Model-Experimental Studies on Next-generation Li-ion Materials

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Lawrence Berkeley National Lab

OVT Merit Review

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Project ID # **ES086**

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Overview

Timeline

- Project start date: October 2008
- Project end date: September 2012
- Percent complete: 50%

Barriers

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

Budget

- FY08: $285k
  - 1 FTE Postdoc
  - 1 FTE Research assistant
- FY09: $400k
  - 0.4 FTE Scientist
  - 1.5 FTE Postdoc (V. Boovaragavan, S. Renganathan, V. Sethuraman)

Partners

- Vince Battaglia
- Gao Liu
- Tom Richardson

(Vince Battaglia, Gao Liu, Tom Richardson: LBNL)

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

Objectives

1. Understand the ultra-fast charge/discharge behavior of some $LiFePO_4$ cathodes
   - What limits $LiFePO_4$ performance at high power densities?
2. Develop a model for silicon anodes
   - What limits the performance under various operating conditions?
3. Quantify conditions under which phase changes can occur in silicon anodes
   - Are life-limiting crystalline phase formation possible under PHEV operation?
4. Understand and quantify the impact of stress on the cycling of silicon anodes
   - How does stress impact the voltage offset and the energy efficiency?
5. Quantify mechanical failure of electrodes
   - What mechanisms contribute to electrode failure and poor life?

Milestones

- Quantify kinetic parameters for lithiation/delithiation reaction and the side reactions in silicon anode for different electrolytes. (Jan. 2009)

  Completed

- Estimate activation energies for lithiation/delithiation reaction and side reactions. (Mar. 2009)

  Completed

- Extract kinetic parameters on porous electrodes fabricated with Si powders and compare to the results obtained on thin films. (Jul. 2009)

  Completed

- 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)

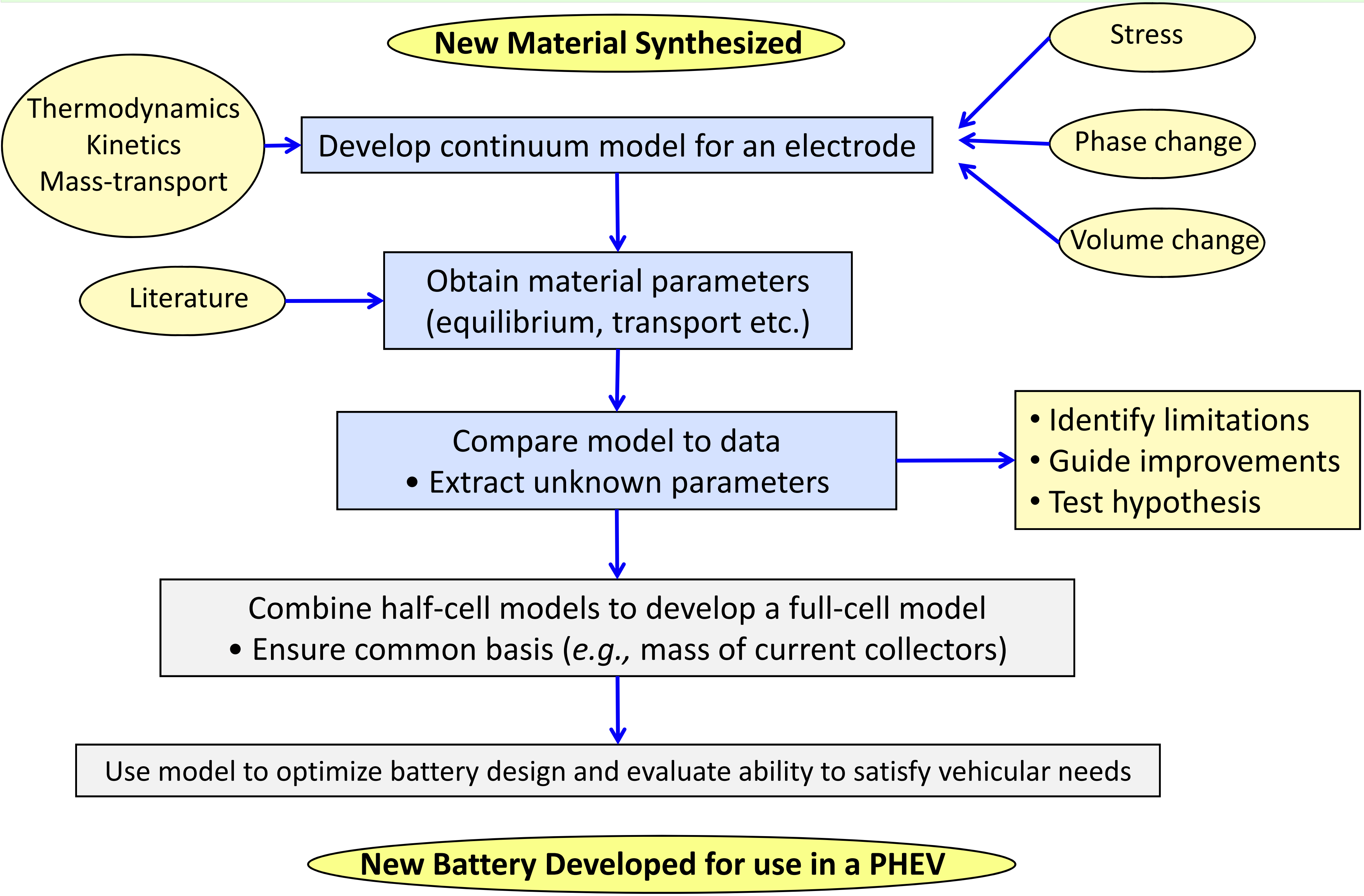
  In Progress

- Develop model for the Si/NCM system to compare to the baseline (September 2010)

  In Progress

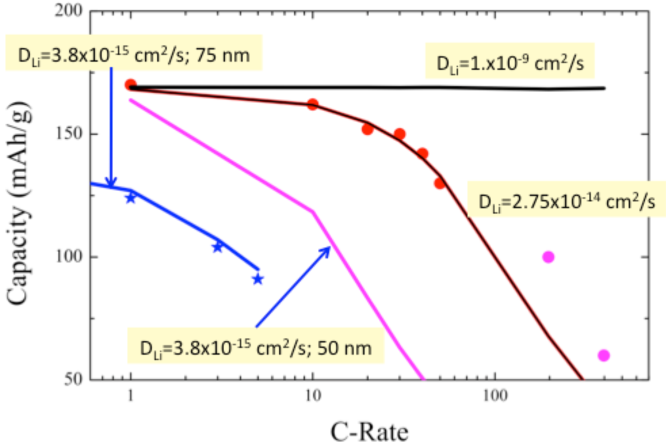
Sept 2008 Sept 2009 Sept 2010

Approach

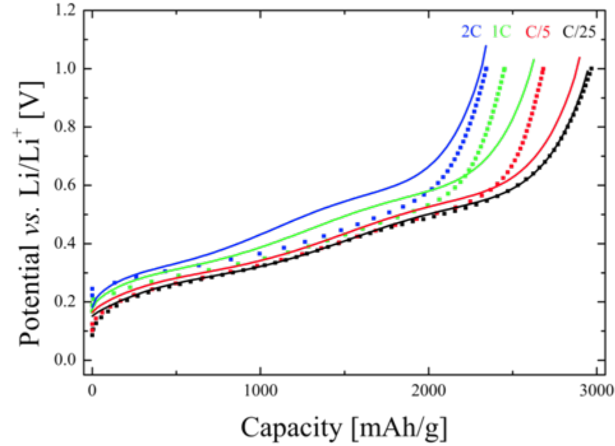

New Material Synthesized
Thermodynamics
Kinetics
Mass-transport
Develop continuum model for an electrode
Stress
Phase change
Volume change
Literature
Obtain material parameters (equilibrium, transport etc.)
Compare model to data
• Extract unknown parameters
• Identify limitations
• Guide improvements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

Collaborations

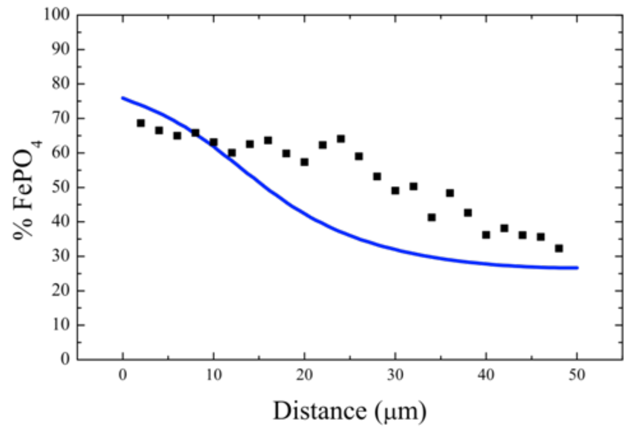
Particle Size Effects
Gerd Ceder, MIT



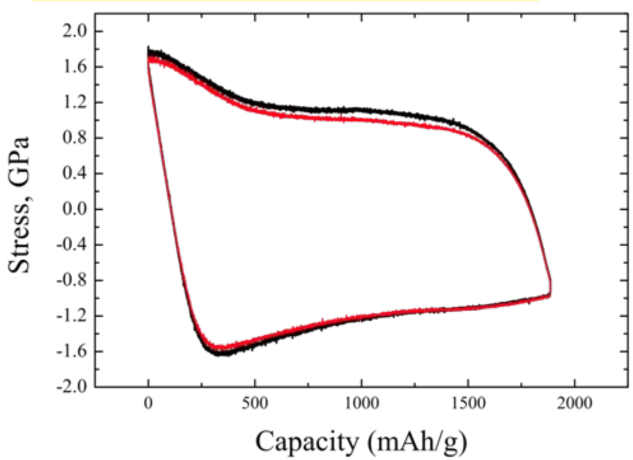
Silicon simulation
Gao Liu, LBNL



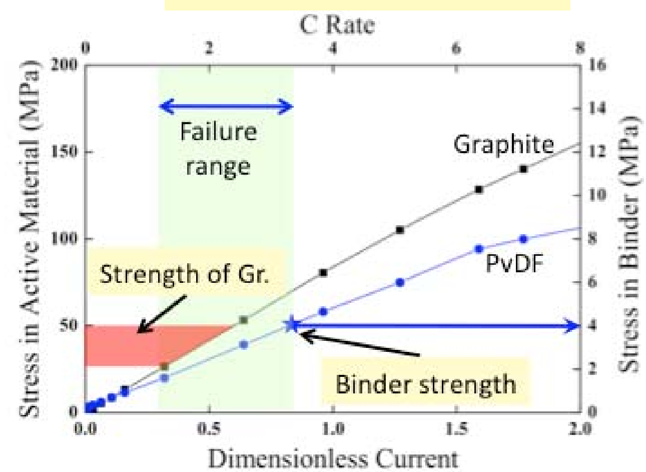
Reaction distributions
Tom Richardson, LBNL



Stress Effects
Pradeep Guduru, Brown U.

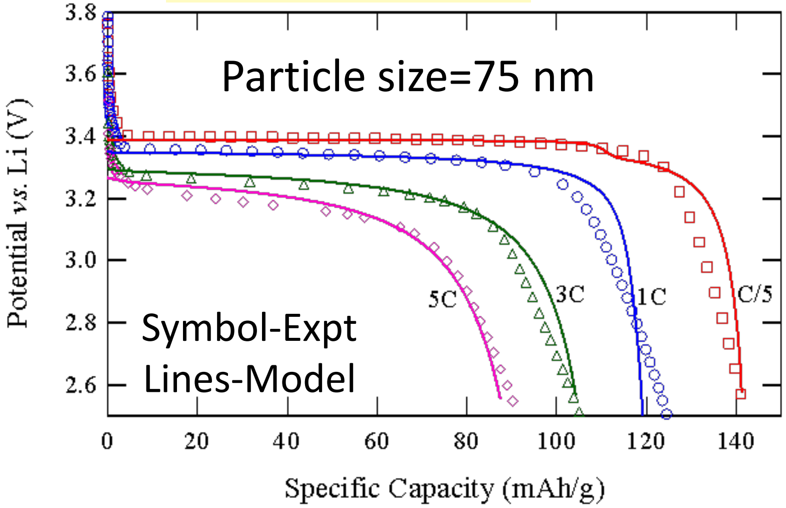


Electrode Failure
Vince Battaglia, LBNL

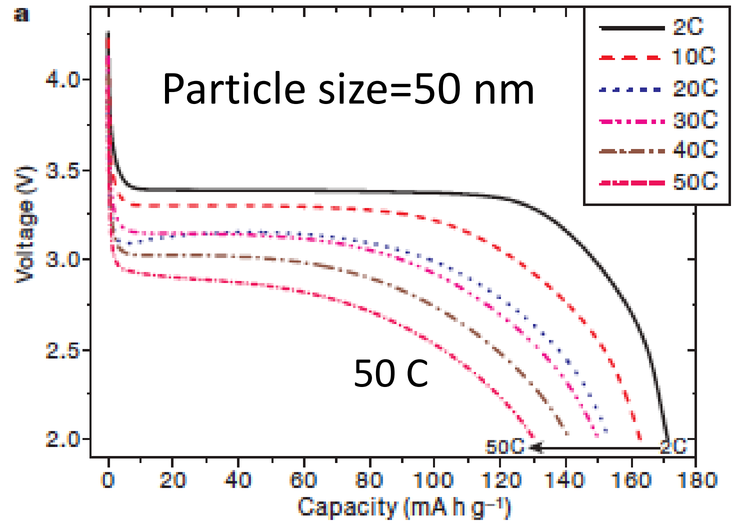


Ultra-high Rate $LiFePO_4$

Baseline $LiFePO_4$

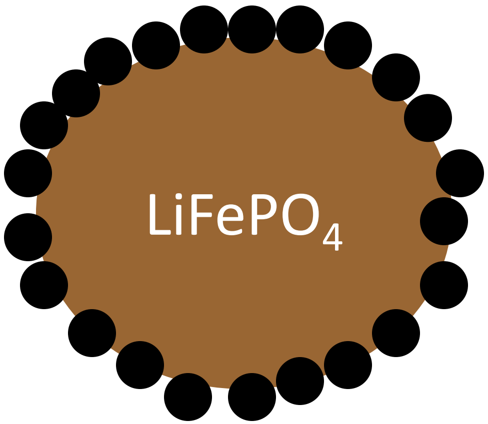


Kang and Ceder, Nature, **458**, 193 (2009)

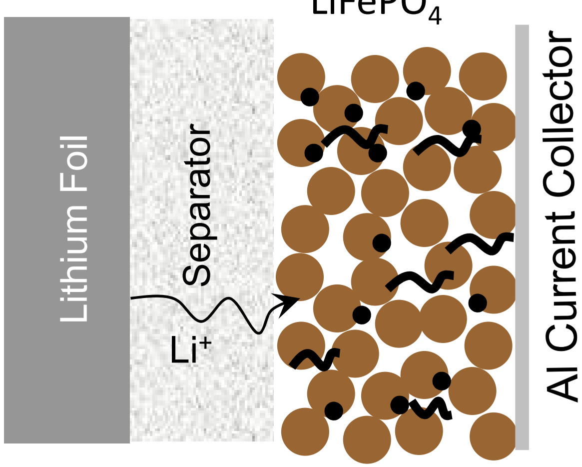


Why are some $LiFePO_4$ particles capable of such high discharge rates?

Methodology

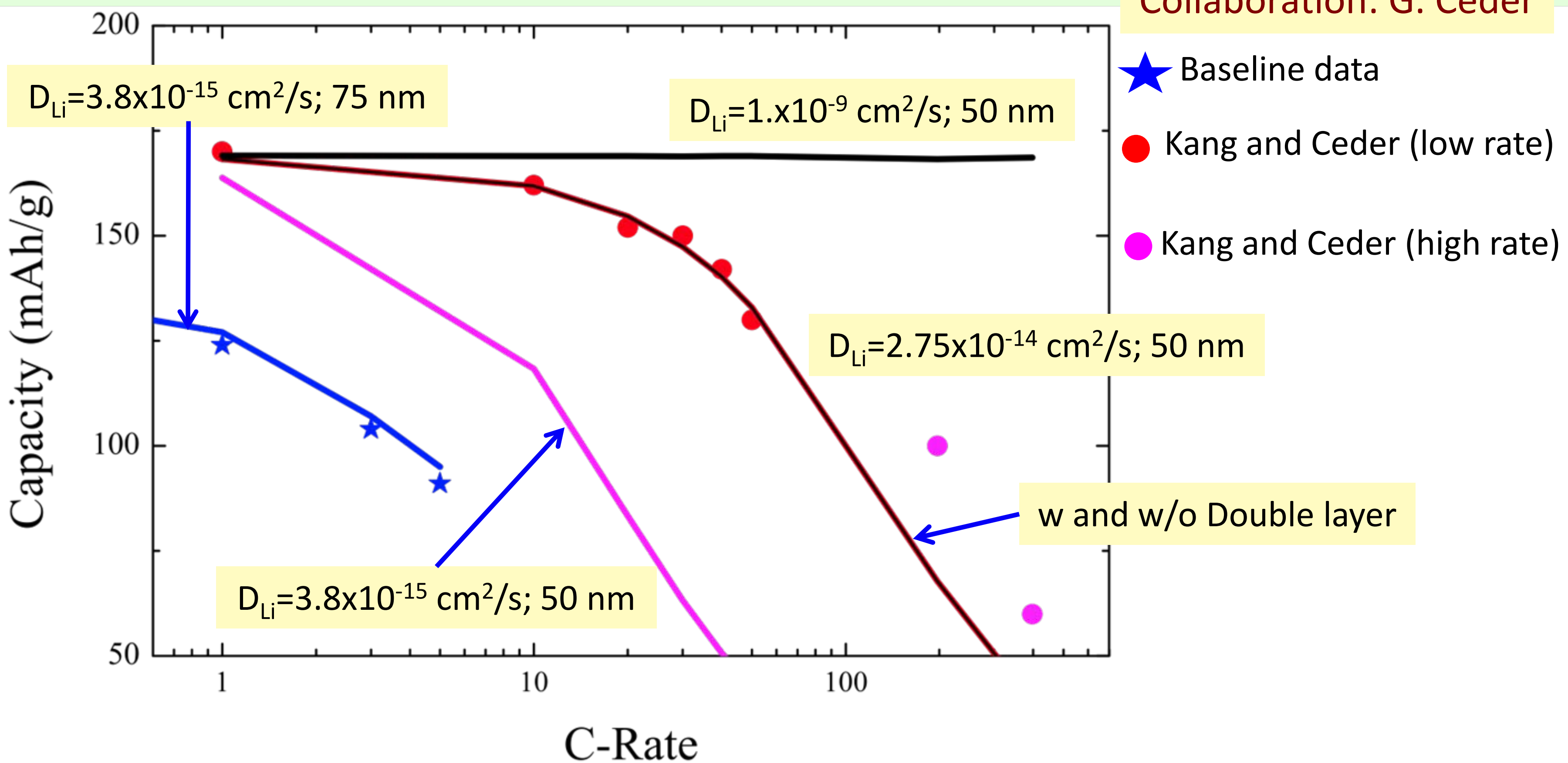


Single particle model with double layer charging



Porous electrode model

Solid-phase Transport Effects



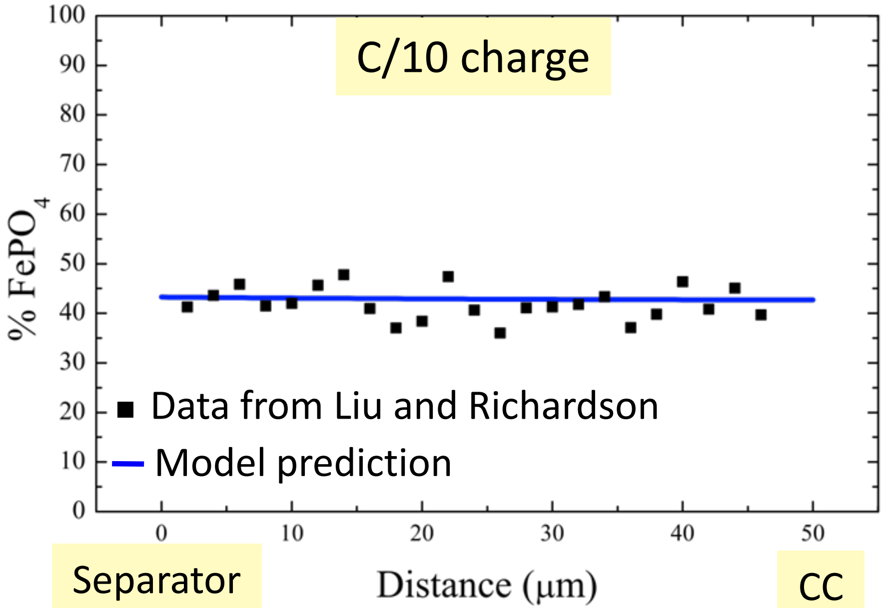
- Smaller particles appear to have a larger diffusion coefficient (defect-related- See Ceder poster)
- Double layer charging does not play a role in high power capability
- Model shows that diffusion coefficient in the order of 10^{-14} cm^2/s predicts data to 50 C

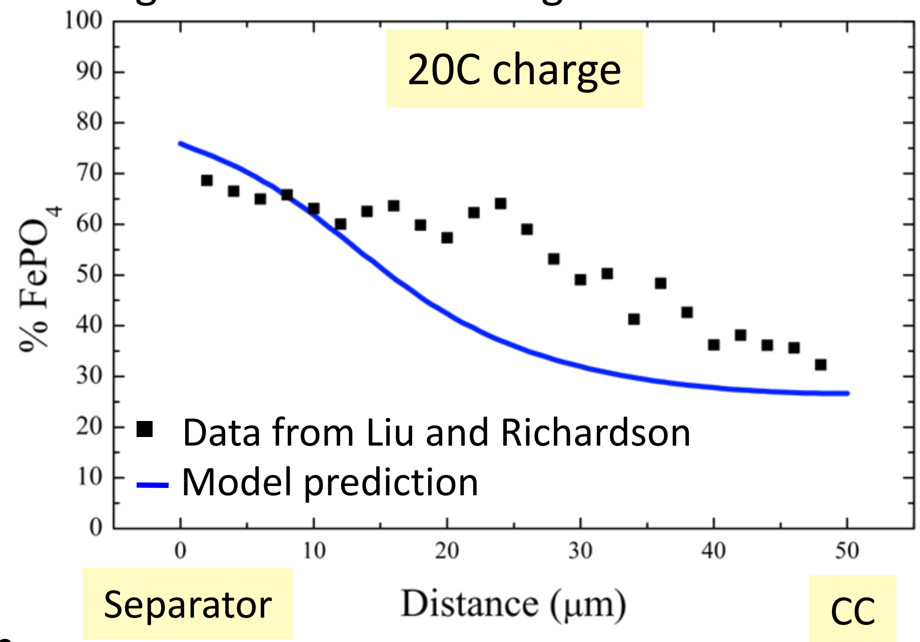
Does electrolyte transport play a role?

Liquid-phase Transport Effects

Collaboration: T. Richardson

- $FePO_4$ distribution obtained by charging at a given rate for a SOC; the SOC is “frozen” because of the flat potential (See T. Richardson’s poster)
    - Cross section microdiffraction analysis used to obtain the profile
- Porous electrode model used to predict the distribution
    - Includes electrolyte transport properties (literature) and design effects (thickness, porosity, and tortuosity). Design similar to ultra-high rate material being studied.



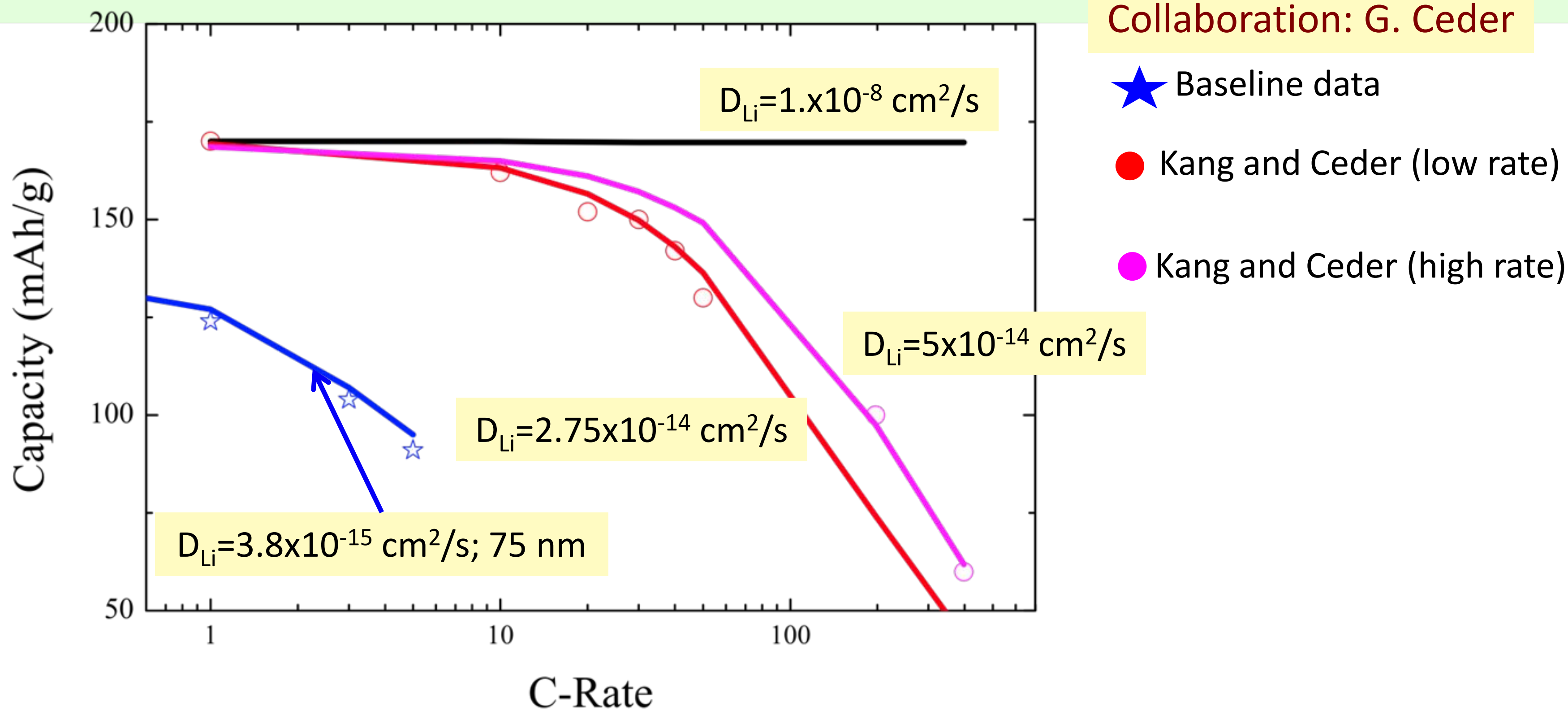


- Model predicts data well for specific cell design
    - Slight overprediction of the impact of electrolyte transport at higher rates
- Data provides a means of tuning the model, especially at low porosities- Future work

Are electrolyte transport losses significant in the ultra high rate $LiFePO_4$ material?

Porous Electrode Model Results

Collaboration: G. Ceder



- For the cell design studied, electrolyte transport does not limit capacity at high rates
  - Electrolyte limitation has a very large impact of the voltage
- Smaller particle size, the resulting larger diffusion coefficient, and thin, highly porous design all contribute to ultra fast rate behavior.
- Larger particles increase energy, but may not meet PHEV power requirements
- It is possible that limitation comes from another source (*e.g.,* nucleation), but manifests itself as a solid-phase transport limitation – Future work

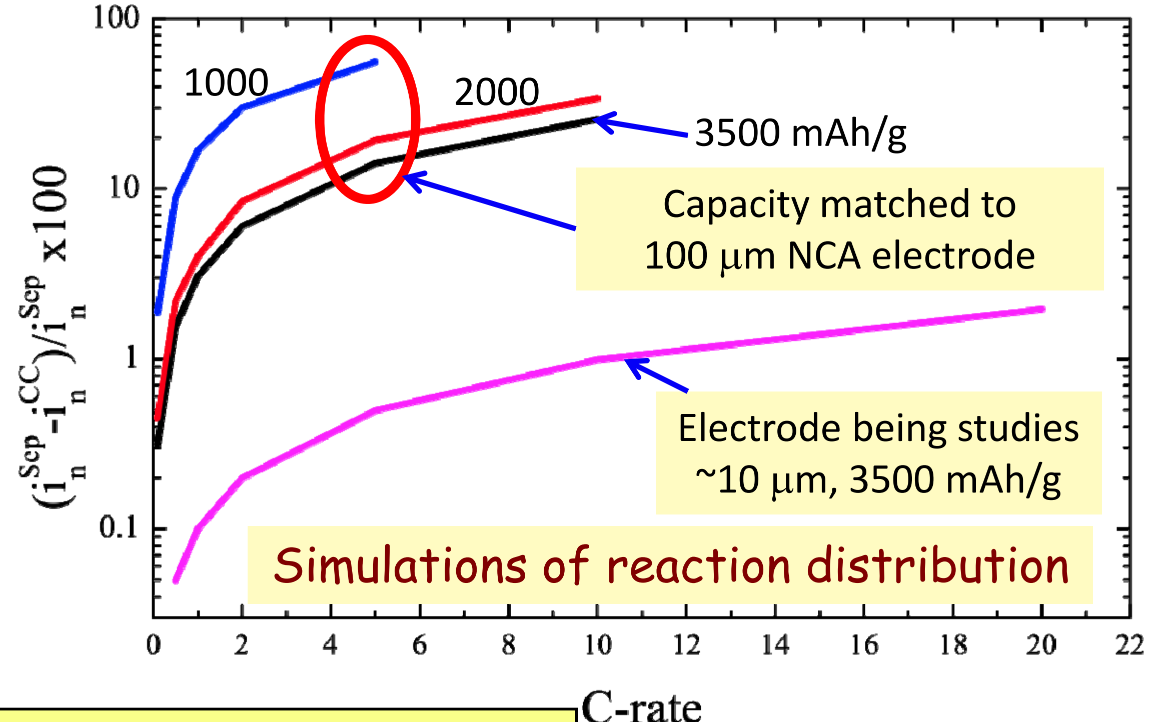
Modeling Silicon Anodes

- Silicon anodes fail due to multiple reasons
  1. Cracking caused by phase transformation both on formation and subsequent cycling
  2. Cracking due to stresses caused by concentration gradients and expansion
  3. Binder/particle interactions

Mathematically describing these requires an accurate description of transport of Li in Si

Focus: Model transport losses in silicon and predict conditions for formation of crystalline phases

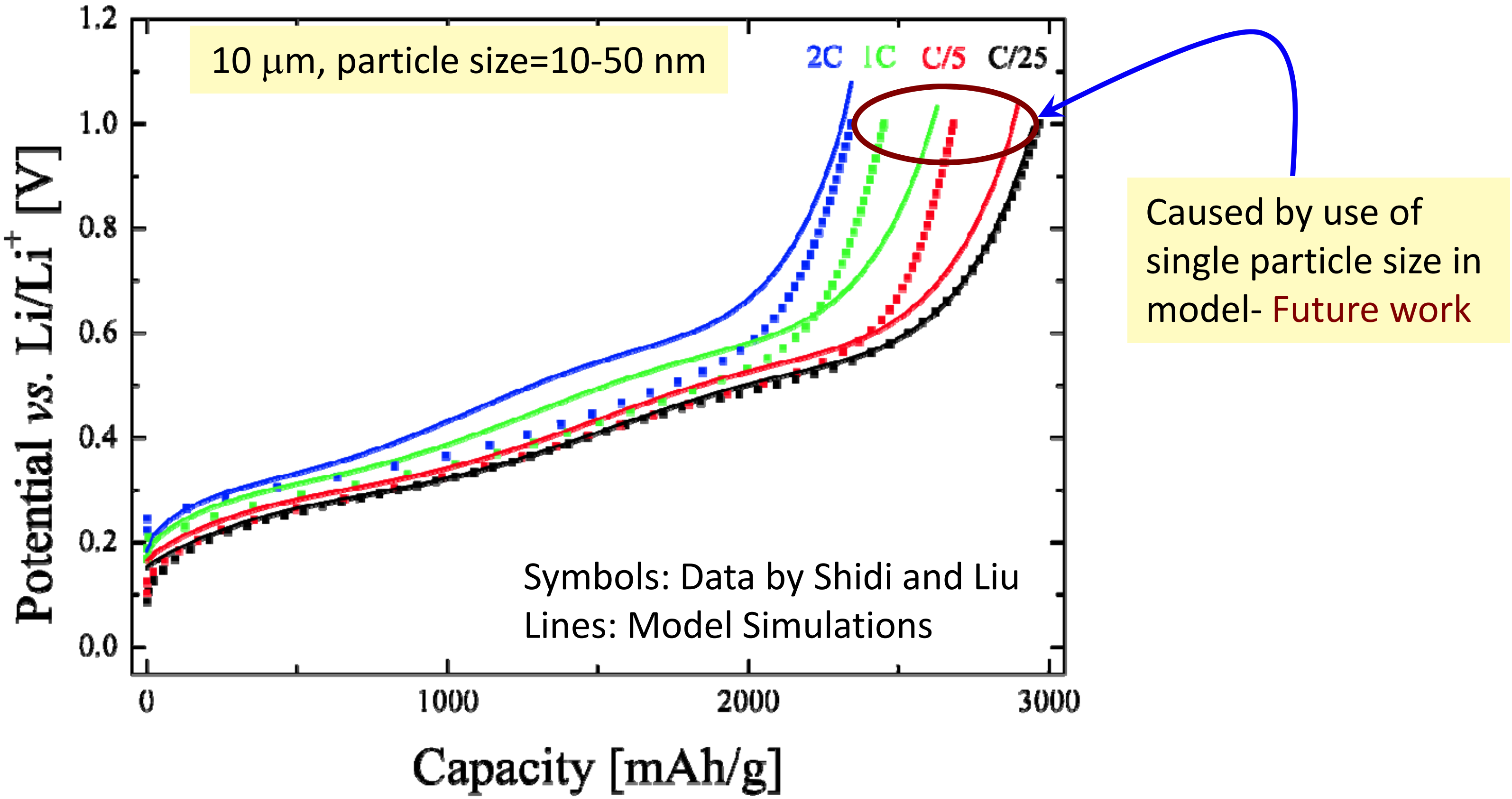
Results suggest that a single particle model adequate for electrodes being studied



Does the model compare well to data?

Comparison of Model to Data

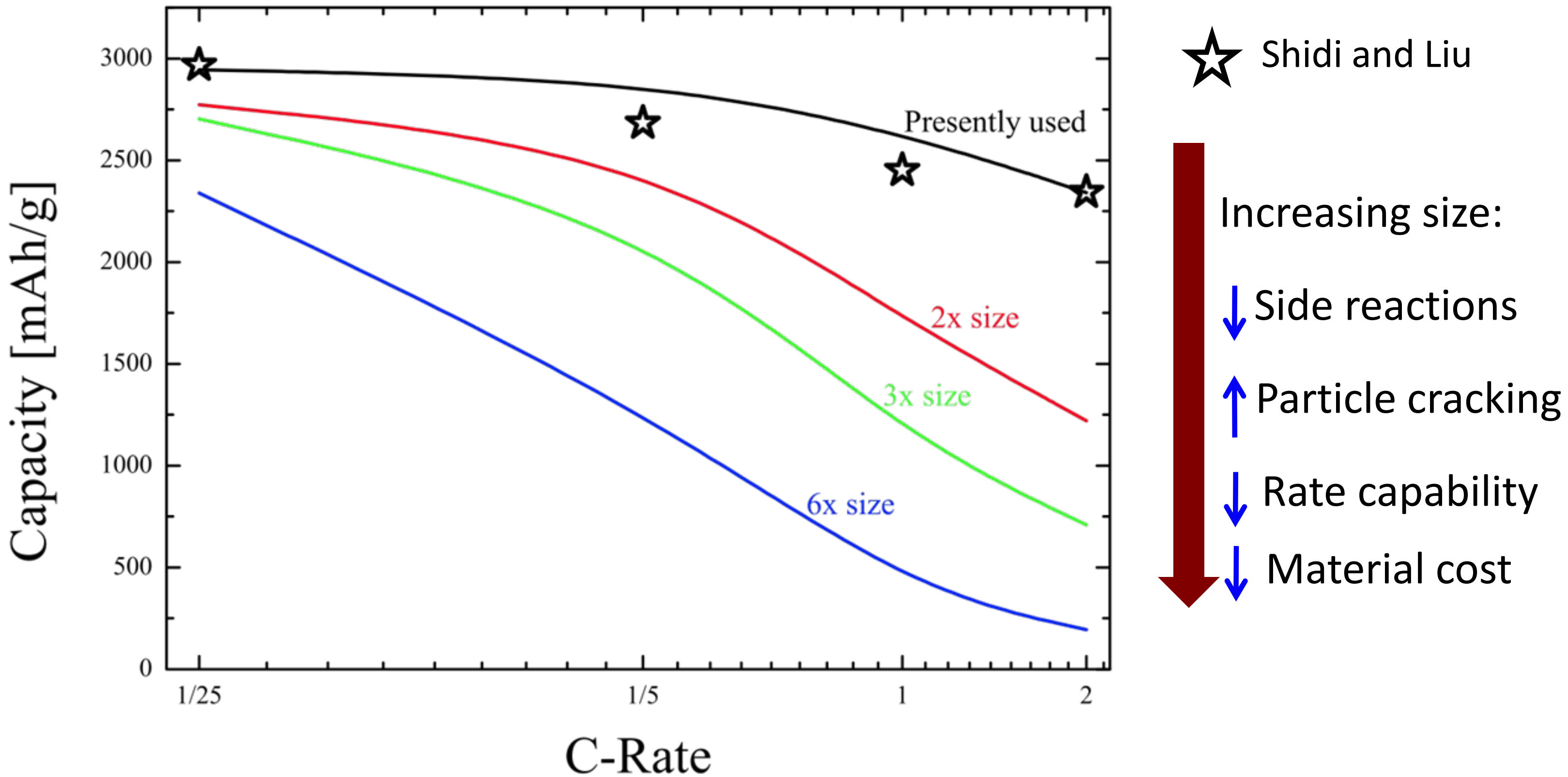
- Model accounts for thermodynamics, kinetics, and mass transport of Li
- Model also accounts for volume change, phase change, double-layer charging and side reactions



- Diffusion coefficient of Li in Si in literature ranges from 10^{-9} to 10^{-16} cm^2/s
  - Model results suggest that lower diffusion coefficient likely the correct value

How does particle size impact performance?

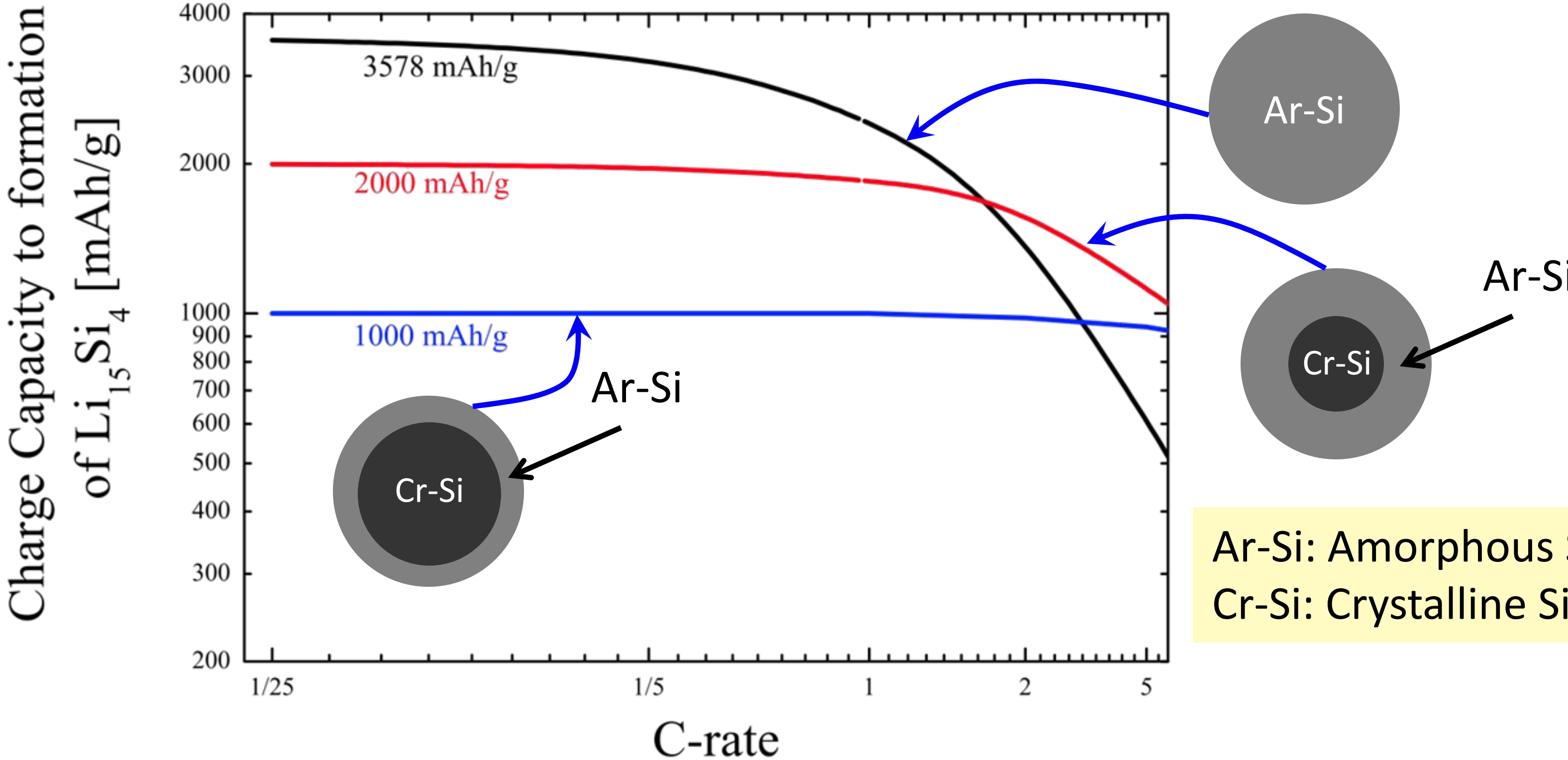
Performance Summary



- Choice of particle size a complex interplay between rate capability, side reactions, stress generation leading to cracking, and cost
    - Stress generation occurs both on 1st cycle amorphatization and on cycling- Future Task
- Particle size also important in dictating conditions under which crystalline phases form on charge

How does silicon behave on charge?

Charging Silicon Anodes at High Rates



Ar-Si: Amorphous Si
Cr-Si: Crystalline Si

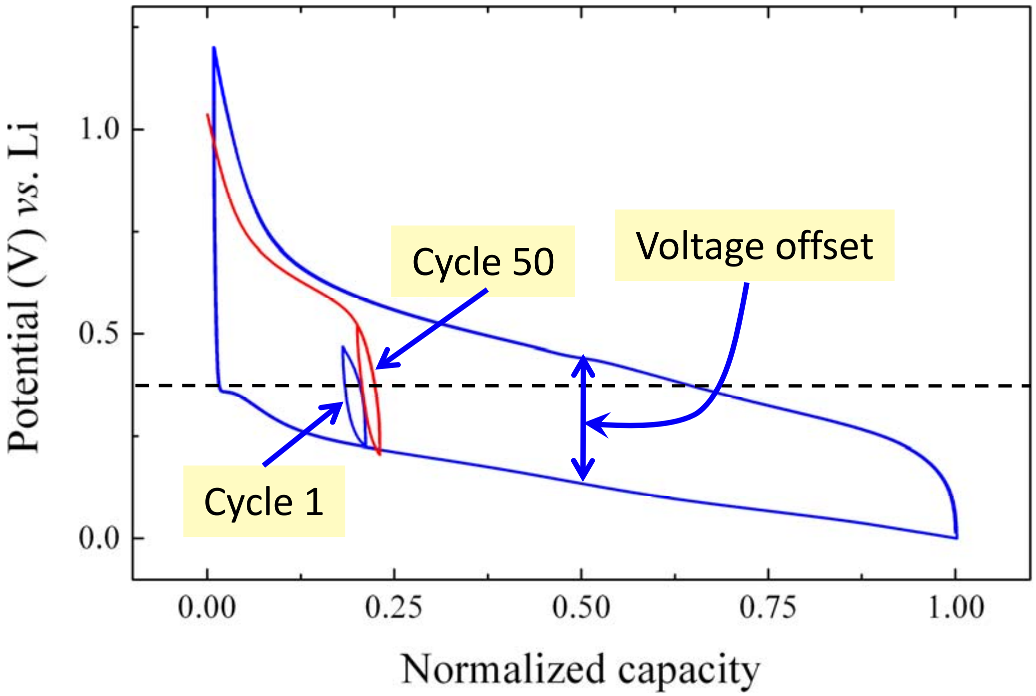
- Model captures maximum capacity before $Li_{15}Si_4$ forms
  - $Li_{15}Si_4$ is a crystalline Si phase that is thought to cause particle cracking

- Formation of phase avoided by cycling battery to 1000-2000 mAh/g
  - Note that cycling above 1500 mAh/g only provides only an incremental increase in cell energy

Model provides guidance on optimal charging conditions to avoid life limitations

Voltage Offset and Stress in Silicon Anodes

- Silicon anodes exhibit a voltage offset (~300 mV)
  - Energy efficiency ~90% at low rates
  - Voltage not an indicator of SOC. Battery management problematic.
  - Voltage drifts with cycling – Peak power changes on PHEV-type cycling



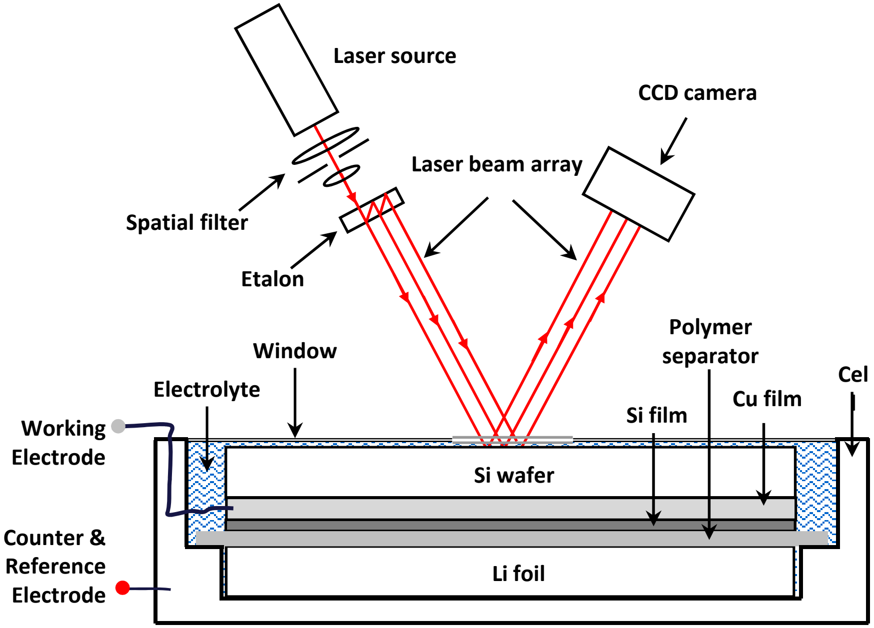
- Voltage behavior consistent with a kinetically limited system

- However, material undergoes significant volume change (stress)

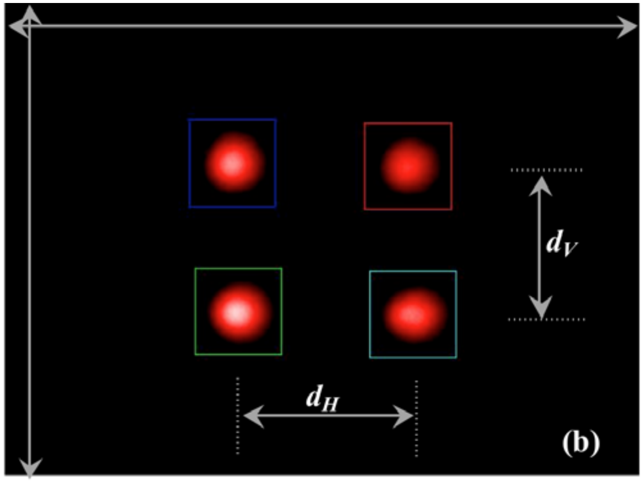
What is the role of stress on the voltage offset?

Stress Measurement Setup

Collaboration: P. Guduru, Brown U.



In situ stress measurement cell



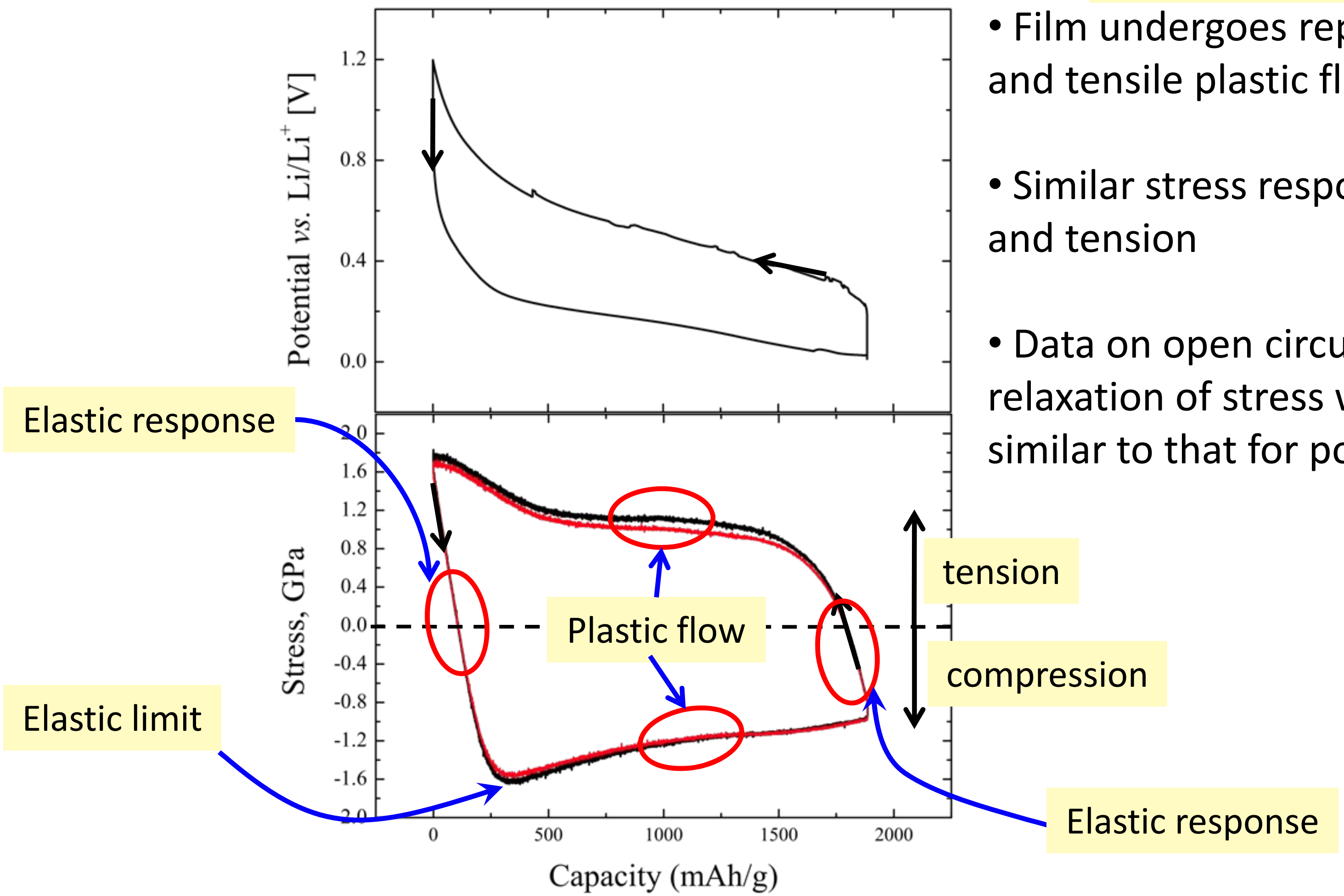
Wafer curvature related to change in spot distance

- Wafer curvature is related to the stress *via* the Stoney equation
- Stress is monitored *in situ* during lithation/delithation
- Experiments were carried out on amorphous silicon thin films.

Cell provides a clear method to understand stress effects during cycling

Stress Evolution on Charge/discharge

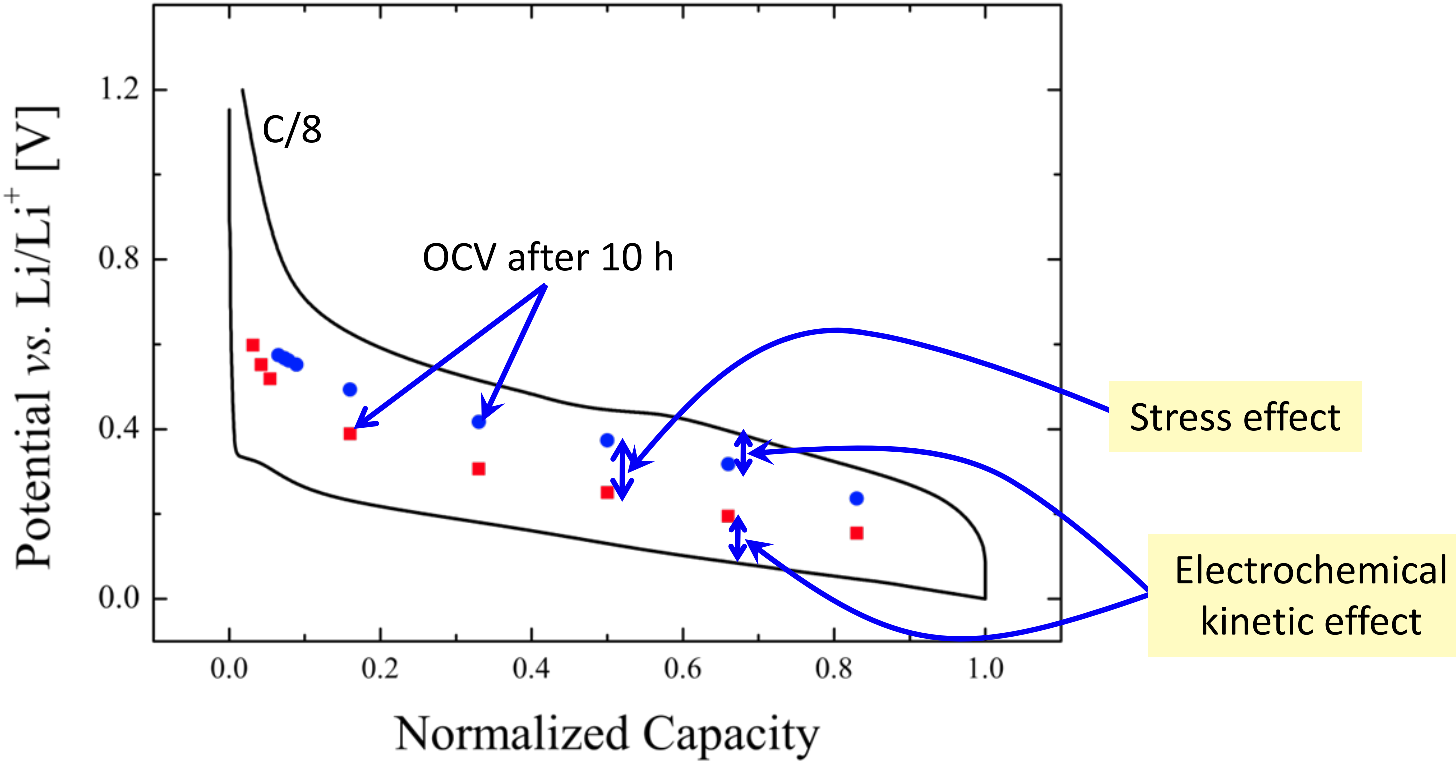
Collaboration: P. Guduru, Brown U.



- Film undergoes repeated compressive and tensile plastic flow
- Similar stress response on compression and tension
- Data on open circuit (not shown) shows relaxation of stress with time constants similar to that for potential relaxation

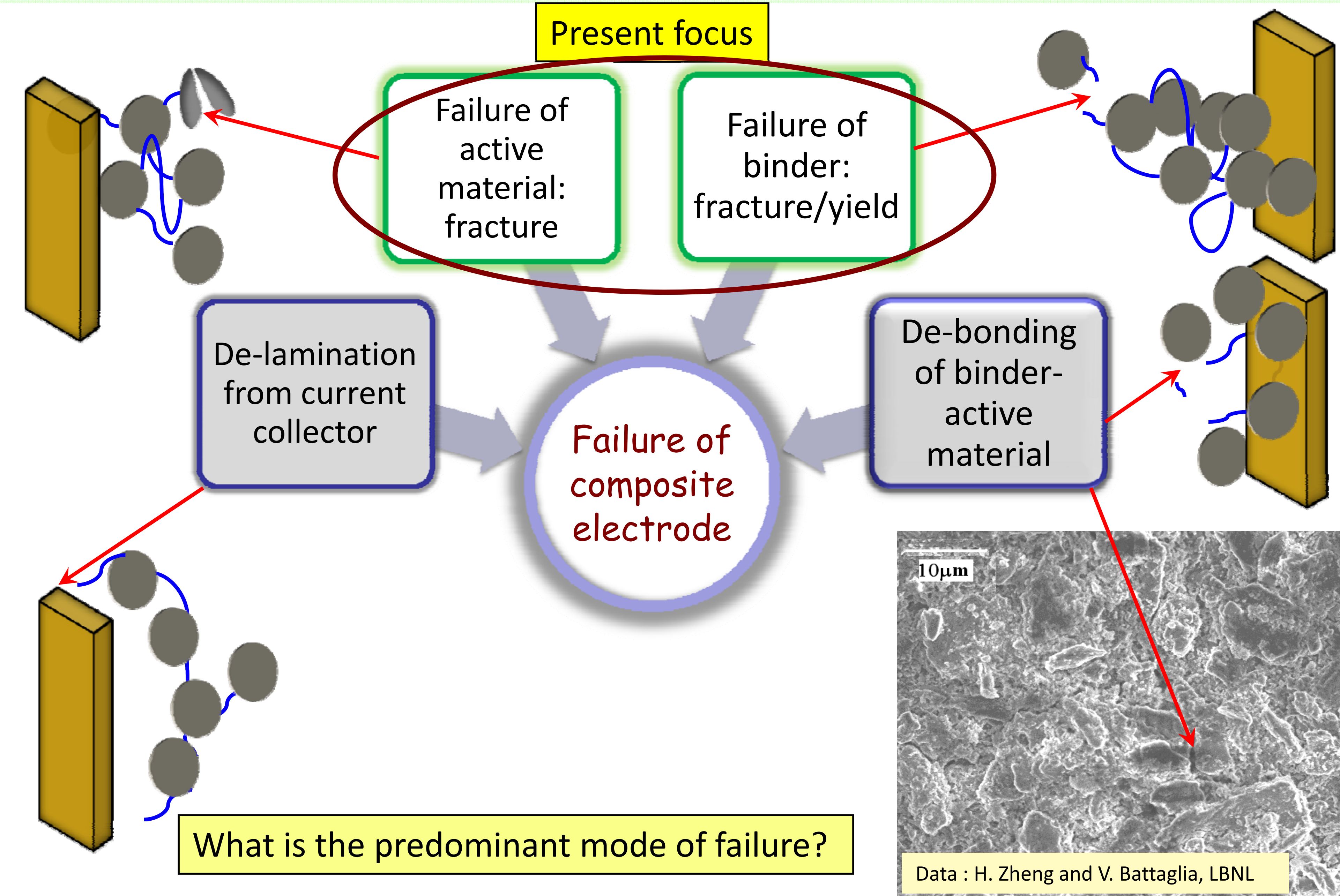
Stress response can be used to quantify the mechanical work and compare this to the electrical work

Stress Effect on Voltage Offset

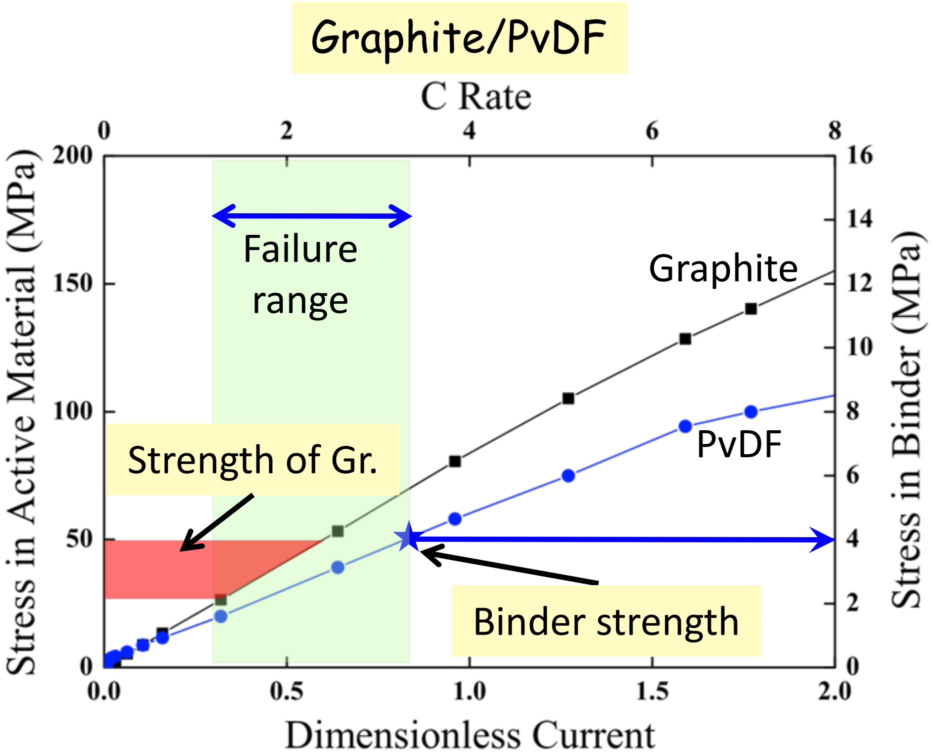


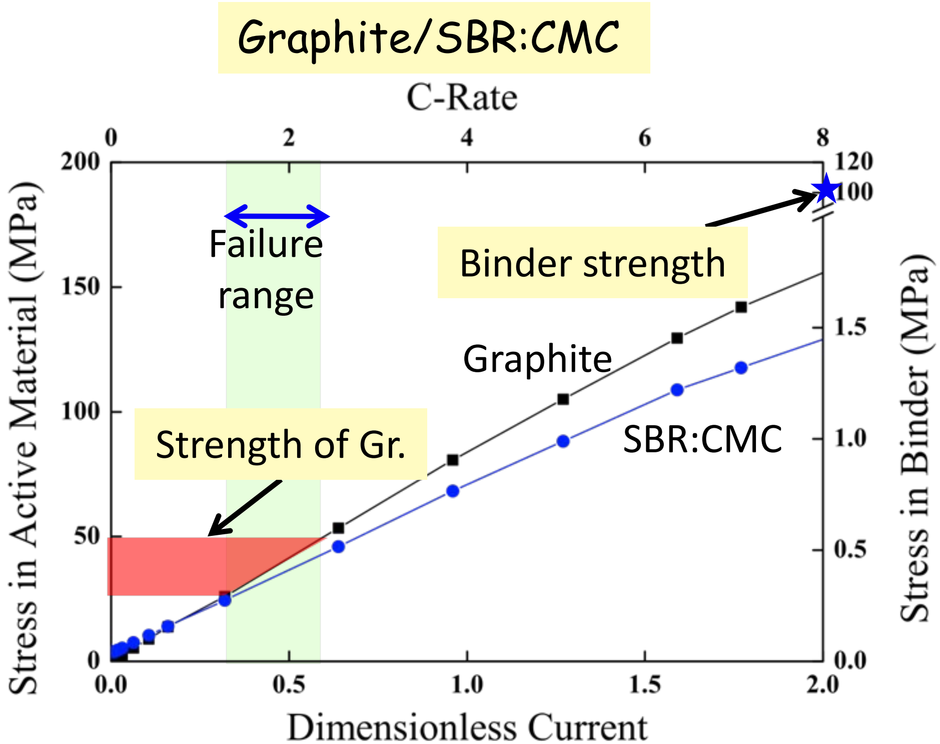
- Stress contributes significantly to the voltage offset (~40%)
- Slow electrochemical kinetics account for the rest- Focus of FY09 research
- Low energy efficiency is unavoidable
- Models need to account for stress effect- Future work

Mechanical Degradation of Electrodes



Simulations of Stress Effects





- Type of binder has a significant impact on failure mode
- Failure can occur under PHEV cycling conditions
- Interface debonding another possible scenario- Future work
- Models can help define ideal binder properties for alloys- Future work

Future Work

1. Understand the performance limitations of battery electrodes during high-rate cycling (*e.g.,* nucleation)

2. Develop a full-cell model for a Si/$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cell and compare it to a Gr/$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cell

3. Examine causes for mechanical failure of electrodes during cycling

4. Extend stress models to silicon anodes to understand binder effects

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

Summary

1. Ultra-fast rate behavior of $LiFePO_4$ result of small particle size, the resulting larger diffusion coefficient, and thin, highly porous design
   - Larger particles, while promising higher energy, may not have the rate required for vehicle applications

1. Silicon anodes show loss in capacity at rates applicable for PHEVs
   - Implications for performance as well as life of electrodes
   - Formation of crystalline $Li_{15}Si_4$ possible under PHEV cycling conditions

2. Stress effects important in describing voltage behavior of silicon anodes
   - Results suggests that low energy efficiency with silicon is unavoidable

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