Performance and Degradation Modeling of Li-ion Batteries

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Lawrence Berkeley National Lab

OVT Merit Review

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Project ID # **ES086**

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start date: October 2008
- Project end date: September 2012
- Percent complete: 75%

Barriers

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

Budget

- FY09: $400k
  - 0.4 FTE Scientist
  - 1.5 FTE Postdoc
- FY10: $400k
  - 0.2 FTE Scientist
  - 2.0 FTE Postdoc (V. Boovaragavan, S. Renganathan)

Partners

- Vince Battaglia
- Gao Liu
- Tom Richardson

} LBNL

- Pradeep Guduru (Brown U.)
- UC-Berkeley Microlab
- Enovix Inc. (formerly *micro*Azure)

Objectives

1. Develop a model to examine the effect of particle size distributions in a flat potential system (*e.g.,* $LiFePO_4$)
   - How is the lithium distributed in the particles?
   - What impact does the distribution have on the rate capability?

2. Develop a performance model for silicon anodes.
   - How do we design a porous electrode to accommodate the large volume change?
   - What is the energy density of the system in comparison to graphite?

3. Develop a mechanical degradation model
   - What impact does the binder have on the electrode degradation?
   - How important are cycling profiles in predicting degradation?
   - What are the failure modes in materials such as graphite and silicon?

4. Develop a mathematical framework to describe battery particles that consist of primary particles agglomerated into secondary particles

Milestones

• Quantify the improvement in cycle life, if any, of silicon thin-film with and without a layer of copper and find the optimum copper thickness to enhance life (Jan 2010)

Completed

• Identify conditions (i.e., current, particle size etc.) under which $Li_{15}Si_4$ forms during charging of silicon anodes (July 2010)

Completed

• Develop model for the Si/NCM system to compare to the baseline (Sept 2010)

Completed

• Compare the performance of the Si/NMC system with the baseline high-energy system and quantify the improvements under PHEV conditions. (Jan 2011)

Completed

• Extend the mechanical degradation model developed for graphite anode to include volume change and pressure diffusion and report on the possible failure modes (March 2011).

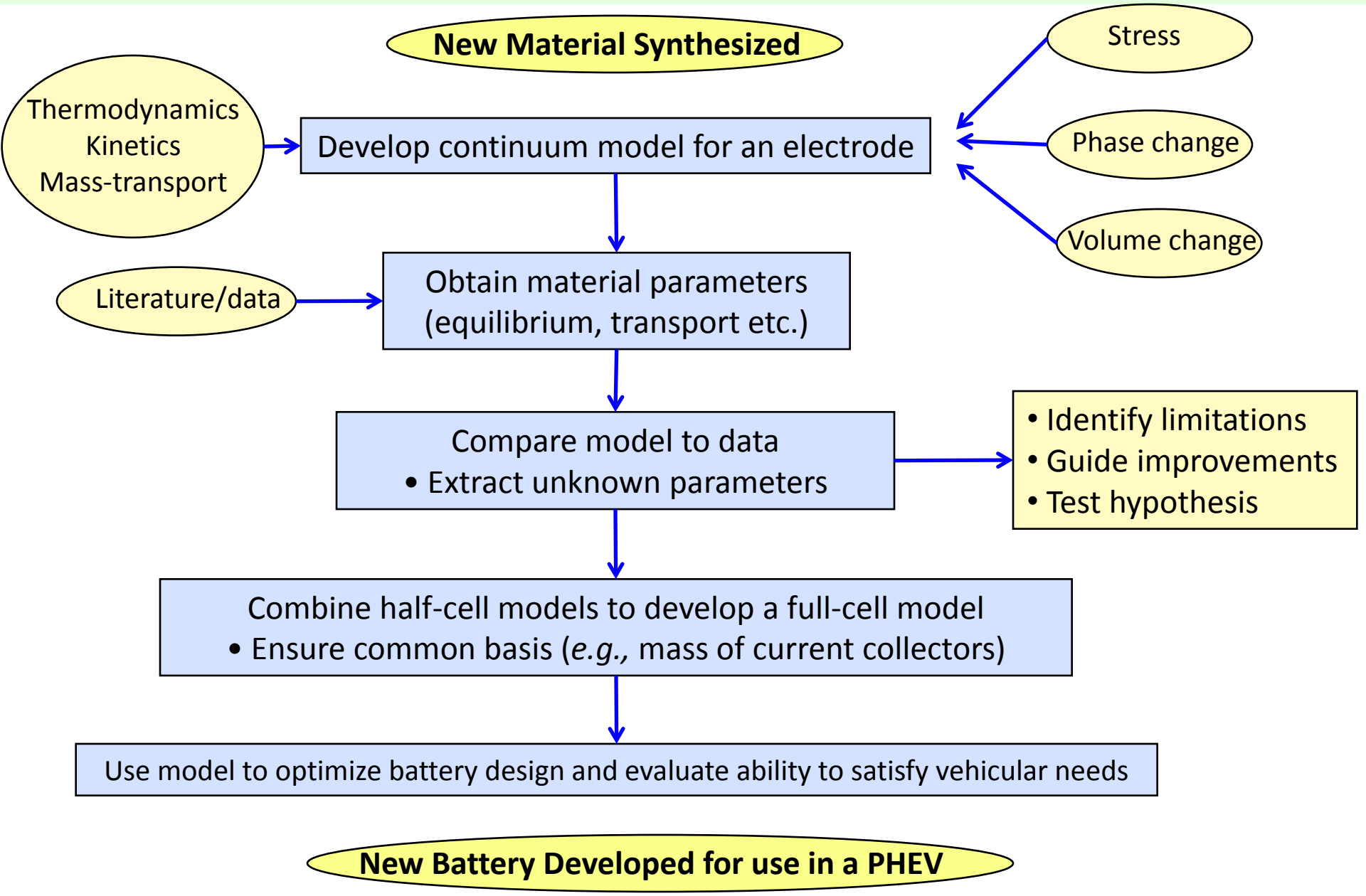
Completed

• Extend the silicon model to include the effect of mechanical stress and interaction of active material and binder and report on the effect of different binders on degradation. (Sept 2011)

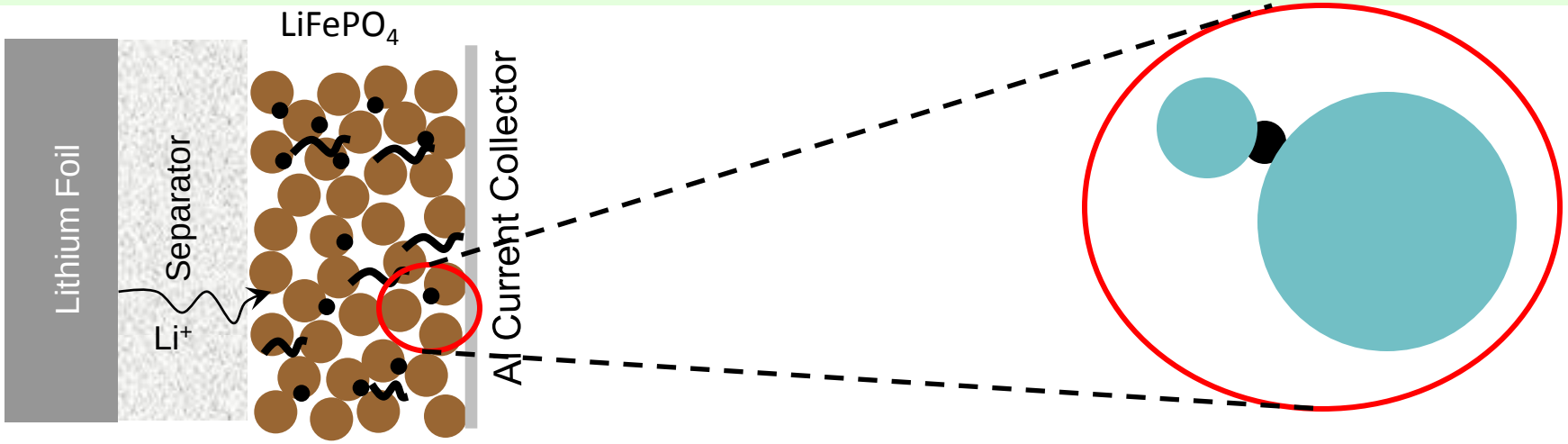
In Progress

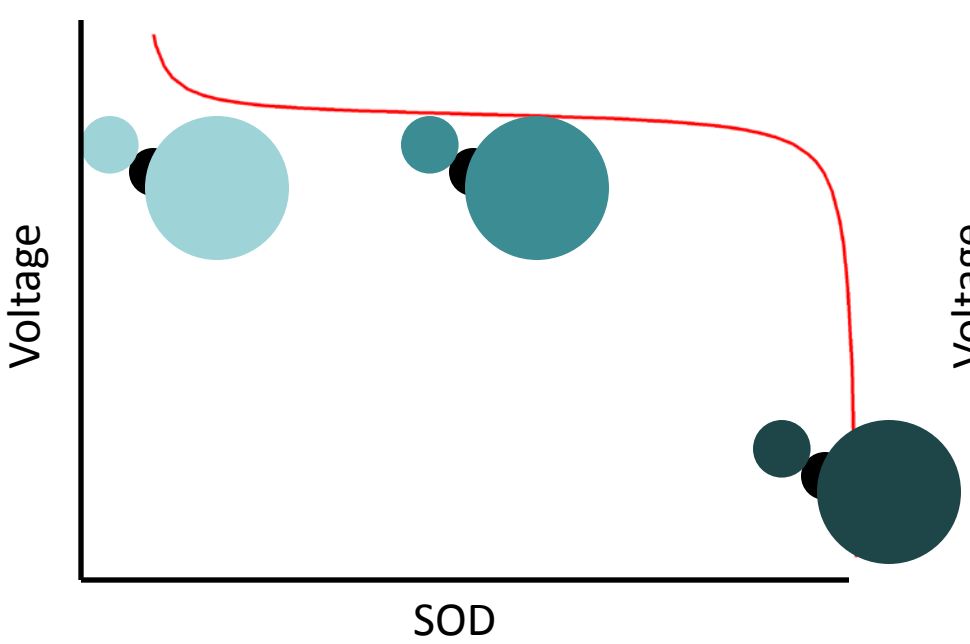
Sept 2009 Sept 2010 Sept 2011

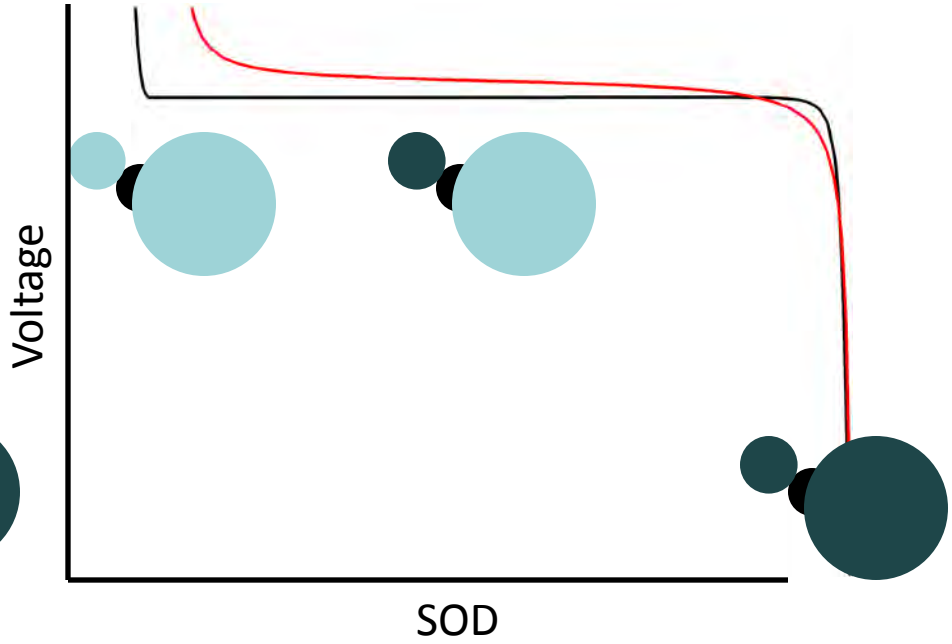
Approach


New Material Synthesized
Thermodynamics
Kinetics
Mass-transport
Develop continuum model for an electrode
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
• Ensure common basis (*e.g.*, mass of current collectors)
Use model to optimize battery design and evaluate ability to satisfy vehicular needs
New Battery Developed for use in a PHEV

Particle-size Effects and Flat Potentials



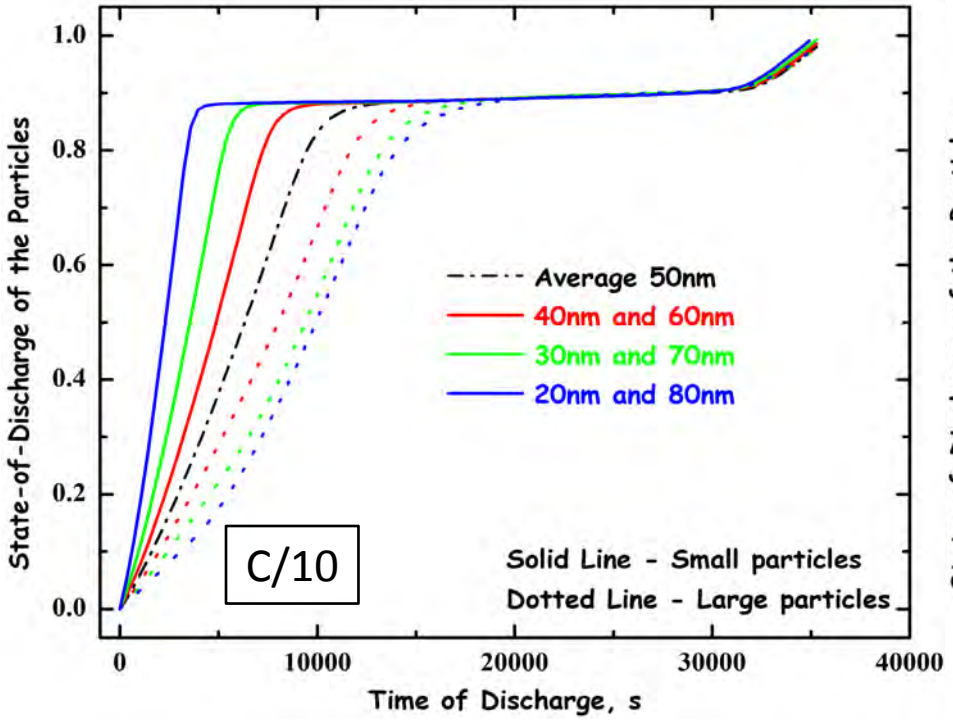


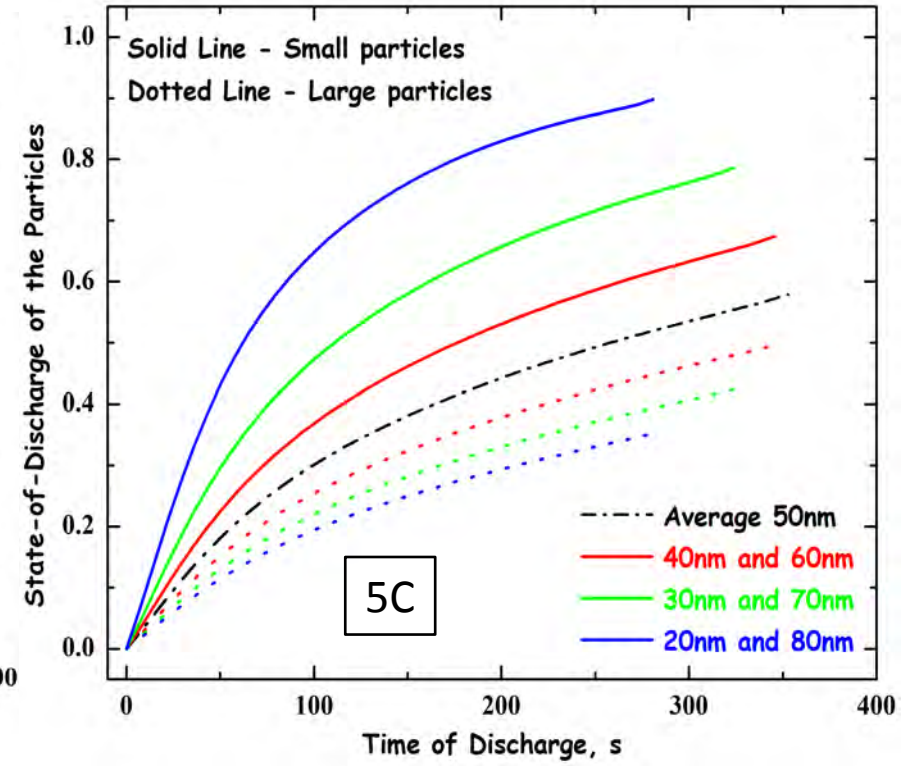


Disparity can exist in lithiation amount between particles of different sizes

Effect of Particle Size Distribution

Case Study using properties similar to $LiFePO_4$



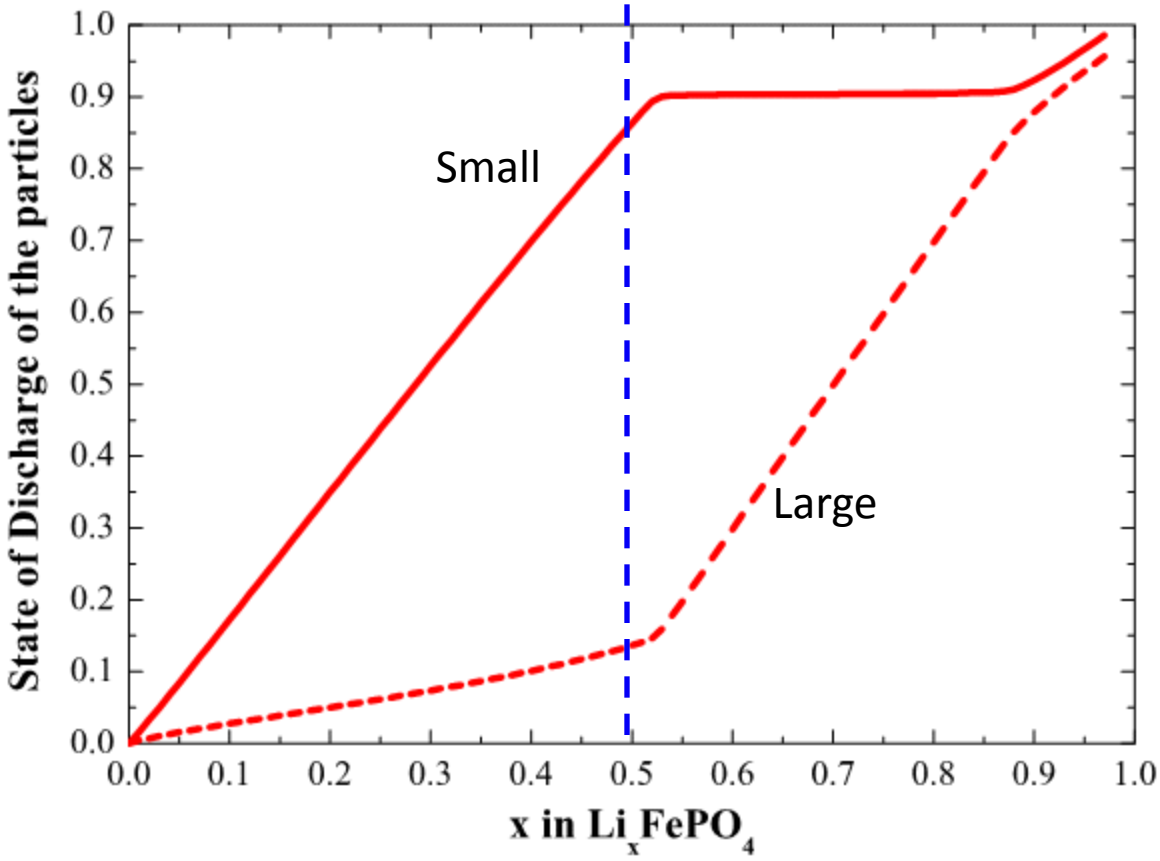


Small particles lithiate until single-phase region; large particles then "catch up"

Transport losses result in deviation from the flat potential; less disparity in lithium content

Disparity in SOC depends on rate and on the size distribution

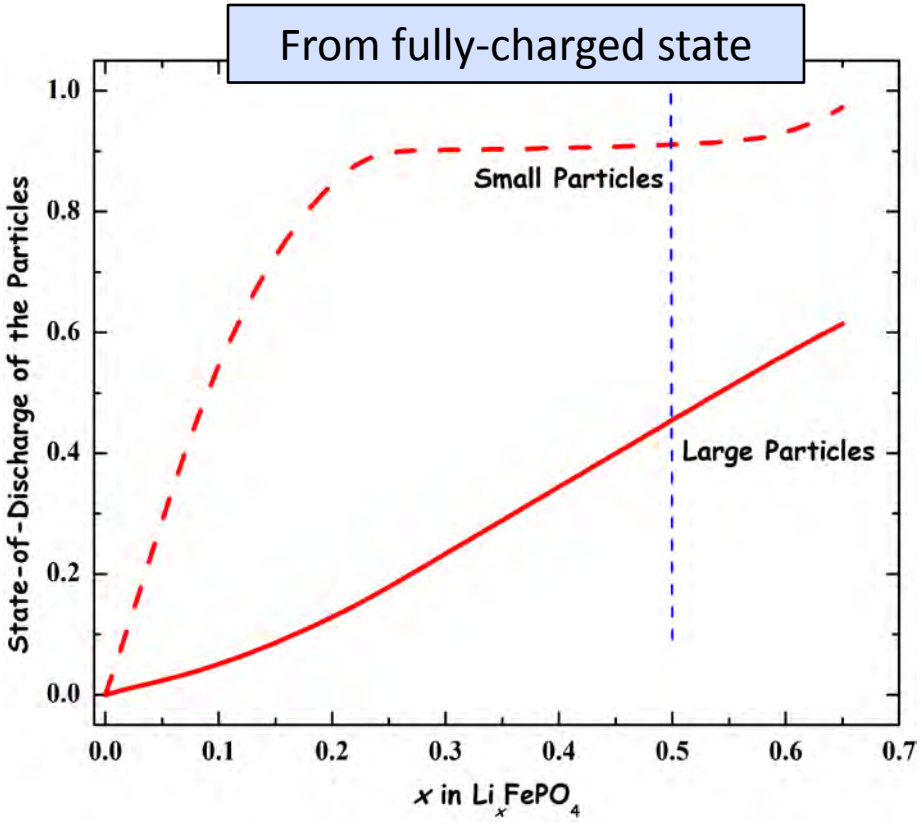
How Wide Can the Disparity be?

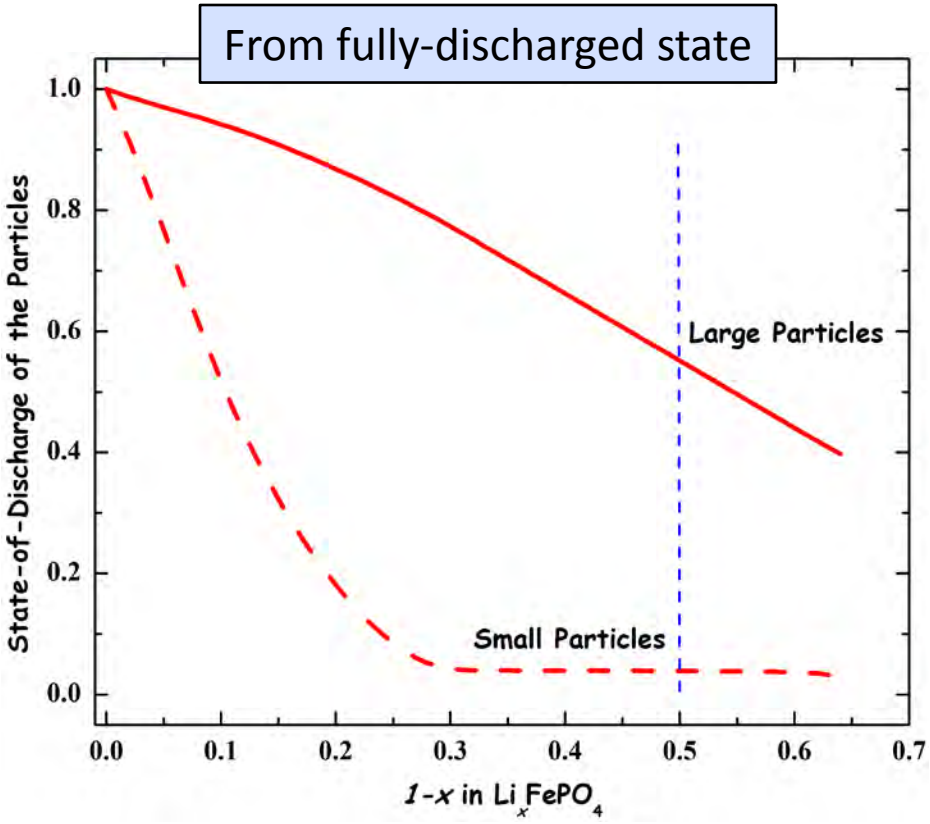


- Under certain conditions, wide disparity can exist between the small and large particles
  - Small particles can be at a “discharged” state when the large particles are “charged”

What is the consequence of this disparity?

Path Dependence



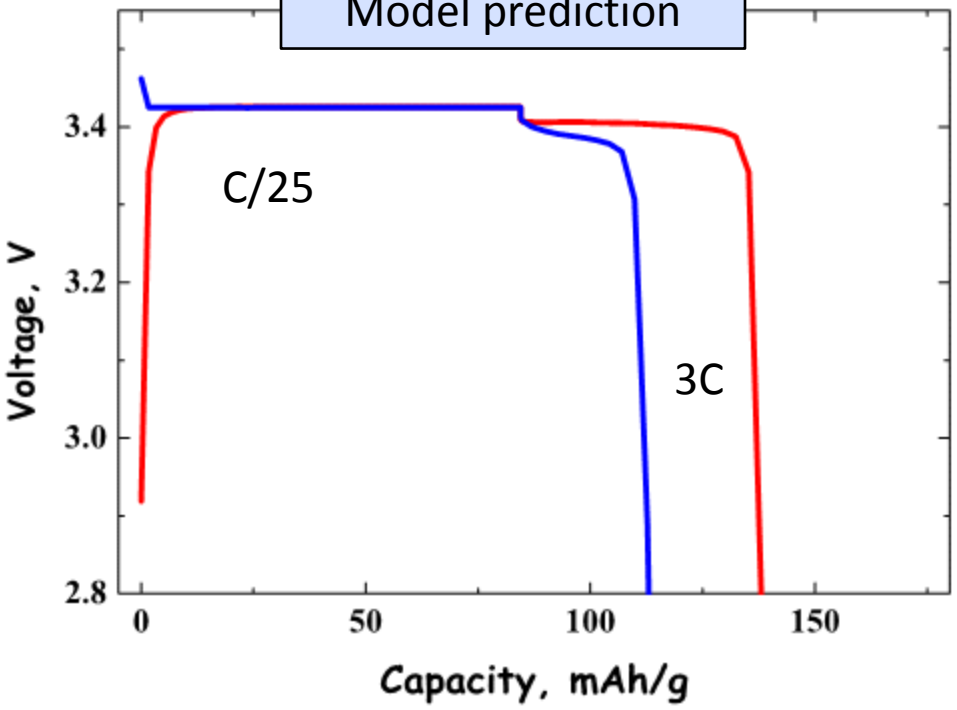


- At 50% SOC, the extent of lithiation depends on the path

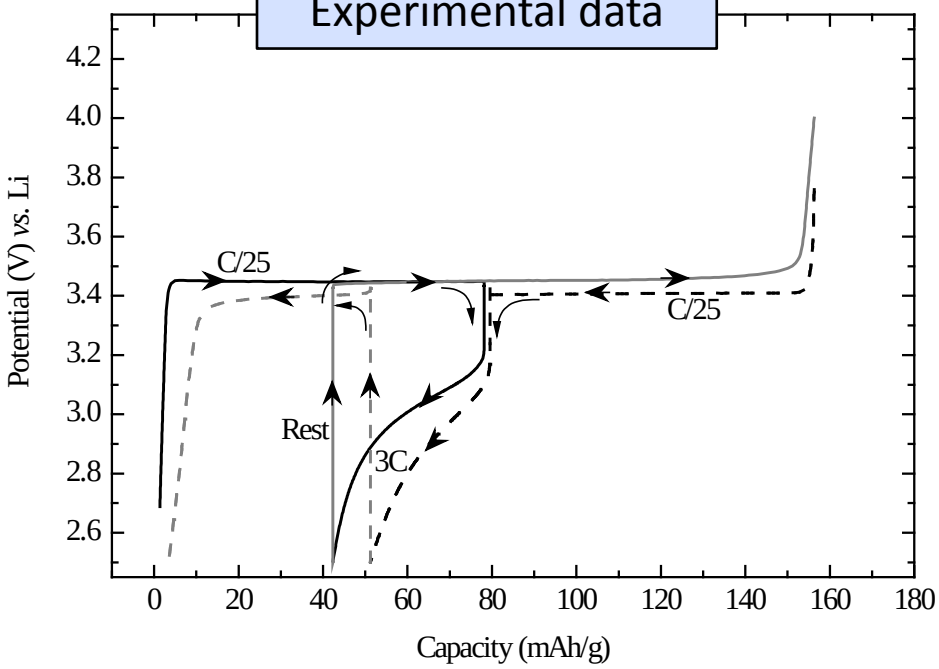
What is the impact of this path dependence?

Impact of Path Dependence

Model prediction



Experimental data



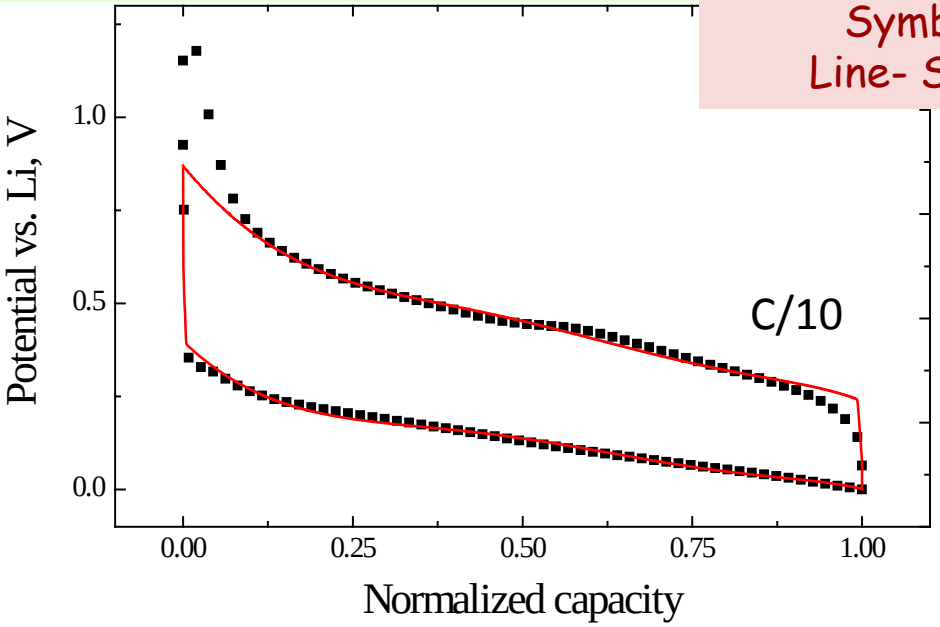
Srinivasan and Newman, Electrochem. Solid-State Lett. 9 A110 (2006)

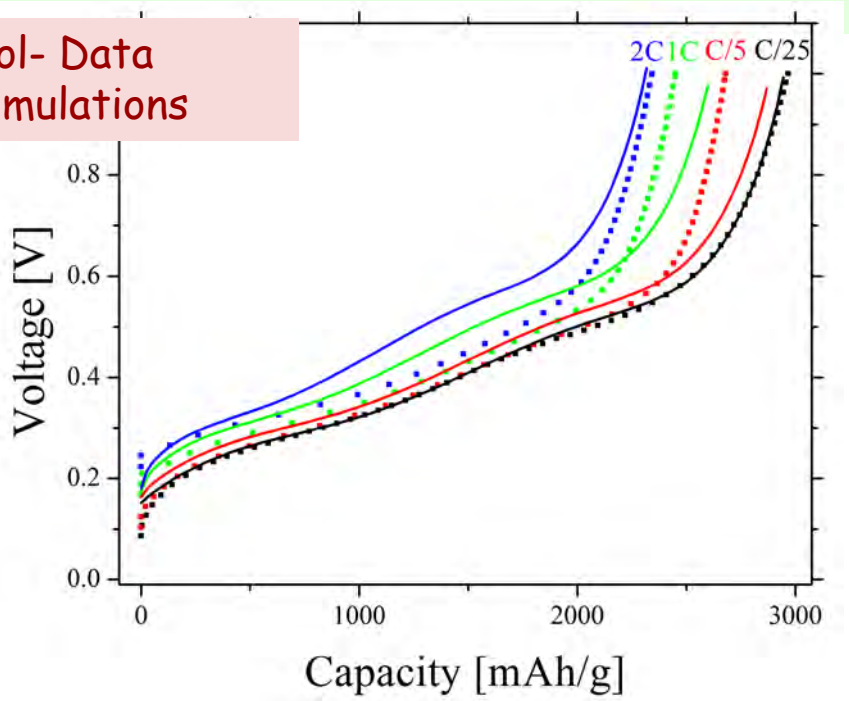
- Path dependence leads to difference in capacity depending on the cycling history
- Difference in capacity depends on particle size distribution and rate.

Path dependence will complicate battery management

Background-Modeling Silicon Anodes

Symbol- Data
Line- Simulations





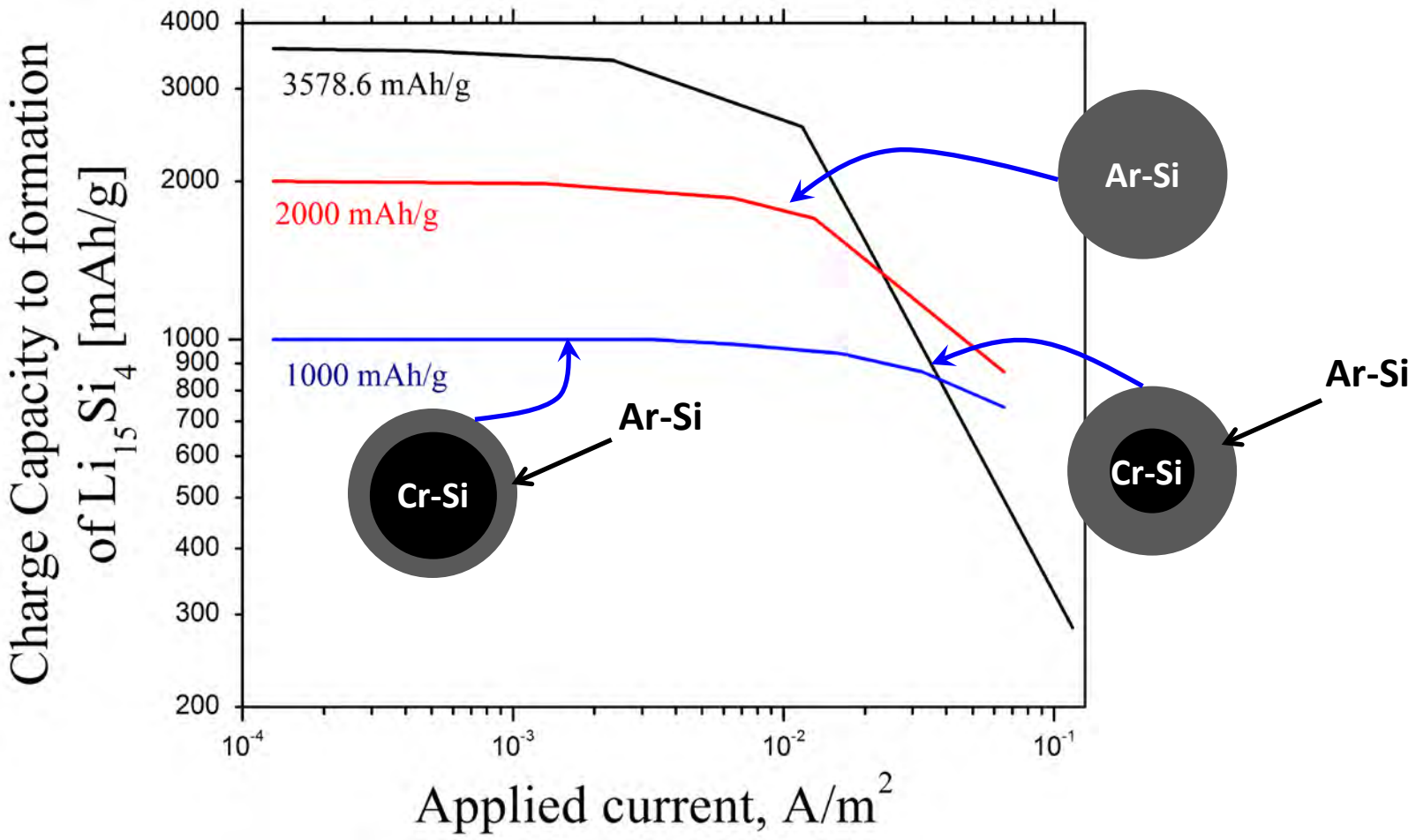
Modeled low-rate hysteresis

Developed a porous electrode model

- Model include volume change in the particles and the associated porosity changes
- Silicon phase diagram taken into consideration
- Anode matched with a NCA cathode (80 μm, 35% porosity)

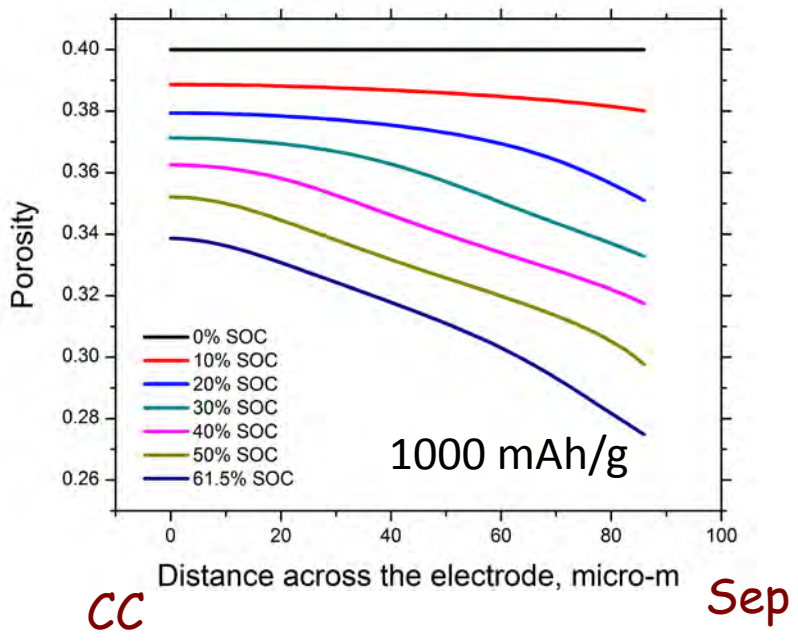
Designing a silicon anode starts with modeling the charging process

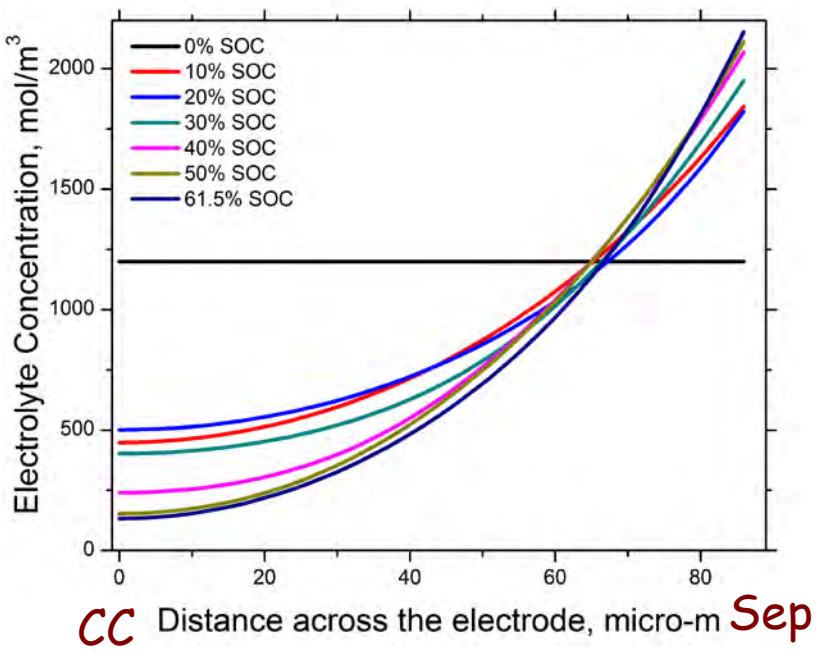
Technical Accomplishments- Considerations on the Particle scale



Capacity obtained determined by extend of cycling and by charge rate

Considerations on the Electrode Scale

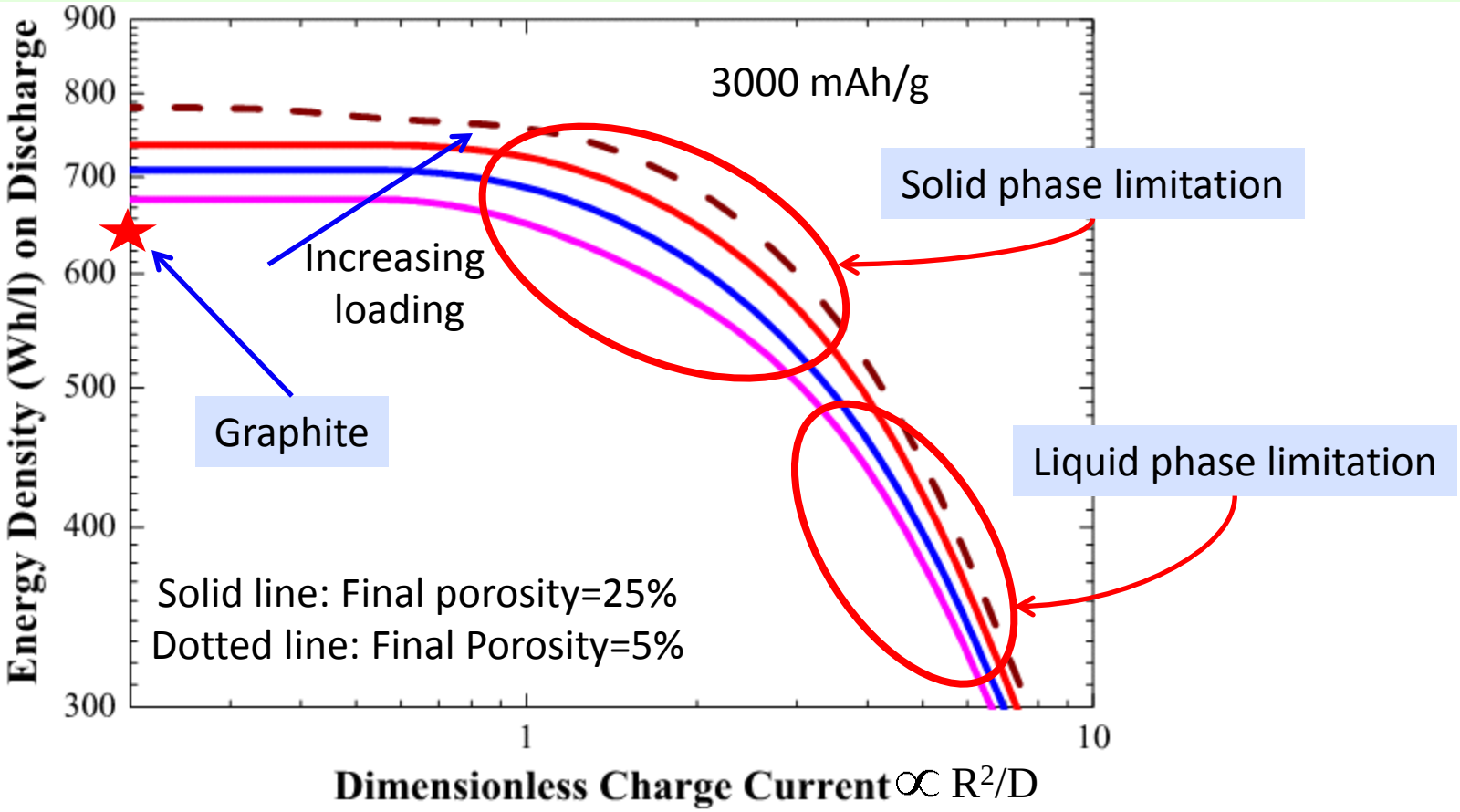




- Capacity of anode matched to cathode
- Assume that final porosity (fully charged state) to be 25% to sustain discharge pulses
- Reaction distributions across porous electrode lead to clogging of the pores and result in electrolyte transport losses.

What is the impact of particle-level and electrode-level issues on the energy density?

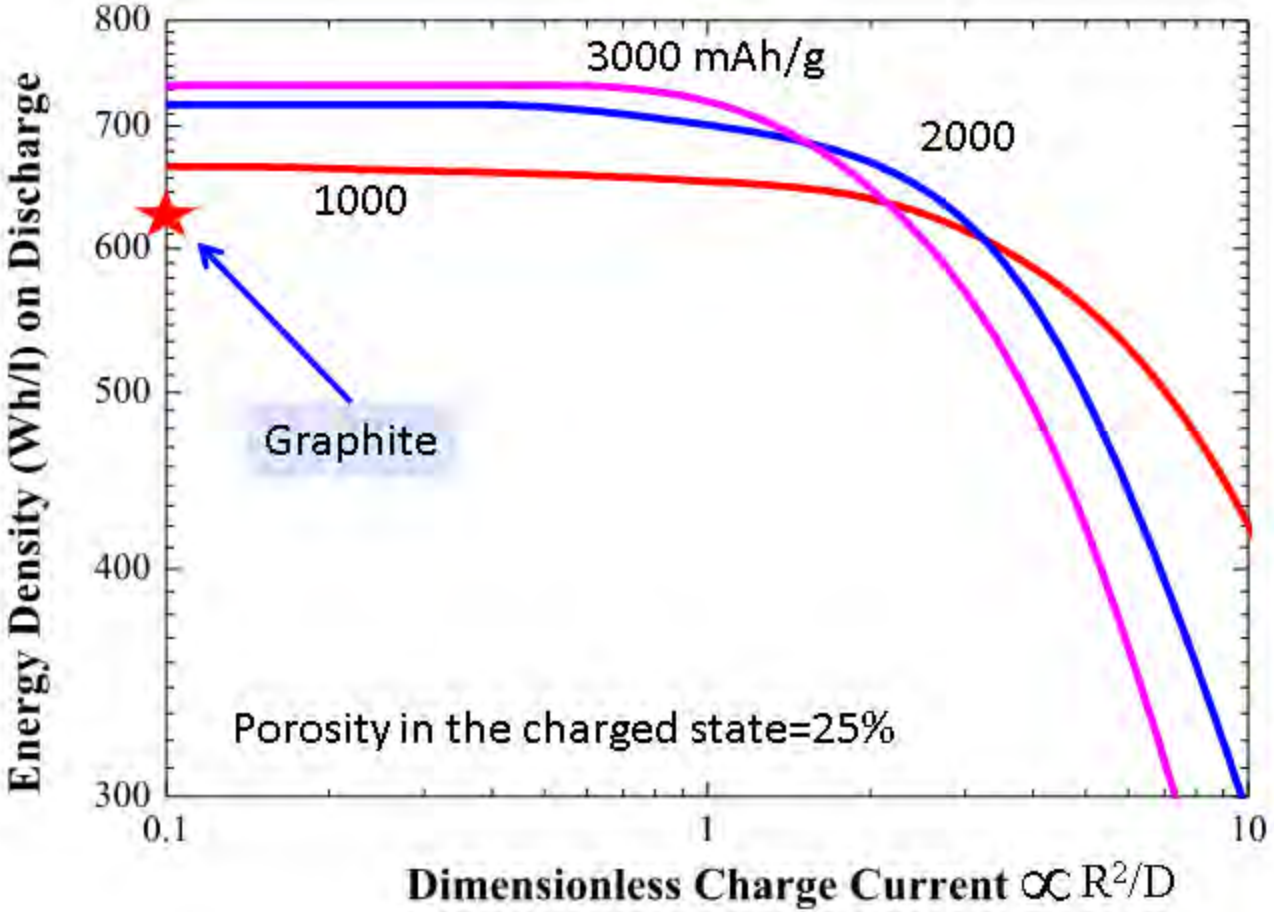
Energy Density Comparison-Loading of Si



- Energy density of a cell level (does not include all header space, tabs, and packaging)
- Energy density improvement of silicon anodes depends on the design

Rate of charging of the anode impacts the volumetric energy density

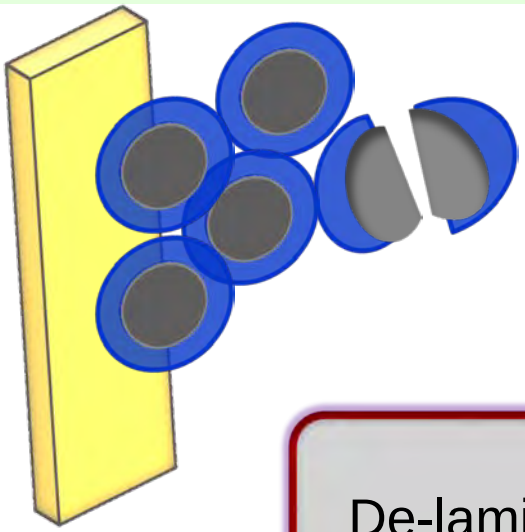
Energy density with Cycling Capacity



- Cycling range should be dictated by the design requirements.
- Volumetric energy density can be maximized by proper design.

Model provides a means of identifying the design to maximizing energy for a given application

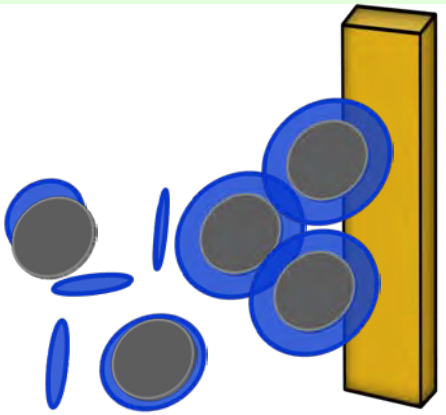
Background-Modes of Mechanical Degradation



Present focus

Failure of active material: fracture

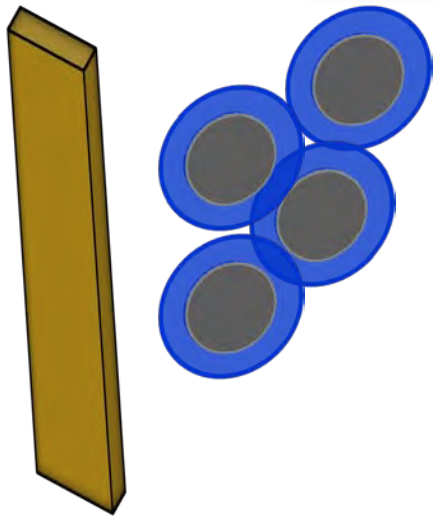
Failure of binder: fracture/yield

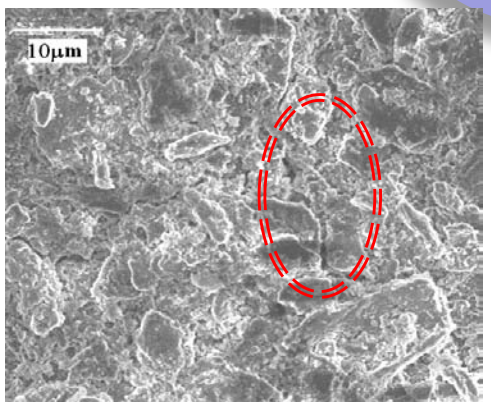


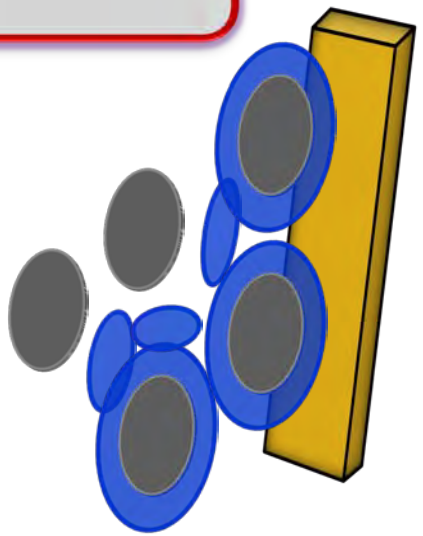
De-lamination from current collector

Failure of composite electrode

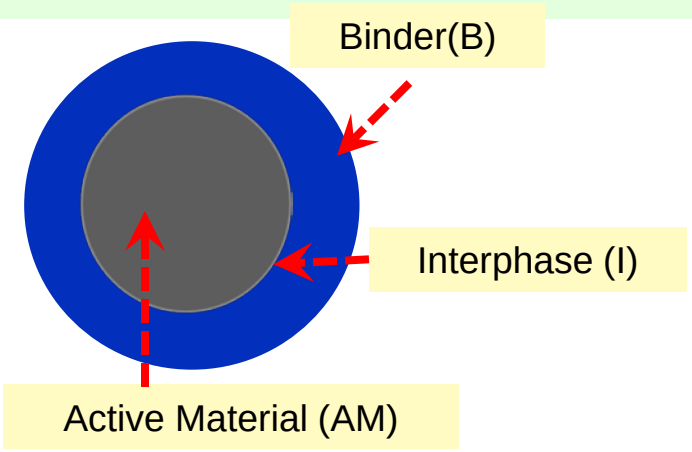
De-bonding of binder-active material

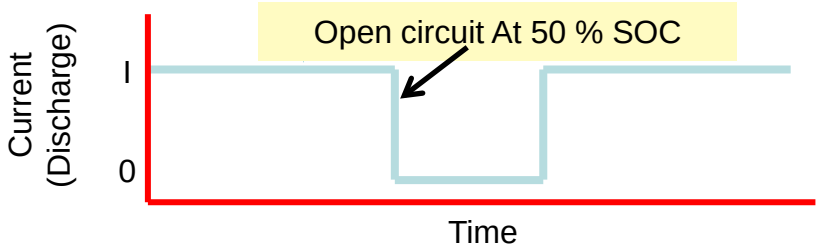


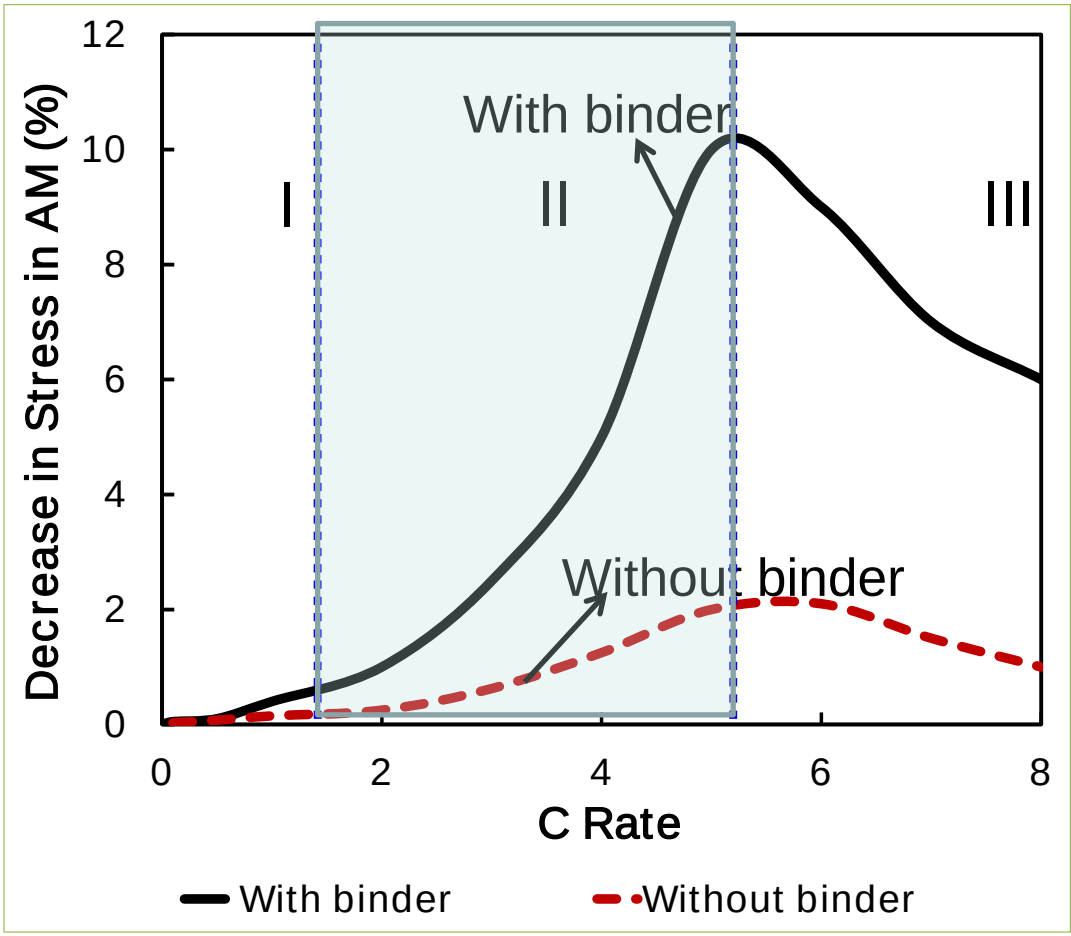




Accomplishments-Effect of Binder

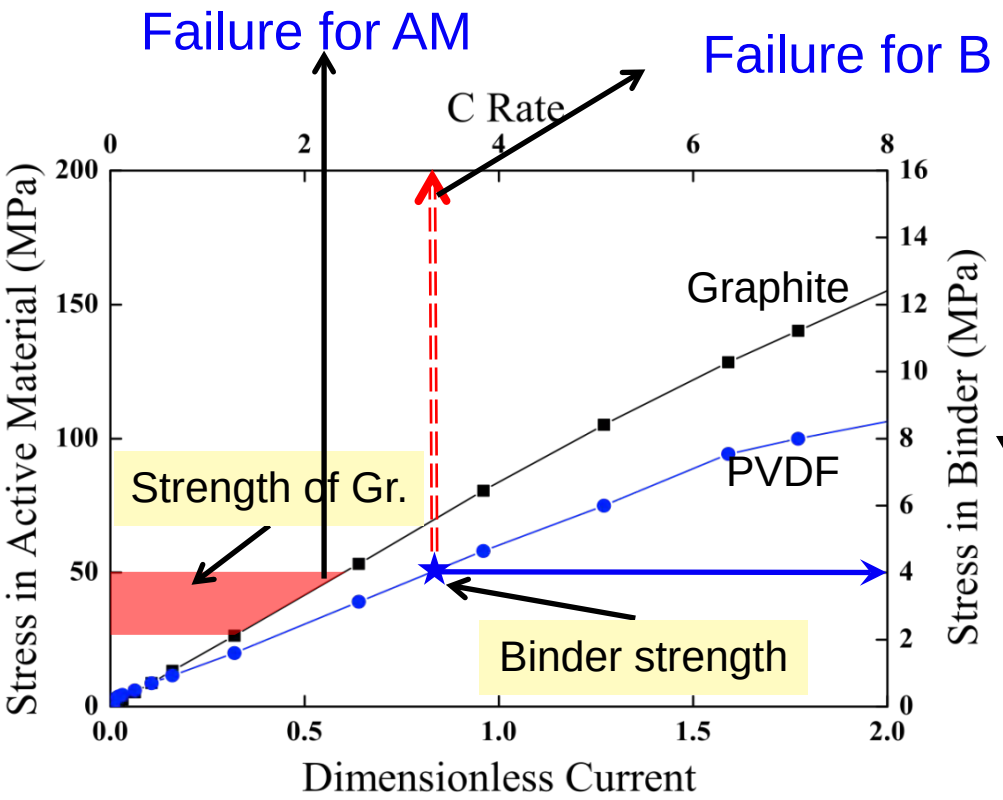






1. Consideration of binder important in predicting stress
2. Cycling protocol influences failure

Failure modes- Graphite/PVdF

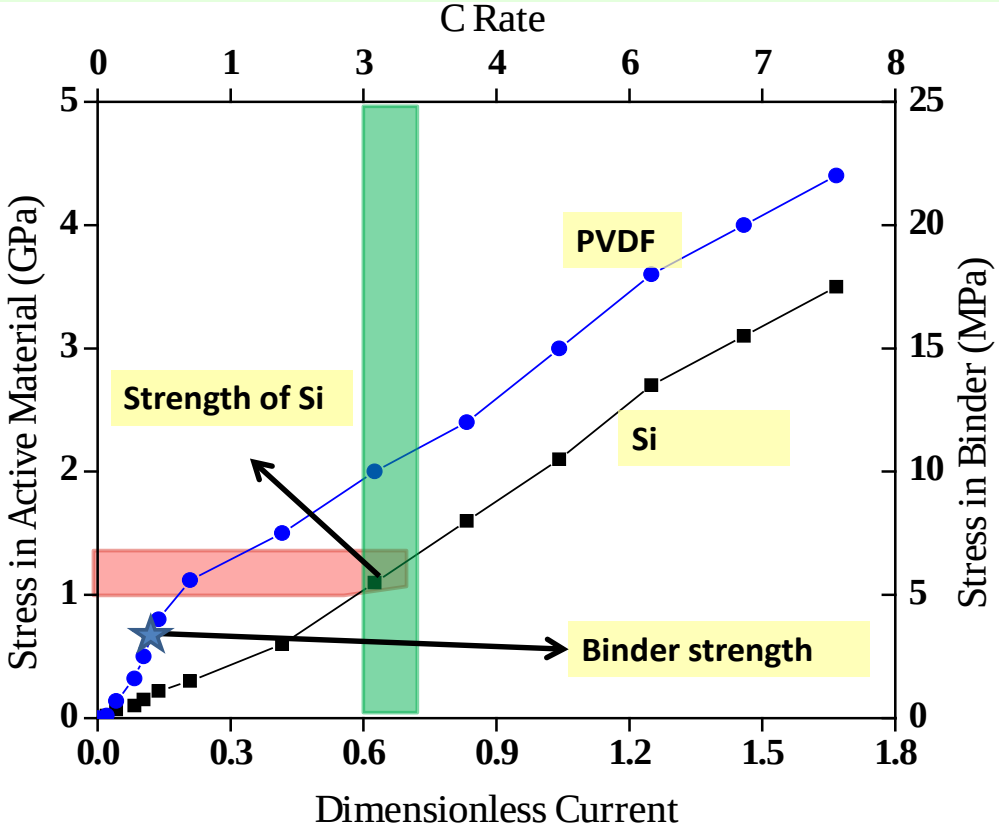


Magnitude of Stress in AM and B depend on the respective mechanical properties: Young's modulus (E) and Poison's Ratio(ν)

- Start of the failure (Fracture or yield initiation) for AM and Binder are very close and in the range of PHEV cycling
- Alternate binders (*e.g.,*SBR/CMC) can change failure modes
- Debonding of binder and particle needs consideration (Future work)

Binder failure needs to be considered when examining electrode failure

Failure modes- Si/PVdF



- Nanomaterials of silicon (<100nm) can be cycled under PHEV conditions
- However binders like PVdF can be the cause of failure
- Consideration of binder/Si interface debonding critical (Future work)

Model provides a way to tune binder/particle properties for a specific application

Future Work

1. Model high-rate behavior of battery electrodes and its relationship with electrode design.

2. Extend models to incorporate microstructure effects (agglomerate vs. primary particle)

3. Extend the silicon model to include side reactions and change in conductivity with lithium content

4. Extend mechanical models to describe debonding at the particle/binder interface.

All studies will be carried out in close collaboration with experimental groups

Summary

1. Flat potential systems, like $LiFePO_4$, can exhibit unique effects related to a particle size distribution
   - Leads to nonuniform lithiation of small *vs.* large particles
   - Nonuniform lithiation can lead to path dependence

2. Volume change in silicon anodes can make electrode design complicated
   - Implications on the practical energy density that is achievable
   - Models can help in designing the electrode for a specific application

3. Binder-related failure important at PHEV operating conditions
   - Models can be used to guide binder development for alloy anodes