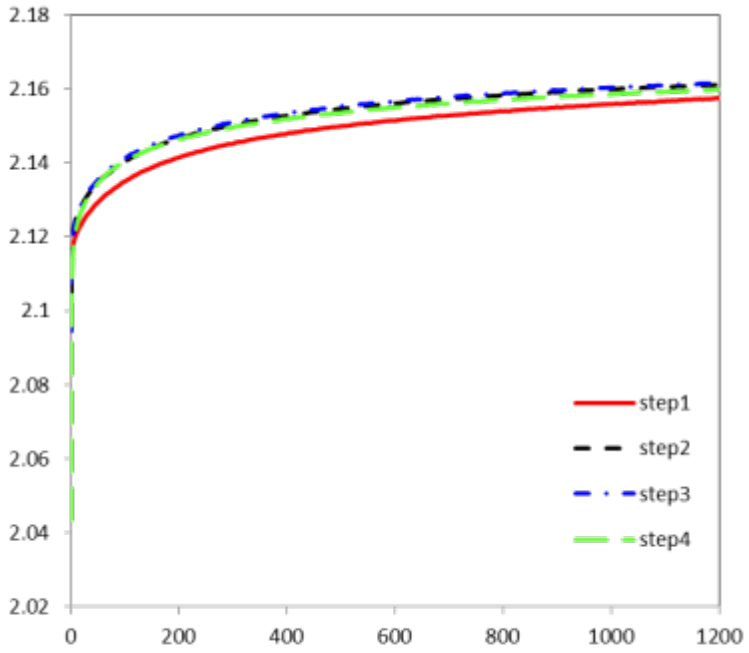
The relaxation kinetics clearly depend on rate of discharge

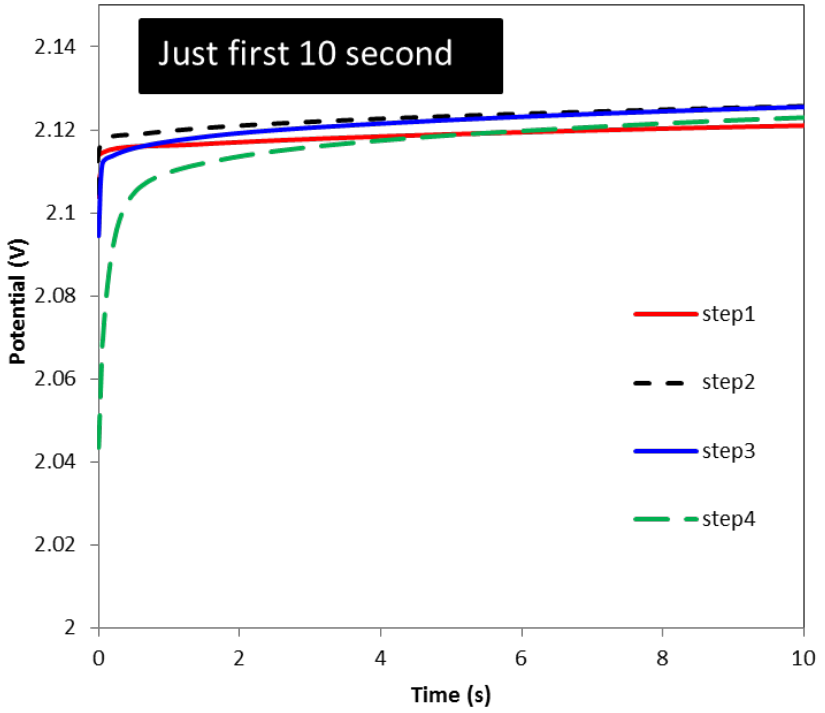
Relaxation behavior: same film thickness



The relaxation behavior is rate-dependent, even with same film thickness

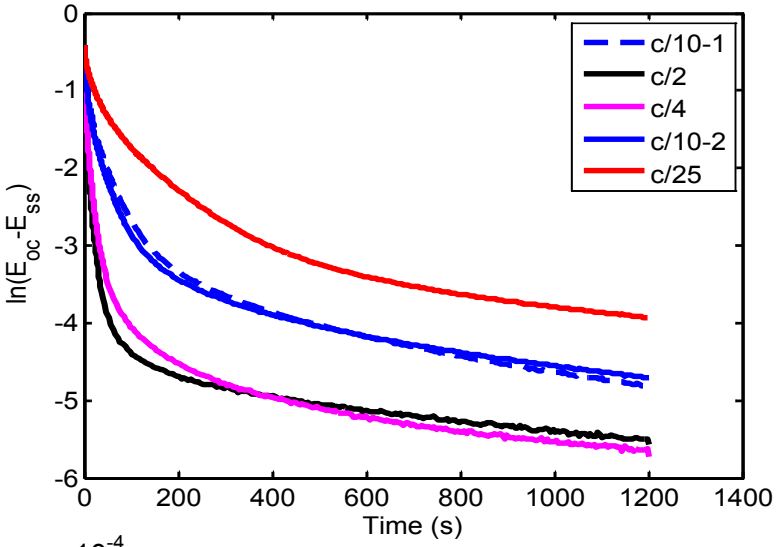
Relaxation behavior: at different SOC

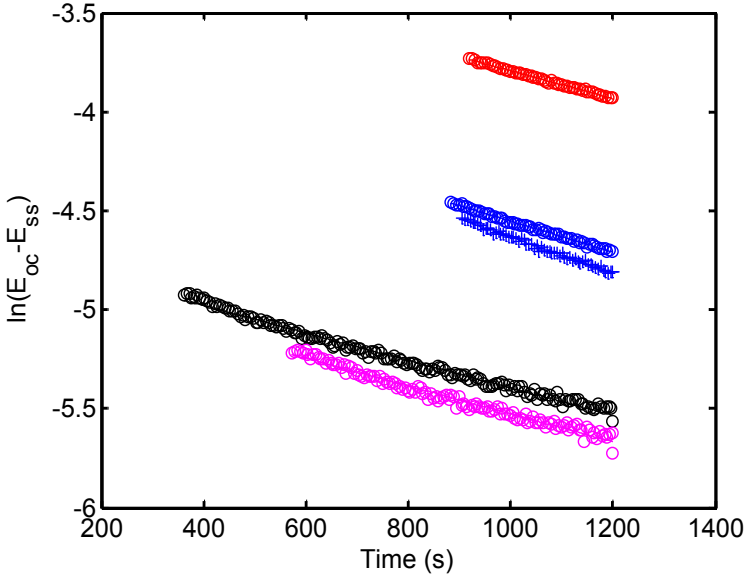


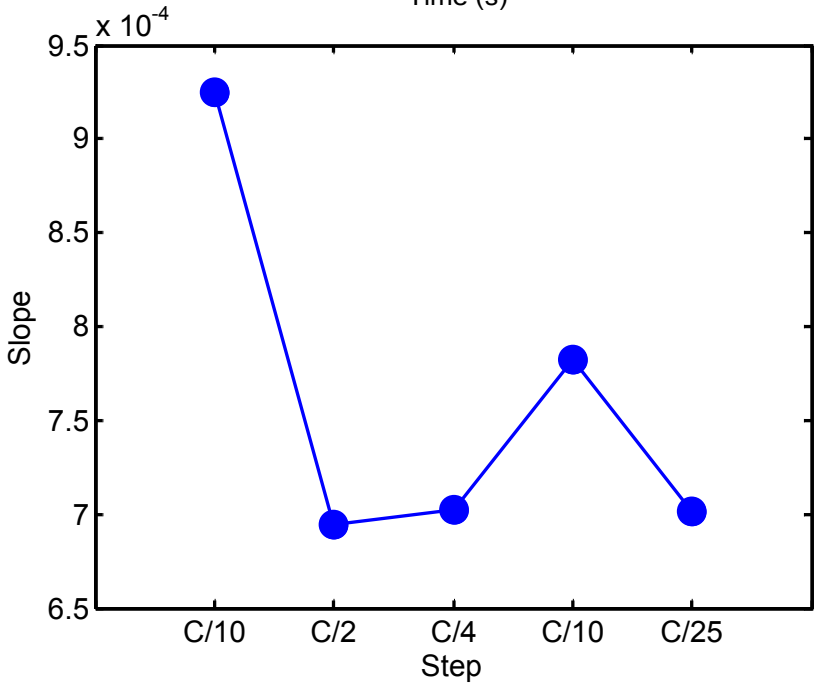


Relaxation kinetics become sluggish only for the lowest SOC (“step4”)

Extract relaxation kinetics



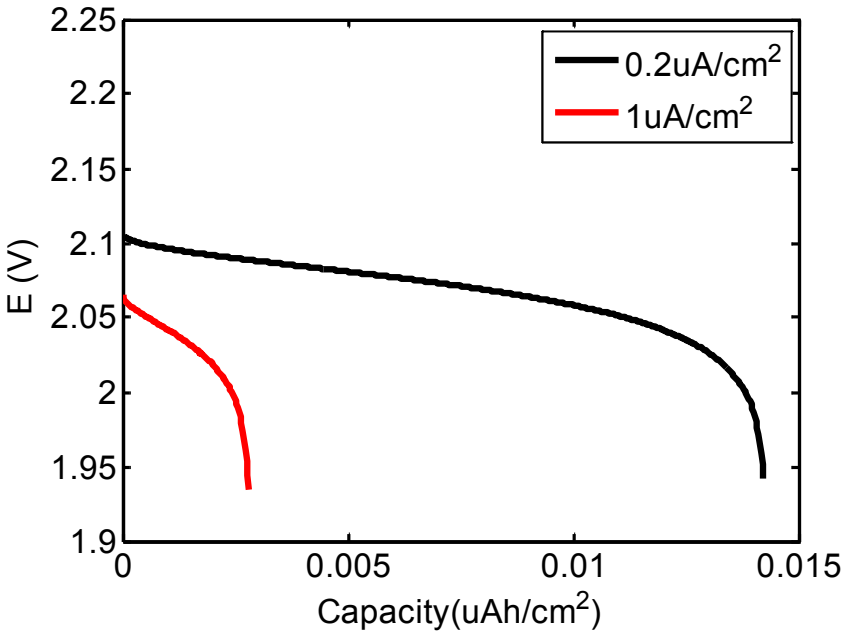


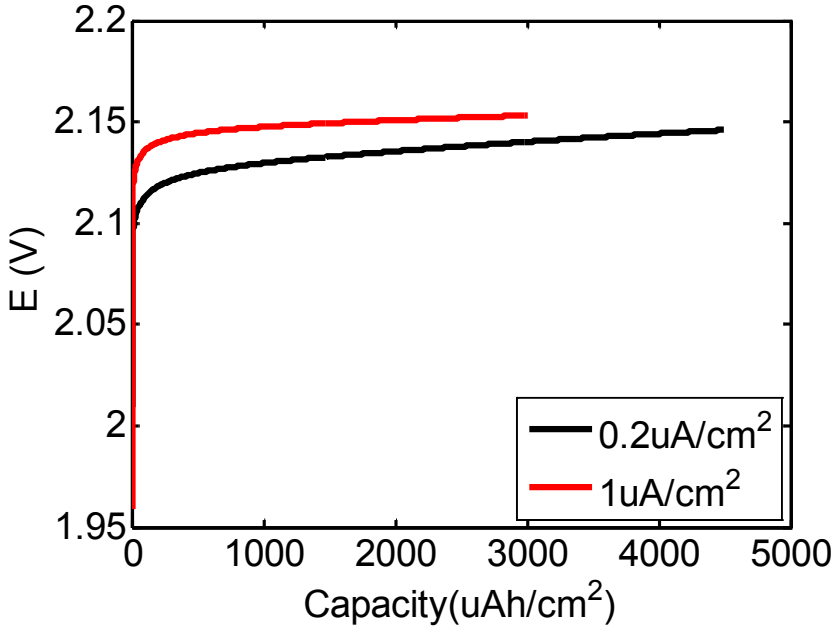


Extract diffusion will be 1x10-18 m2/s by assuming film thickness of 100nm

Simulation based on extracted parameters

- $D_{eff}=D\varepsilon^{Brugg}=10^{-10}\cdot(2.5\times10^{-3})^3=1\times10^{-18}\ m^2/s$
- L=100 nm with C_0=0.3 M

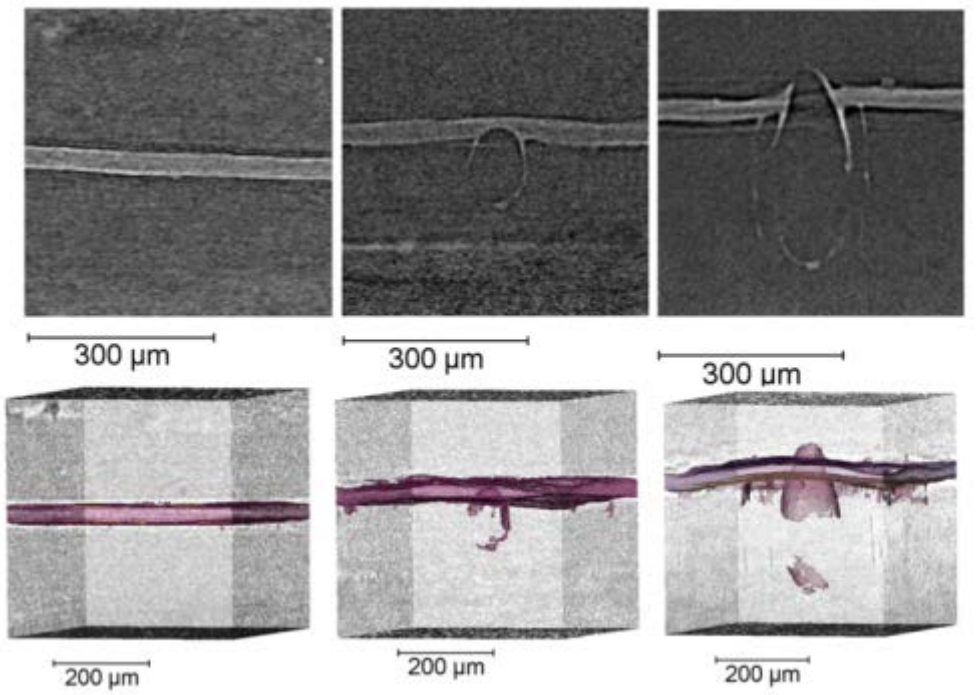




Available capacity limited by slow transport; relaxation behavior is rate-dependent.

Li metal: dendrite growth

- Collaboration with Katherine Harry, Nitash Balsara (UCB and LBNL)
- Li-Li symmetric cells with polymer electrolyte
- *In situ* imaging by hard X-ray microtomography (LBNL ALS beamline 8.3.2, Dula Parkinson)
  - Dendrite growth observed as function of charge passed
  - Dendrites approximately axisymmetric
  - Electrolyte experiences severe deformation
  - Dendrites push through electrolyte and eventually short cell

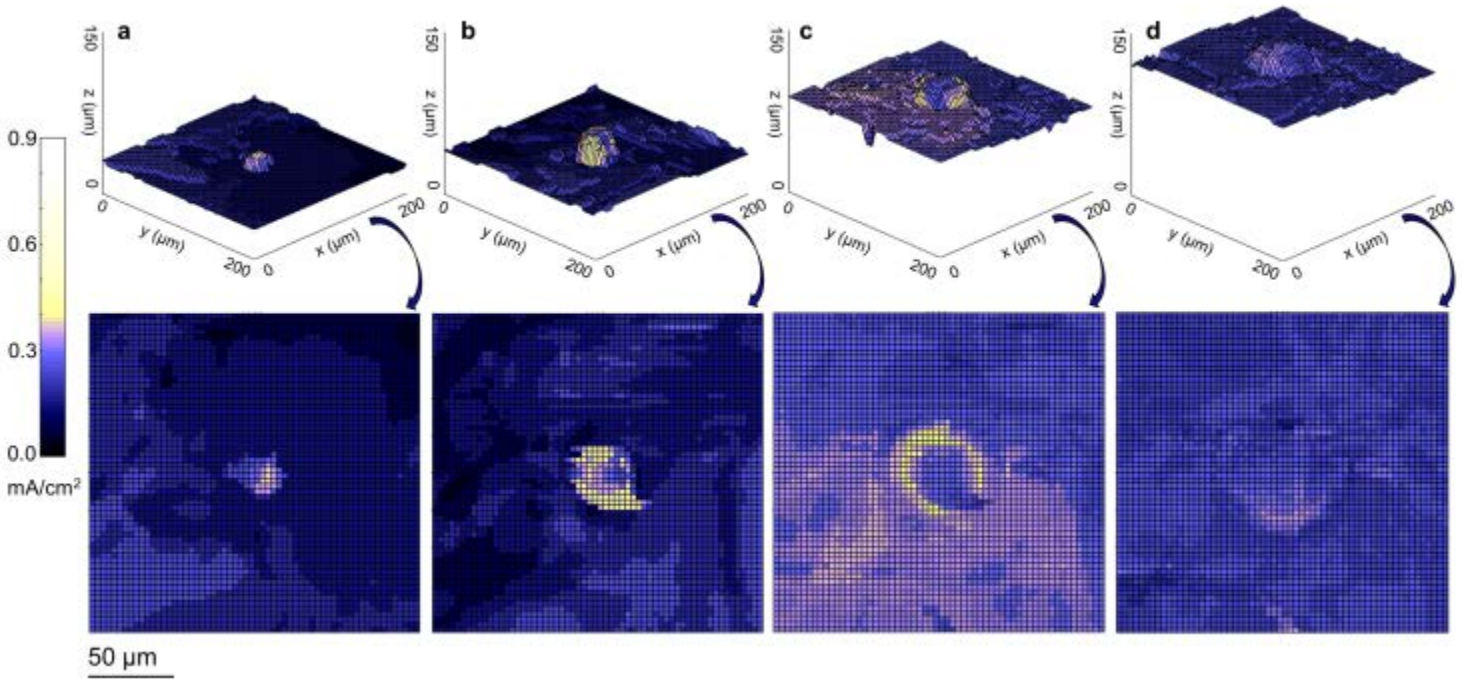


Harry and Balsara (UCB and LBNL)

Dendrite growth experimentally monitored

Li metal: current density

- Continued dendrite stress suggests non-uniform current density distribution
  - Time-resolved tomography data allows estimation of spatial distribution of current density (Harry and Balsara)

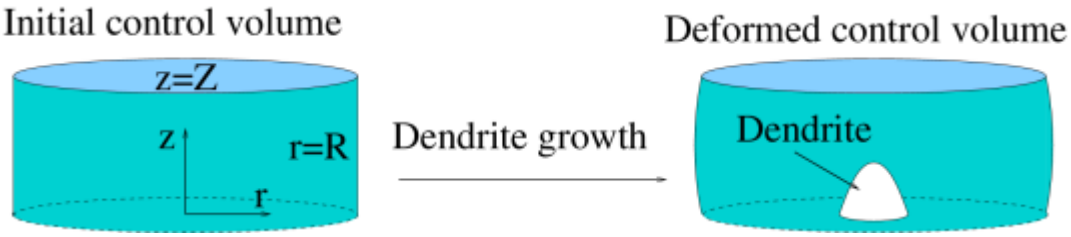


Harry and Balsara (UCB and LBNL)

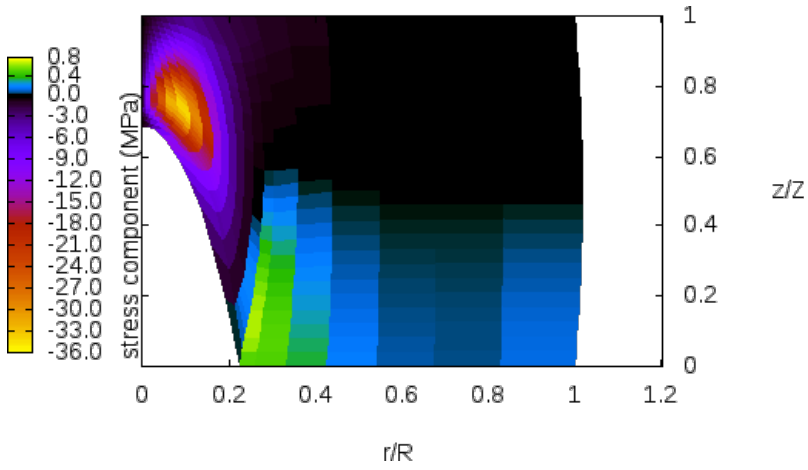
What factors influence current density/dendrite growth?

Li metal: mechanical stress

- Electrolyte deformation due to dendrite growth suggests stress buildup
  - Strain energy expected to influence reaction rates
  - Dendrite/electrolyte interface locations extracted
  - Electrolyte shear modulus measured experimentally (Harry and Balsara)
  - Dendrites approximately axisymmetric



  - Mechanical stress model developed for cylindrical electrolyte region around dendrite
  - Adapted from our large-deformation silicon/binder model (Higa and Srinivasan, 2015), using open-source PyGDH software package https://sites.google.com/a/lbl.gov/pygdh/



Stresses appear to influence dendrite growth

Responses to Previous Year Reviewers' Comments

The project received uniformly positive responses

- The reviewer said that the PI has an excellent approach where relevant problems are attacked in a number of areas important to advanced battery development. The reviewer noted that approach has a good marriage between modeling and experimental work
- The reviewer stated that the simulation work at cell level for the Li-S battery is inspiring
- The reviewer commented that good collaboration is that best blend of theoreticians and practitioners.
- The reviewer said that future work includes broad selections of systems and tools.
- The reviewer noted that the project provides a deep understanding and guidance for the potentially high-energy systems.

Collaboration and Coordination

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

Remaining Challenges and Barriers

- Microstructure model:
  - Need more accurate resolution of phase identity
  - Need to consider much larger problem domains requiring much more computational time

- 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.)

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

Summary

- Microstructure models may allow better predictions compared to the macro-homogeneous approach
  - Sufficient spatial resolution eliminates need for porosity and tortuosity
  - Larger simulation domains needed for accurate results

- 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