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

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OVT Merit Review
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Project ID # **es_34_srinivasan**

Overview

Timeline

Modeling Silicon Anodes

- Project start date: August 2007
- Project end date: June 2009
- Percent complete: 60%

Barriers

- Barriers addressed
  - Low energy efficiency (due to voltage hysteresis)
  - Low energy (due to SEI formation)
  - Low cycle/calendar life (due to volume change and side reactions)

Budget

- FY07: $400k
  - 0.7 FTE scientist
  - 1 FTE postdoc (Vijay Sethuraman)

- FY08: $285k
  - 1 FTE postdoc (Vijay Sethuraman)
  - 1 FTE research assistant (Kristin Kowolik)

Partners

- John Newman
- Vince Battaglia
- Gao Liu
- Robert Kostecki
- Ramesh Ramamoorthy (UCB)
- Sam Mao (LBNL)
- UC-Berkeley microlab
- Keith Kepler ((Farasis Energy)

Objectives

1. Understand, and mathematically describe, voltage hysteresis in silicon anodes and quantify the energy efficiency under rates relevant for vehicle applications

2. Quantify the impact of electrolyte solvents and additives on the voltage hysteresis, 1st cycle loss, and steady state efficiency in silicon to enable higher energy and longer life

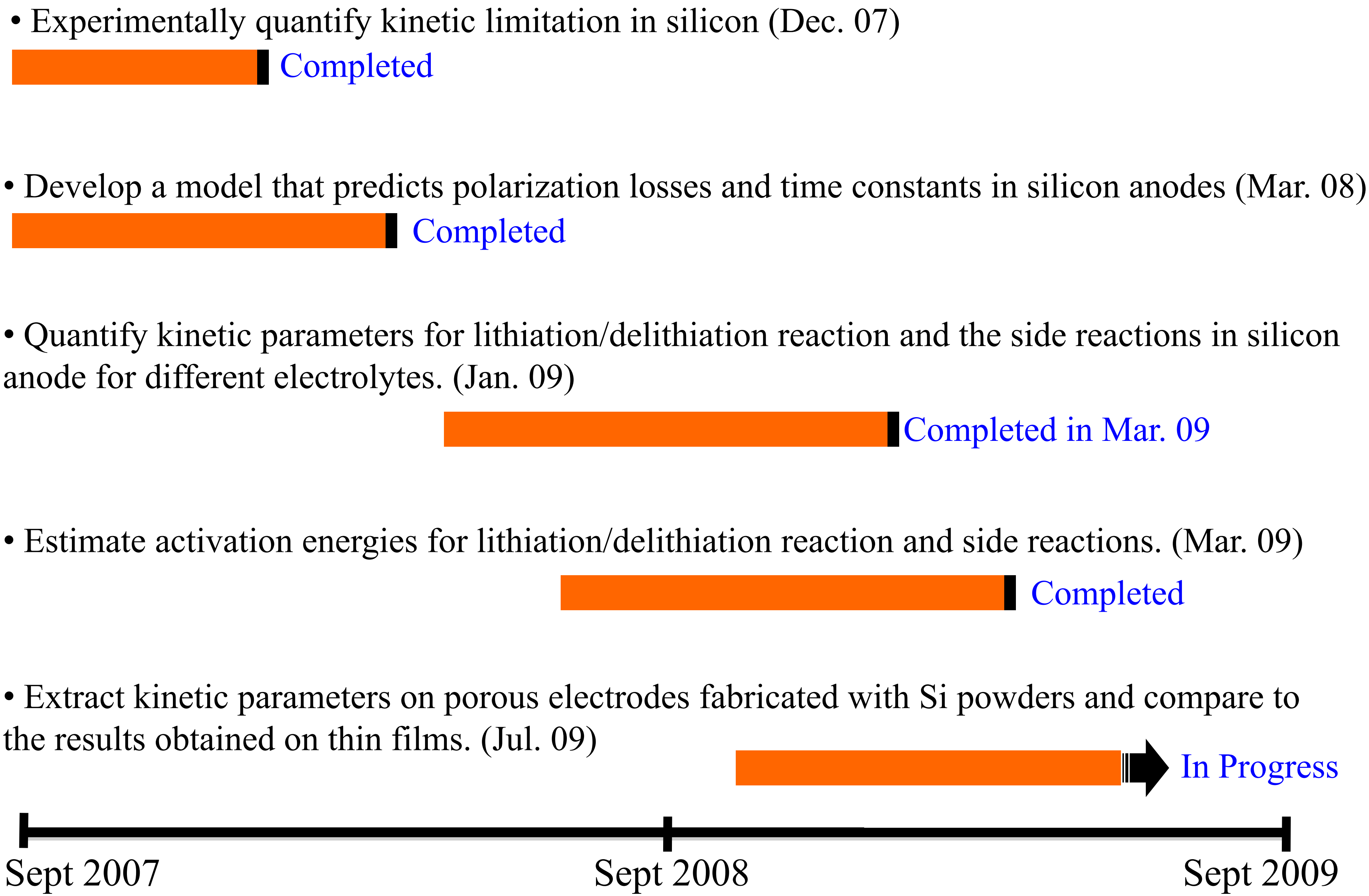
3. Quantify impact of voltage hysteresis on small SOC cycling, with emphasis on changes during cycling

4. Study the impact of surface coatings to enable better cycling characteristics to improve life without sacrificing power capability

5. Extend kinetic model for silicon anodes to include phase behavior and transport in order to predict conditions under which life-limiting crystalline phases form

6. Use continuum models to understand the use of cathode materials in PHEVs with emphasis on $LiMnPO_4$

Milestones



- Experimentally quantify kinetic limitation in silicon (Dec. 07)

Completed

- Develop a model that predicts polarization losses and time constants in silicon anodes (Mar. 08)

Completed

- Quantify kinetic parameters for lithiation/delithiation reaction and the side reactions in silicon anode for different electrolytes. (Jan. 09)

Completed in Mar. 09

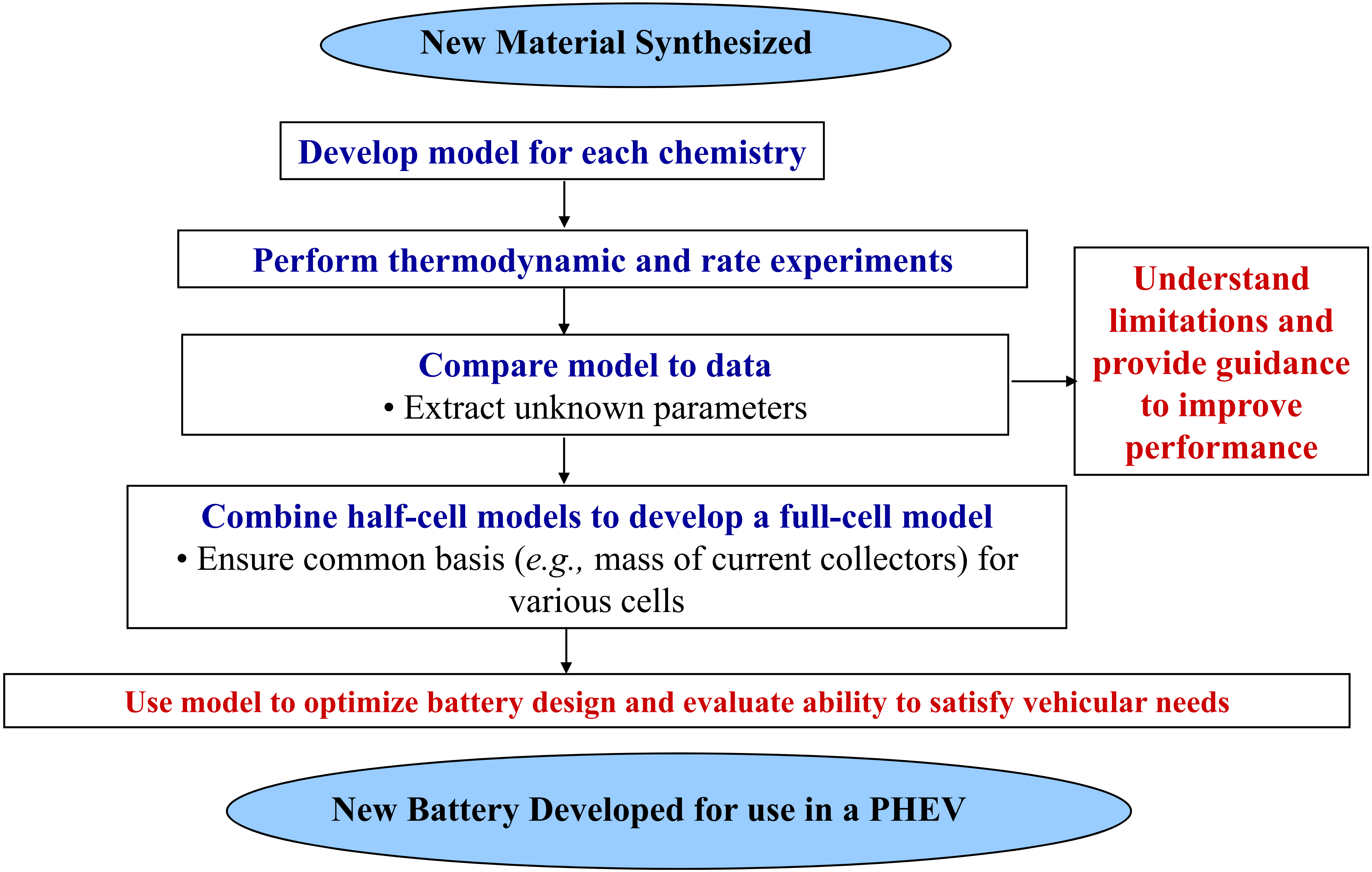
- Estimate activation energies for lithiation/delithiation reaction and side reactions. (Mar. 09)

Completed

- Extract kinetic parameters on porous electrodes fabricated with Si powders and compare to the results obtained on thin films. (Jul. 09)

In Progress

Approach



New Material Synthesized

Develop model for each chemistry

Perform thermodynamic and rate experiments

Compare model to data
- Extract unknown parameters

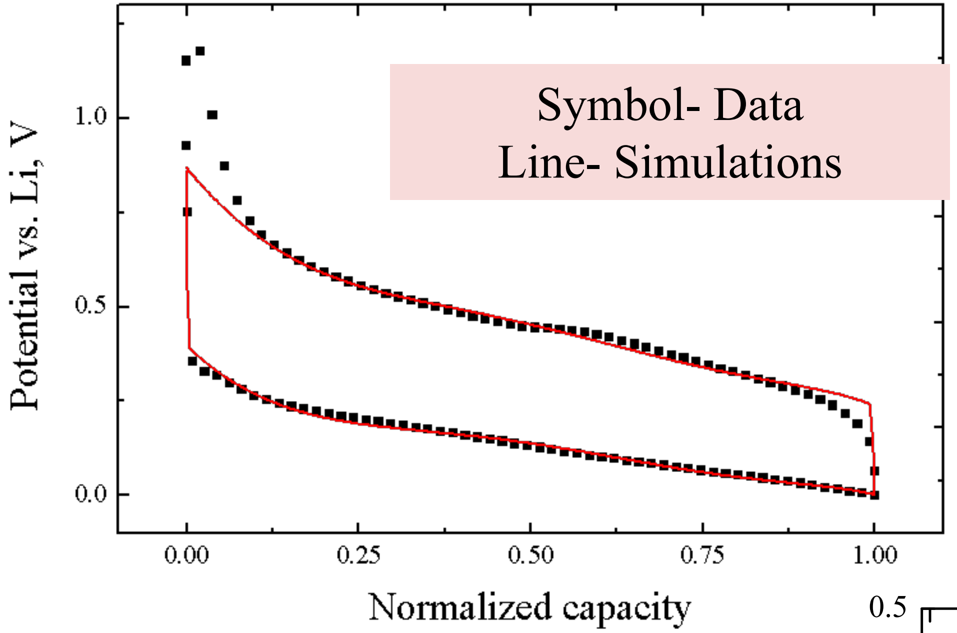
Understand limitations and provide guidance to improve performance

Combine half-cell models to develop a full-cell model
- Ensure common basis (*e.g.*, mass of current collectors) for various cells

Use model to optimize battery design and evaluate ability to satisfy vehicular needs

New Battery Developed for use in a PHEV

Background-Modeling Voltage Hysteresis

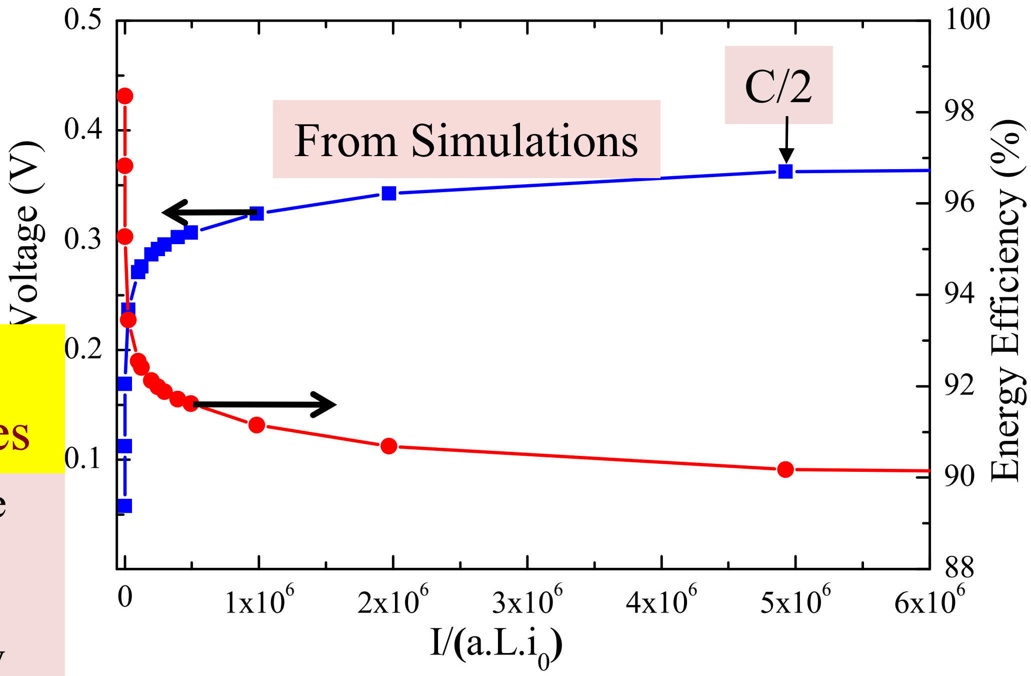


- Developed a kinetic model to predict the voltage offset in silicon.
- Parameters in model were obtained from open-circuit experiments.

However, data was impacted by side reactions, which were not included in the model.

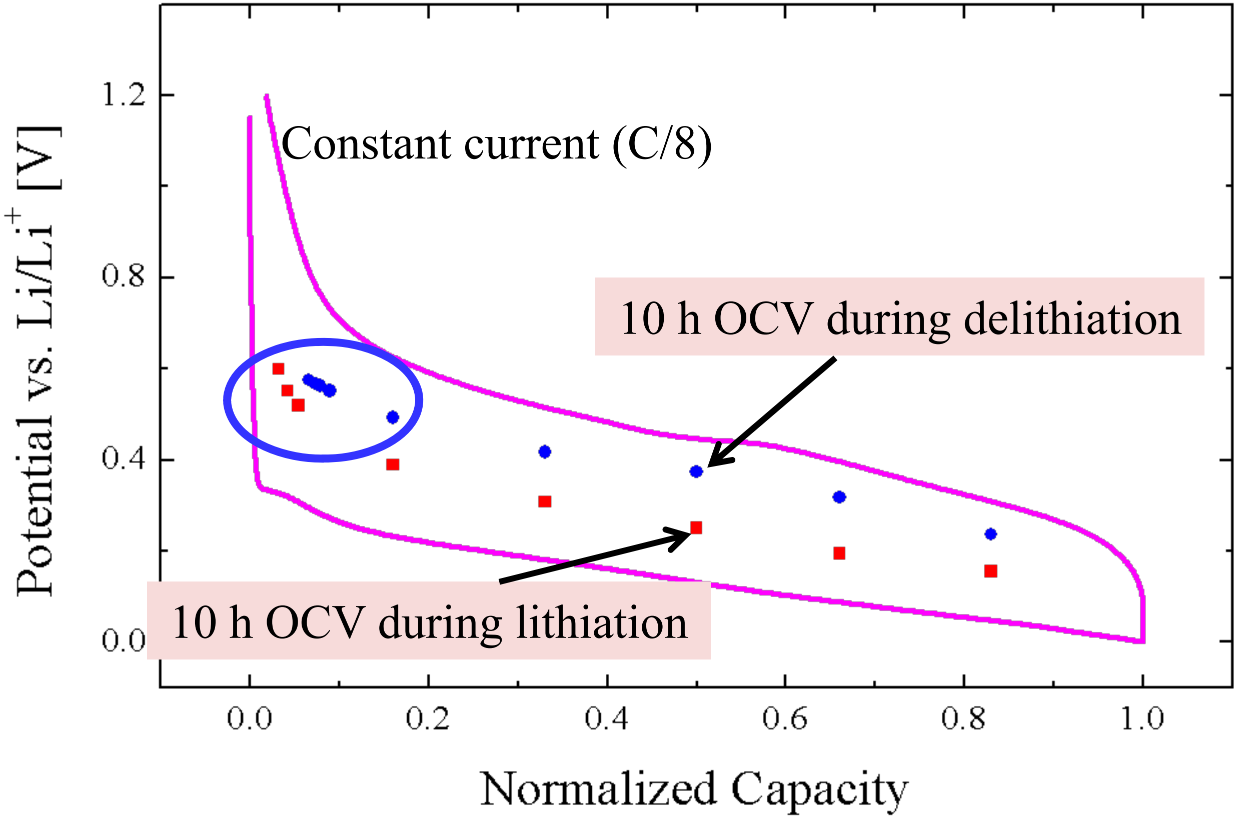
- Model was used to estimate the energy efficiency with rate.
- Shows that voltage relatively insensitive to area at PHEV conditions

Model does not include mass transfer; expected to be important at higher rates



a-surface area per volume
L- thickness
i_0 - exchange CD
I- Applied current density

Technical Accomplishments- Equilibrium Potential



- Note that OCVs do not collapse
  - ➢ Side reaction complicates estimation of a true equilibrium potential
  - ➢ Not clear if the equilibrium path is different, or if curves will collapse if side reaction can be eliminated.
- Note that closeness of the curves at low SOCs- consistent with a side reaction effect

In FY09 we have examined two ways of dealing with the side reaction, (i) *via* correcting for the reaction using a mathematical mode and (ii) using additives

Side Reaction Correction

Marching caused by a side reaction

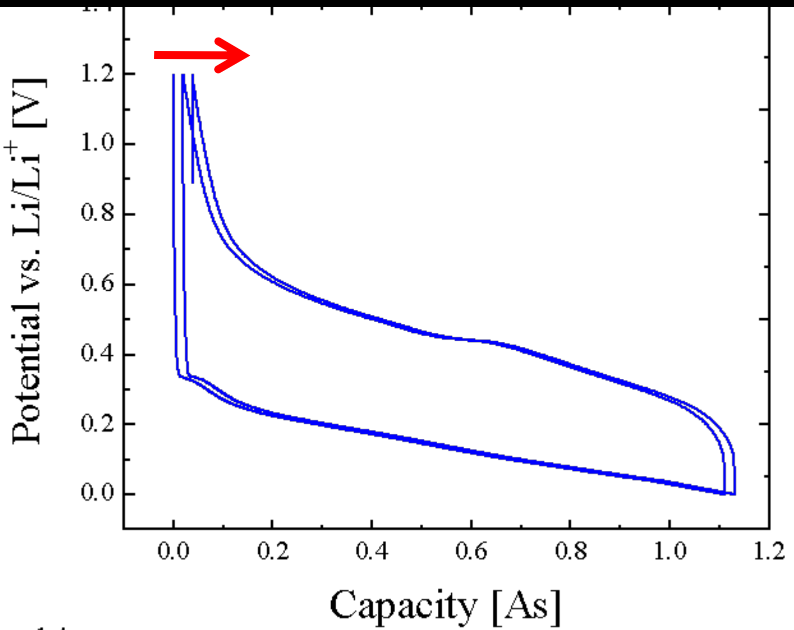
Total Current(i)=lithium insertion(i_{Li})+solvent reduction (i_{side})

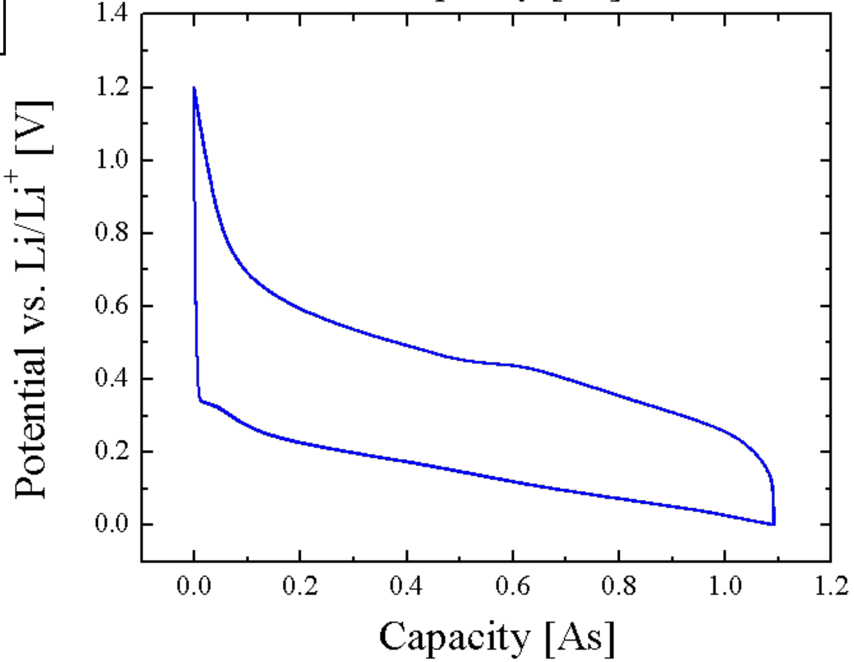
Assume Tafel Kinetics for side reaction (U_{side}=0.8 V)

$$i_{side} = i_{0,side}\exp\left(-\frac{\alpha_{side}F}{RT}(V-U_{side})\right)$$

Calculate i_{side} through the cycle assuming $i_{0,side}$ and α_{side} (0.5)

Find $i_{0,side}$ that eliminates the marching





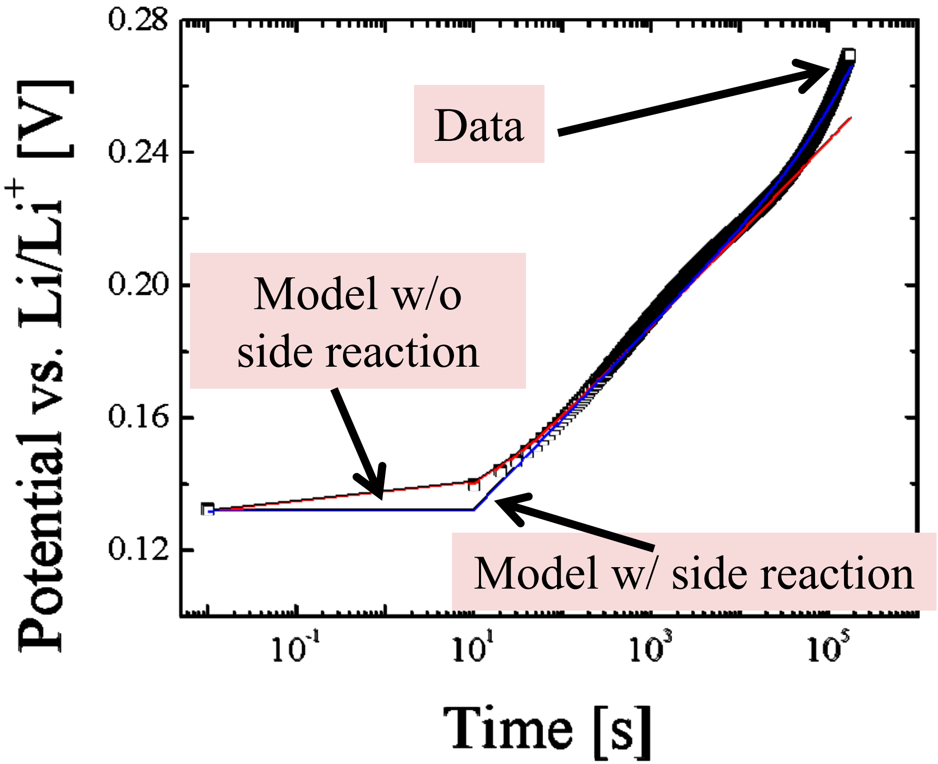
Estimating the Kinetics of the Main Reaction

Assumptions:

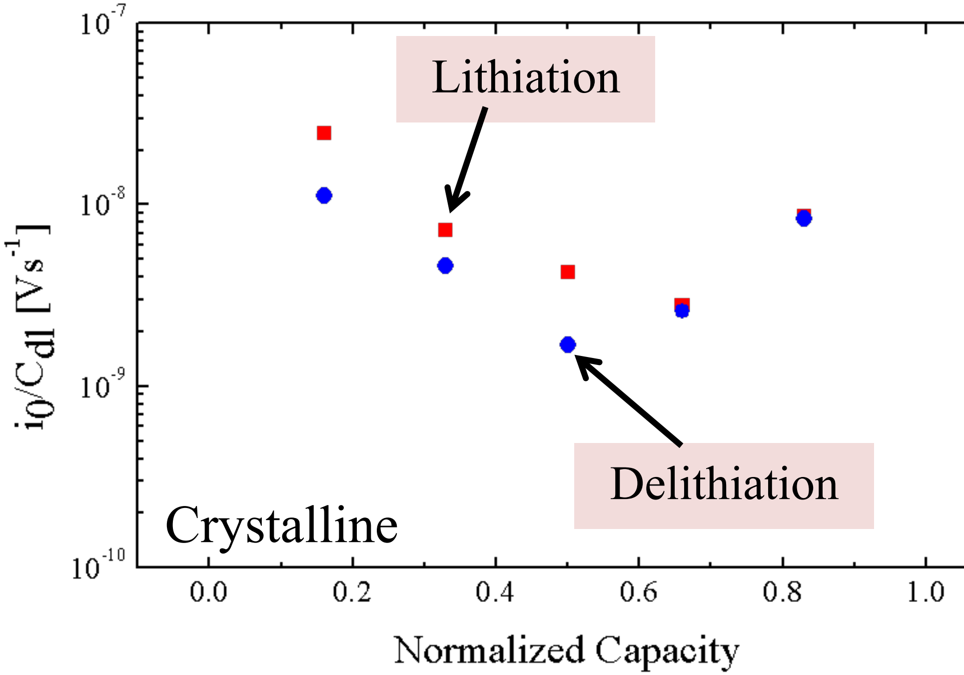
1. Ignore porous electrode effects- thin film
2. Use tafel to represent main reaction kinetics- very small i_o
3. Current small enough to ignore diffusion losses- We are now relaxing this assumption

On open-circuit, solve for: $C_{dl}\dfrac{dV}{dt} = i_o \exp\left(-\dfrac{\alpha_c F}{RT}(V-U)\right)$

Plot of V *vs.* ln(t) should be a straight line at intermediate times.



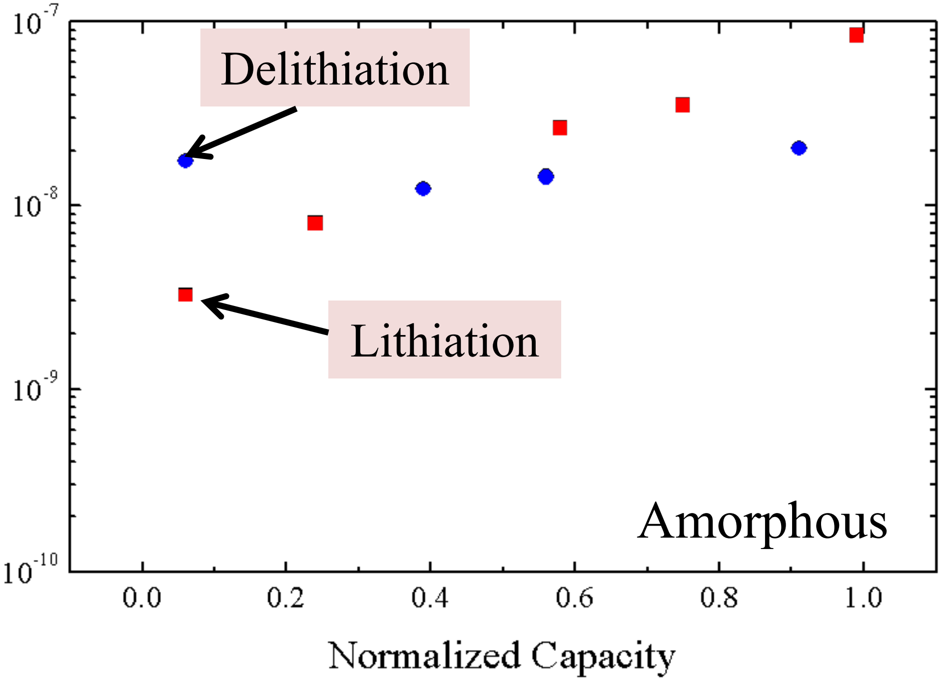
Main Reaction Kinetics Estimated with Model



- Assuming C_{dl}=10 μF/cm^2, i_o O(10^{-13} A/cm^2)
  - On graphite, at room temperature, i_o O(10^{-3} A/cm^2)
- Crystalline films known to undergo amorphatization on the 1st cycle

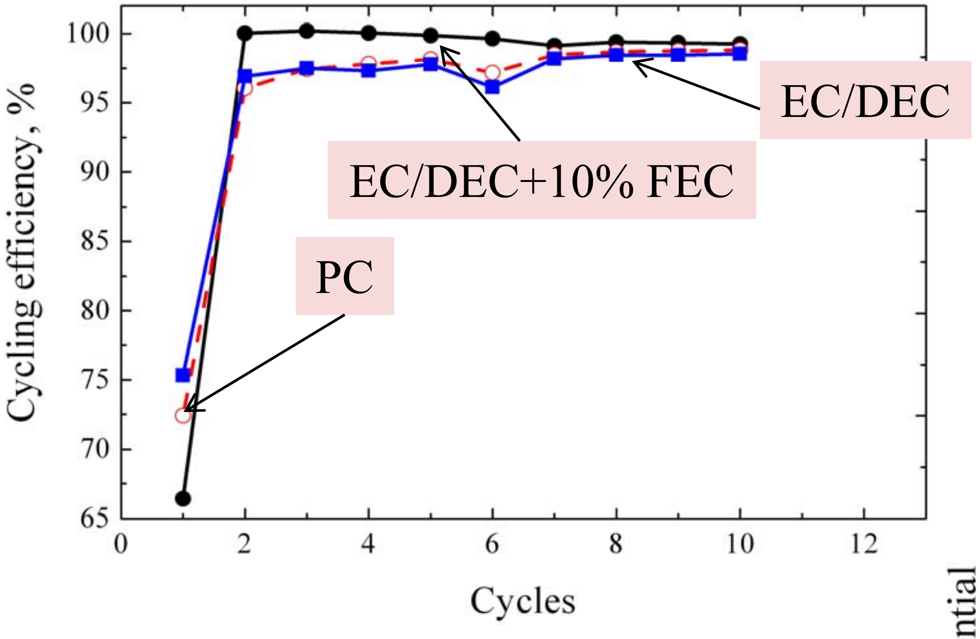
- Values estimated in amorphous films similar to those in crystalline films.
- Small quantitative differences seen; attributed to differences in the equilibrium potential values used.

Methodology established to estimate kinetic parameters for both main and side reactions



Effect of Solvent on Side Reactions

- We have studied the side reaction rate in PC and using Fluoroethylene Carbonate (FEC) as an additive



FEC: 99.26%, $i_{0,s} = 4.05 \times 10^{-13}$ A/cm^2

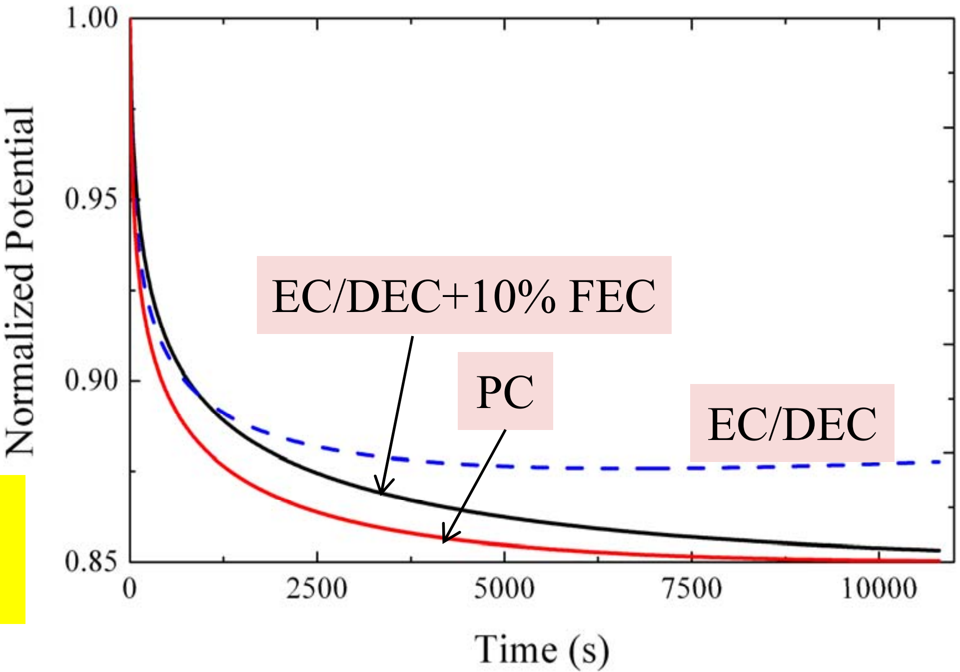
PC: 98.82%, $i_{0,s} = 7.25 \times 10^{-13}$ A/cm^2

EC:DEC: 98.55%, $i_{0,s} = 9.55 \times 10^{-13}$ A/cm^2

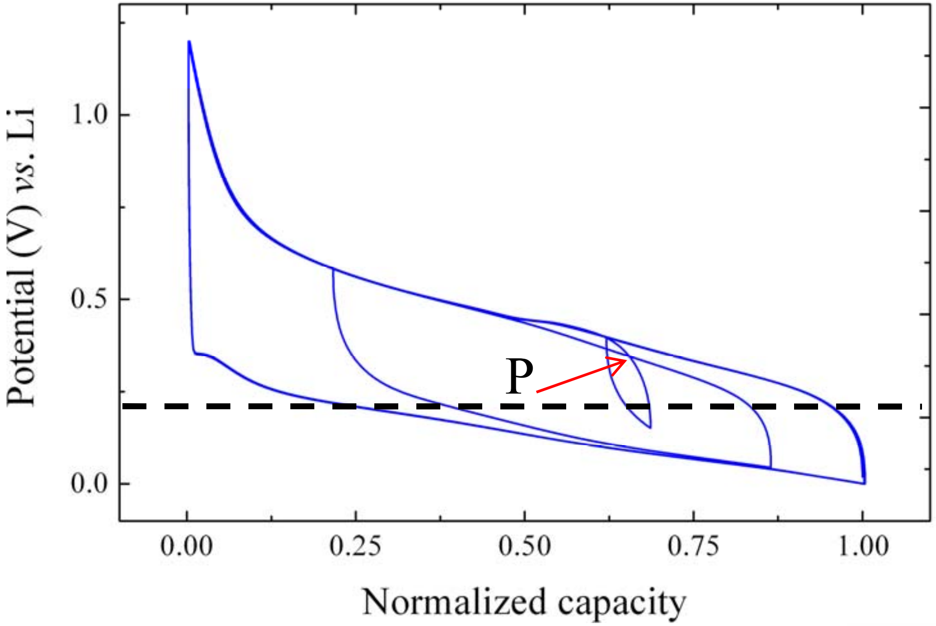
Significant increase in efficiency with FEC additive

- Solvents appear to make a better SEI.
- No change in offset potential

FEC-based electrolytes provides a means of identifying true equilibrium potential



Cycling of Silicon Anodes under PHEV Cycling



- Note that the point “P” can be approached in two different ways

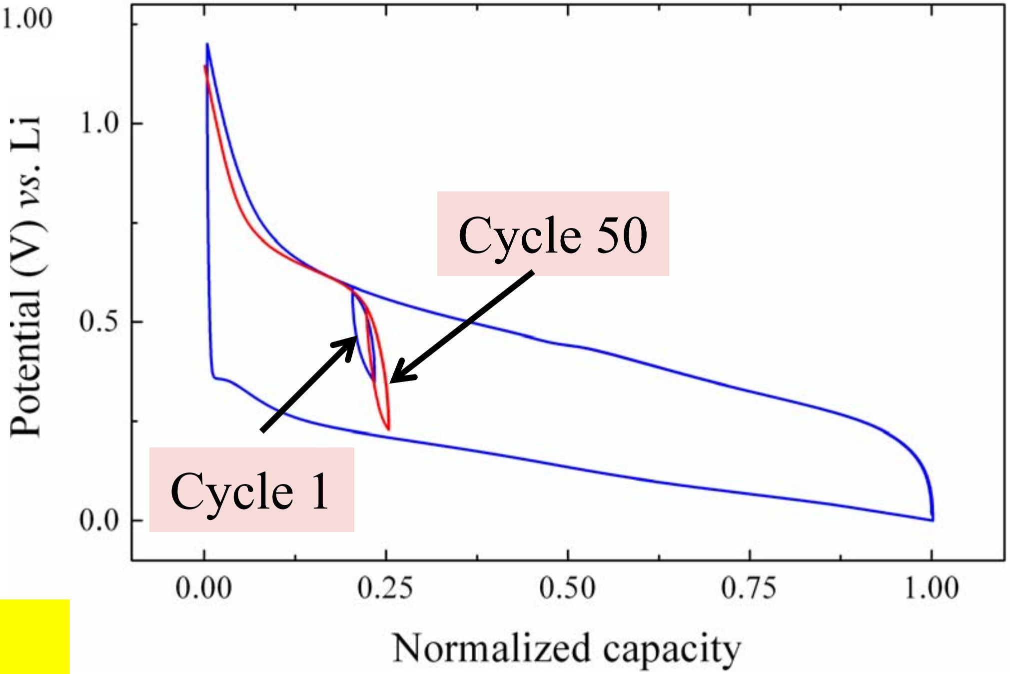
- Path after crossing the point dictated by the past history

- Predicting the voltage made very difficult because of hysteresis.

- On continuous HEV or PHEV-type cycling, voltage “drifts” to lower values
  - ➢ <u>Not due to side reactions</u>

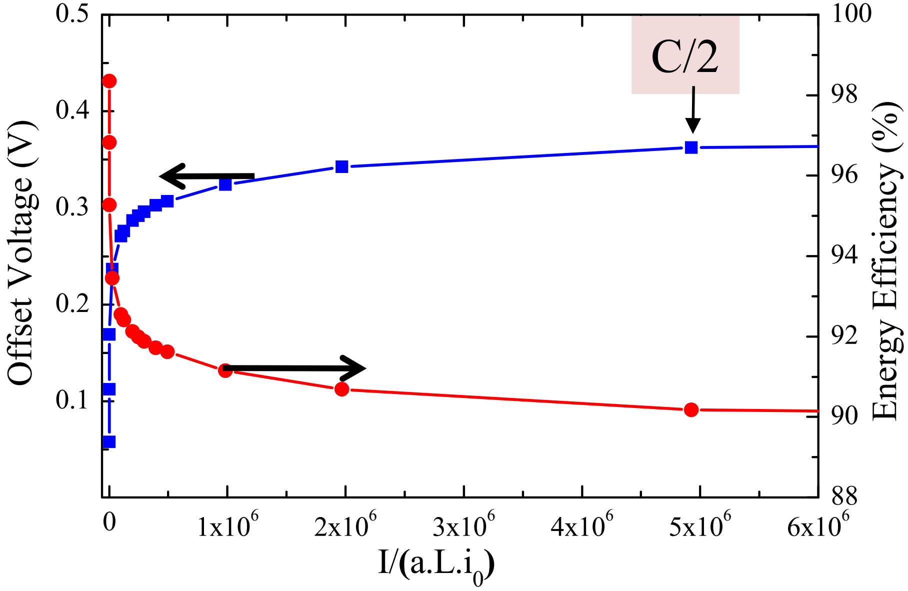
- Note that peak power would change during the cycling.

- May indicate that the “true” equilibrium potential is closer to the charging voltage.



Path dependence complicates battery management systems

Effect of Copper-coating on Cycling of Silicon



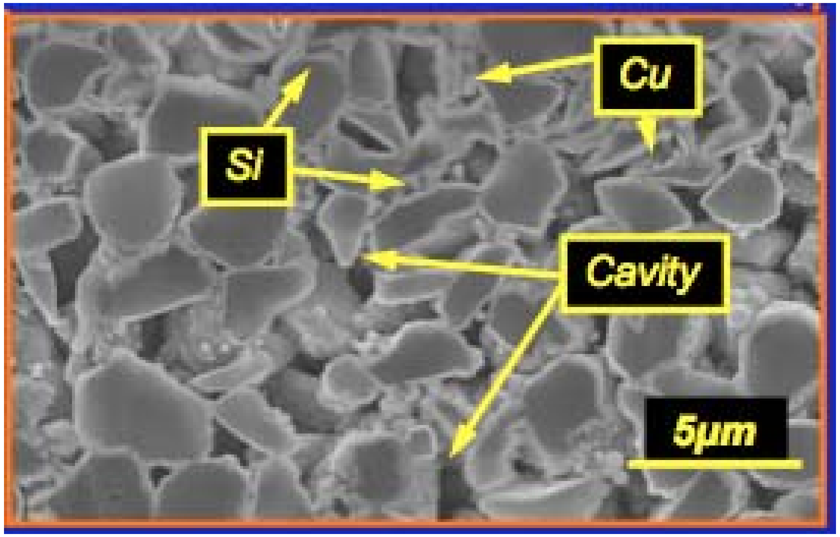
- Model predicts that under PHEV conditions, energy efficiency should be relatively insensitive to area.

- Mitsui has announced introduction of SILX® technology for vehicle market.

- Technology allows doubling of capacity over graphite.

- 20% fade in 500 cycles (100% DOD)

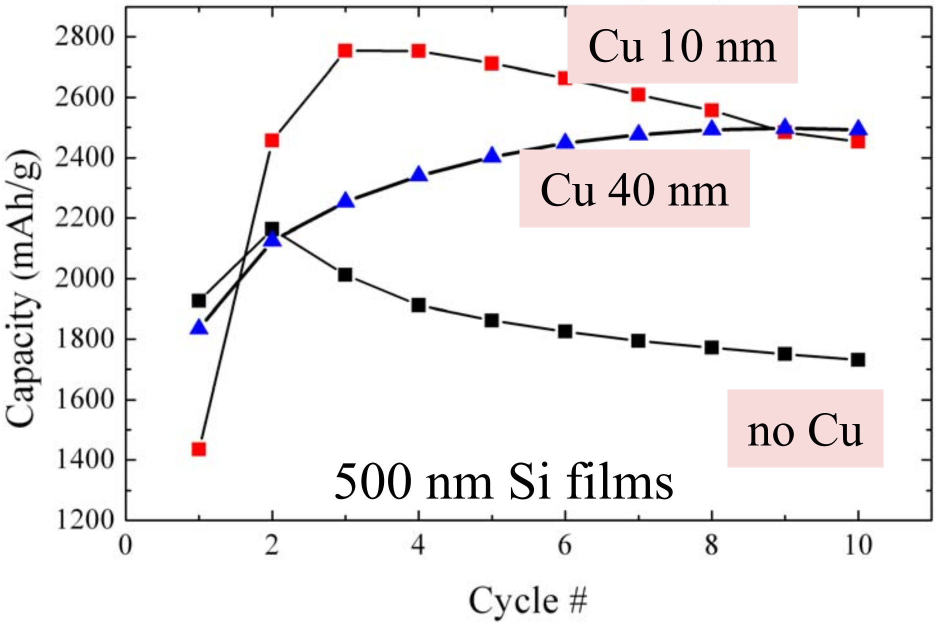
- Significantly lower fade in HEV-type cycling



SILX® technology developed by Mitsui Mining and Smelting Co., Ltd

Final Goal: Develop model for this chemistry.
Progress to date: Experimentally examine impact of Cu coating on Si thin films

Studies on Copper-coated Silicon



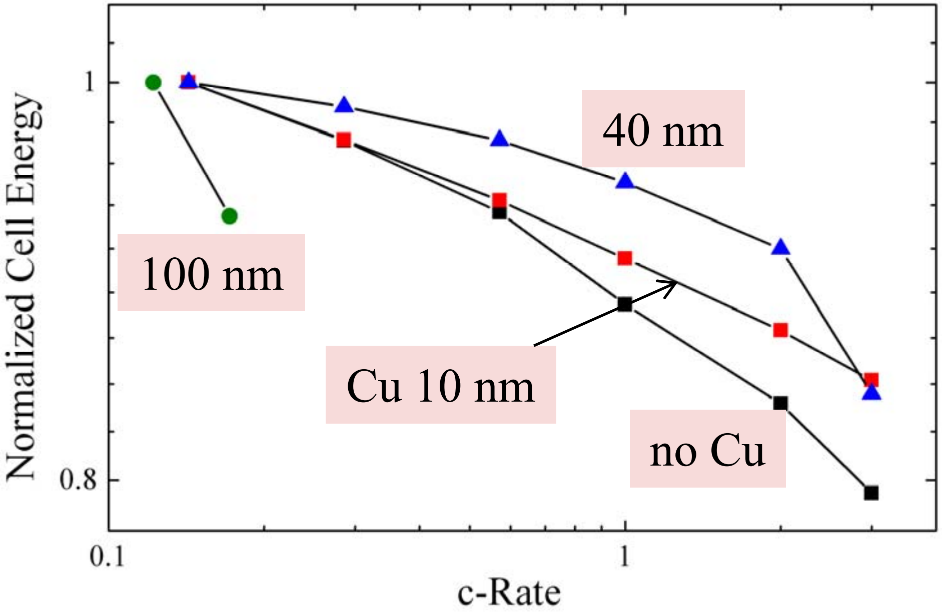
- Discharge curves at different rates suggest that ohmic limitations decrease with addition of copper (leading to better performance).

- However, rate decreases significantly at higher Cu thicknesses as capacity of silicon is not accessible.

- Silicon films fade rapidly with cycling.

- Copper layer appears to prevent particle isolation caused by the volume expansion and cracking.

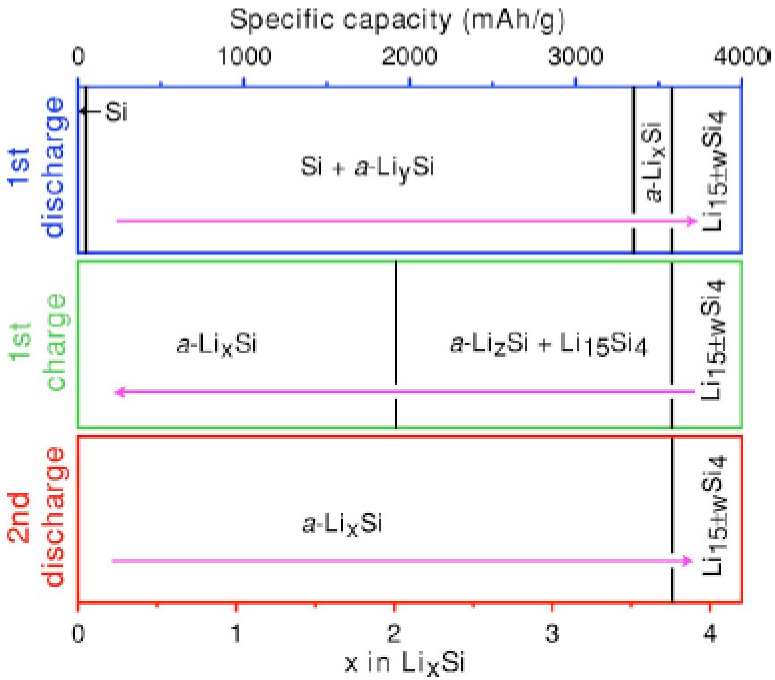
- However, a critical amount of copper is needed.



Study suggests that copper layer prevent particle isolation
However, surface cannot be covered with copper

Modeling Mass Transport in Silicon

Phase Diagram



Source: Li and Dahn, *J. Elec. Soc.*, **154**, A156 (2007)

- During the 1st lithation, crystalline silicon undergoes solid state amorphatization.

- Subsequent cycling occurs in the amorphous range.

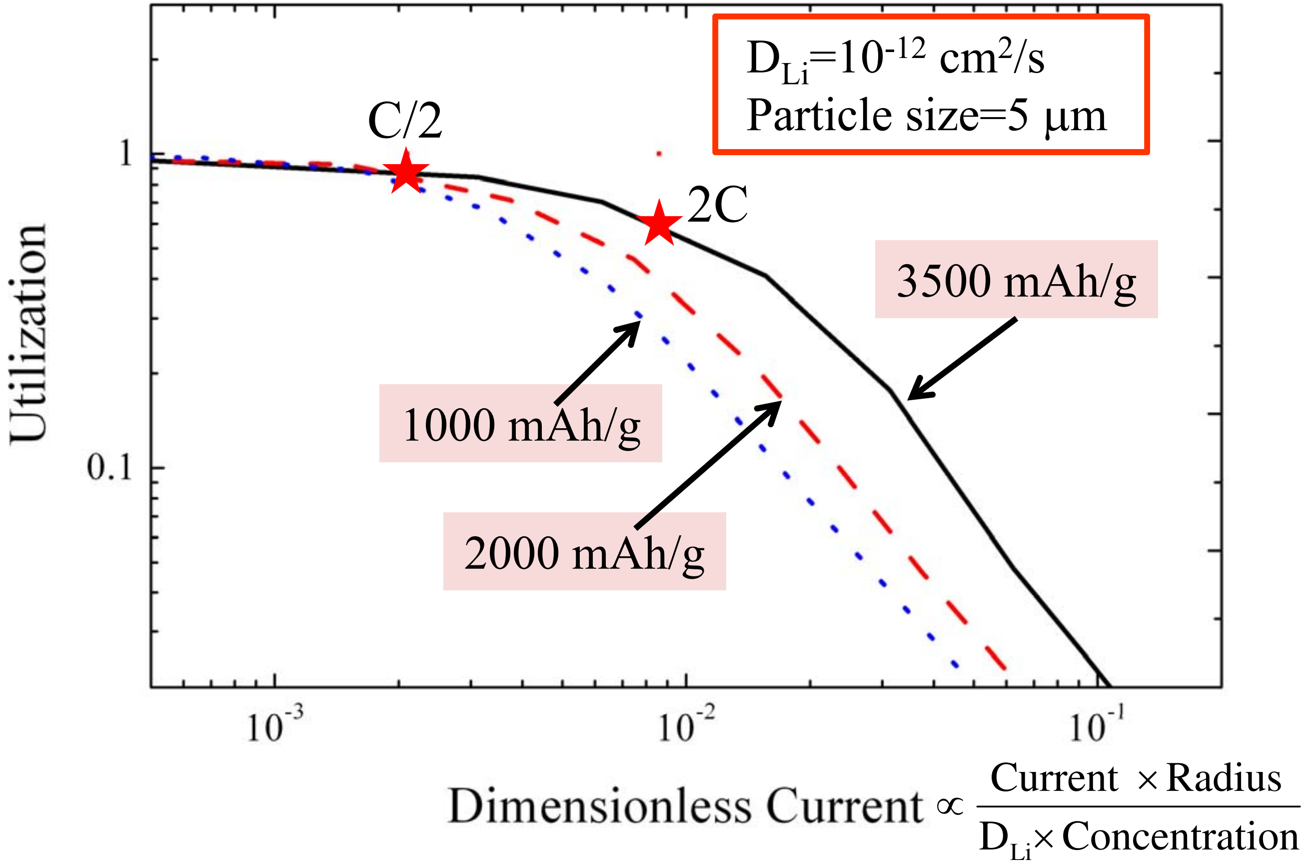
- However, at high concentrations of Li in the lattice, crystalline $Li_{15}Si_4$ phase forms

  - ➢ Thought to be detrimental to cycling [Obrovac and Krause, *J. Elec. Soc.*, **154**, A103 (2007)]

We are developing a mathematical model to identify conditions under which the crystalline phase forms, with emphasis on PHEV operation.

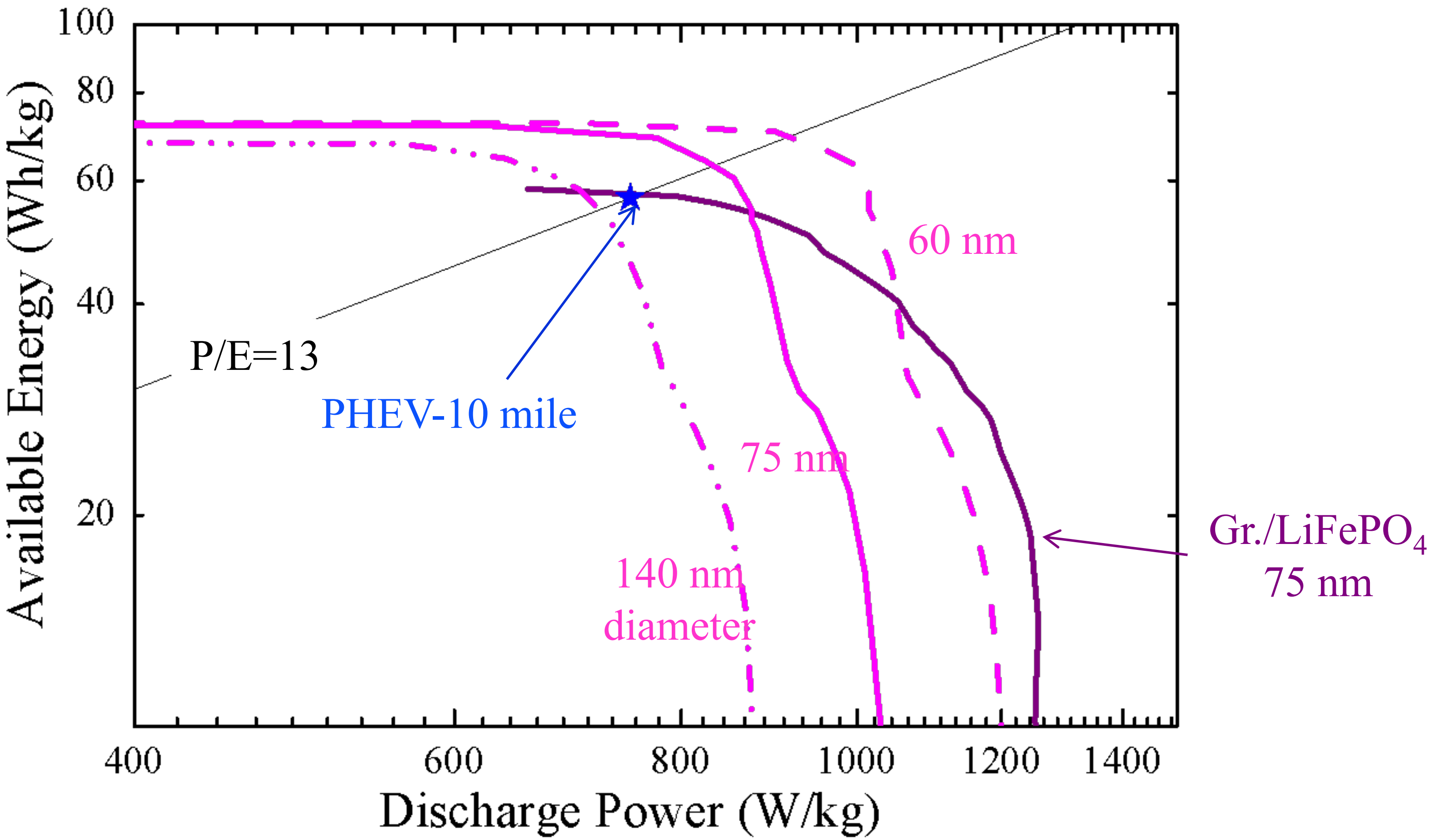
Modeling Mass Transport in Silicon

- Model does not explicitly account for the 1st lithiation cycle
  - Analysis performed for cycling in the amorphous region after formation
  - 1st cycle accounted to identify the extend of formation of the amorphous region
- Wide disparity in reported values of diffusion coefficient (10^{-8} to 10^{-13} cm^2/s)



Model suggests that silicon electrodes could have rate limitations when used in PHEVs
Note that pulse operation would exacerbate effect.

Studies on $LiMnPO_4$ cathodes



- Properties for $LiMnPO_4$ assumed to be similar to $LiFePO_4$
    - Note that in reality conductivity of $LiMnPO_4$ less than $LiFePO_4$

- However, the closeness of the flat potential to the cut-off potential means that performance has to exceed that for $LiFePO_4$ to truly take advantage of the higher potential

Future Work

- Incorporate the kinetic and mass transfer models into a porous electrode model and simulate the performance of a NMC/Si cell under PHEV conditions

- Work with Cell Analysis group to obtain experimental data on silicon powders to compare to the model.

- Complete the study on the copper-coated silicon samples and develop a mathematical model that accounts for the decreased area for reaction and increasing diffusion length on PHEV operation.

- Develop a model for $LiMnPO_4$ that incorporates the recent understanding of phase behavior obtained in $LiFePO_4$

Summary

- The large voltage offset in alloy anodes decreases the energy efficiency and complicates SOC prediction.

- Mathematical model was developed that can be used to estimate the kinetic properties that characterize the main and side reactions.

- Additives and solvents have a large impact on the side reaction and can help minimize them, presumably, by making a better SEI.

- Copper coatings on silicon appears to hold the electrode together during cycling, enhancing cycling capability
  - ➢ While the tafel-like behavior of silicon suggests that small changes to the area for reaction will not have a big impact on polarization, fully covering the surface will lead to no access.

- Mass-transfer model allows identification of cycling conditions under which life-limiting phenomenon can occur