Kinetics of Lithium Insertion into Silicon Anodes

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OVT Merit Review

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This presentation does not contain any proprietary or confidential information

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Purpose of work

1. Compare the performance of various lithium-ion cathodes when used in HEV and PHEV applications using mathematical modeling

2. Understand the limitations in using alloy anodes (specifically silicon) in PHEV applications

Responses to reviewers' comments- June 2006

1. "Extend the modeling to other systems"
   - *Research has been directed to next-generation systems (alloy anodes) in keeping with BATTs emphasis in this area*

2. "The PI should interact with and guide the staff who are building cells"
   - *Close interaction exist with cell analysis group*

3. "Not clear what info the models will give to the experimentalists"
   - *Models have provided guidance to material developers (how small a particle is needed to achieve HEV-like power?) and cell developers (how thick should the electrode be for a PHEV?)*

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

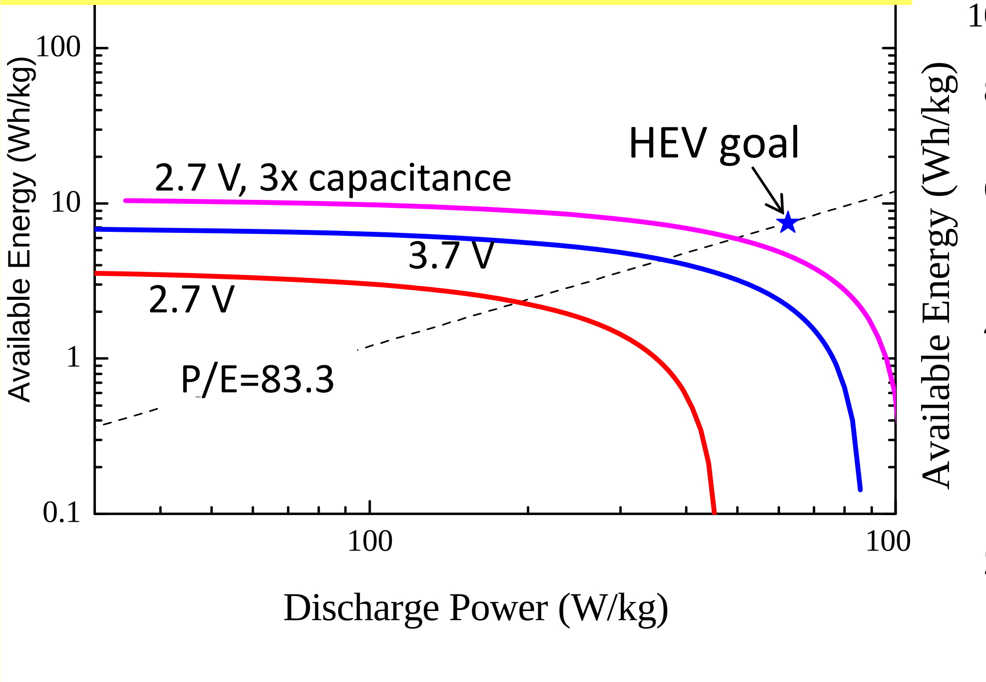
Use model to optimize battery design and evaluate ability to satisfy vehicular needs

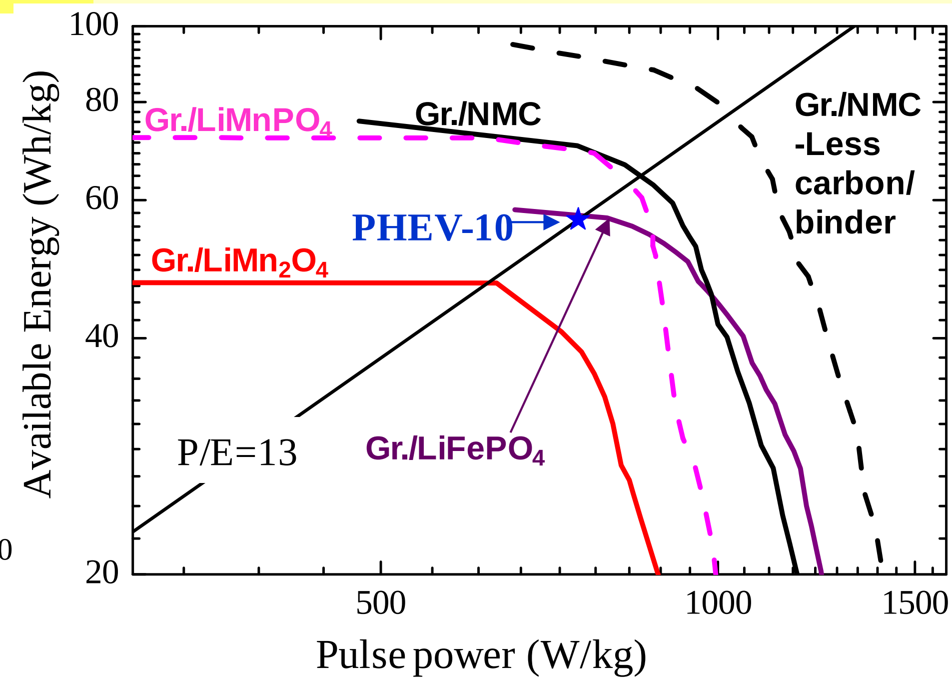
New Battery Developed for use in a PHEV

Accomplishments

New Material Synthesized

symmetric carbon capacitors with tetraethlyammonium tetrafluoroborate in acetonitrile





New Battery Developed for use in a PHEV

Approach

New Material Synthesized

Develop model for each chemistry

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Understand limitations and provide guidance to improve performance

We have been using this approach to model silicon anodes.
All experiments are conducted on thin films as opposed to porous electrodes

New Battery Developed for use in a PHEV

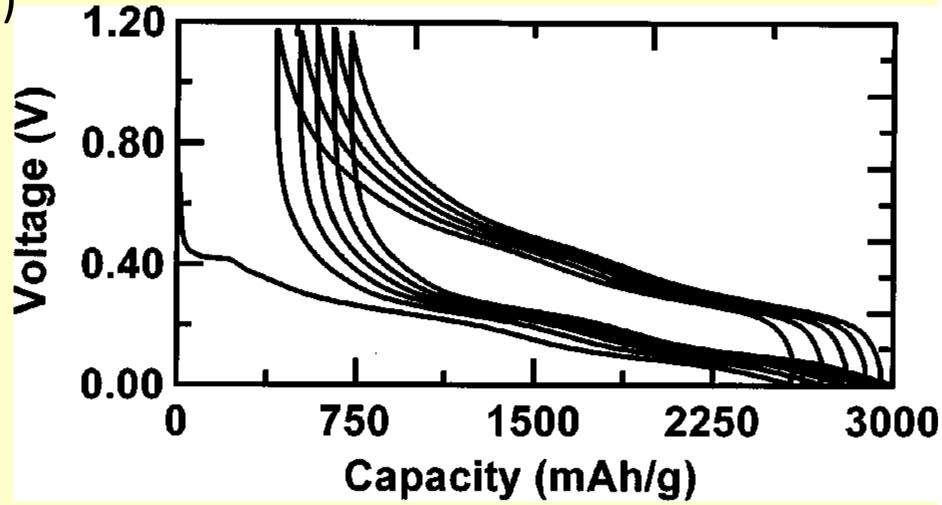
Why silicon?

- High capacity compared to graphite (3579 *vs.* 372 mAh/g)
  - Theoretical energy of the cell *could* increase by ~35% (lower $/kWh)

Barriers

- Large irreversible capacity loss (1000 mAh/g)
- Large volume change during cycling (280%)

J. Electrochem. Soc., **150**, A1457 (2003)

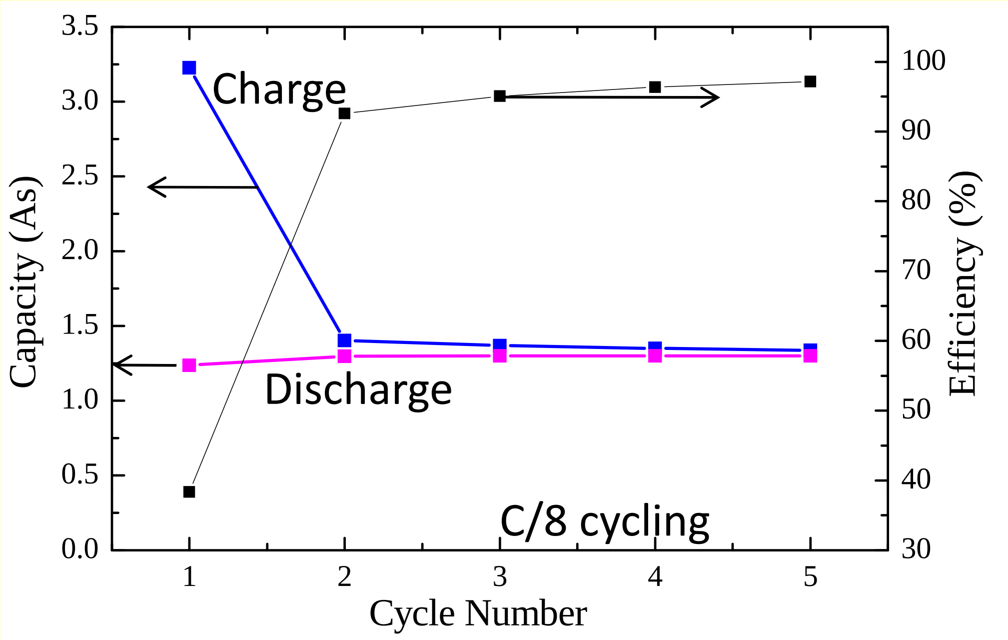


- Even at low rates (C/10), the voltage during lithiation is lower than during delithiation by ~0.32 V

Impact:

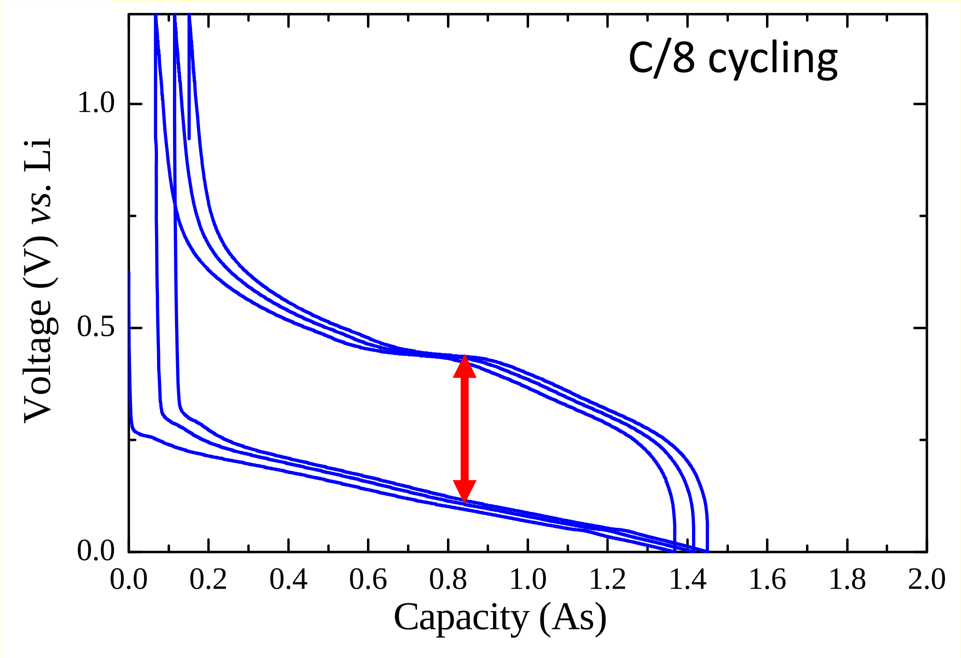
1. **Round trip energy efficiency**=91% (at C/10). VT goal is 90% on HEV cycling (10C)
2. Resistance estimate=~7000 Ω-cm^2 ! Typical resistance of electrodes=15 Ω-cm^2
   Has impact on VT **power goals**.

Film behavior

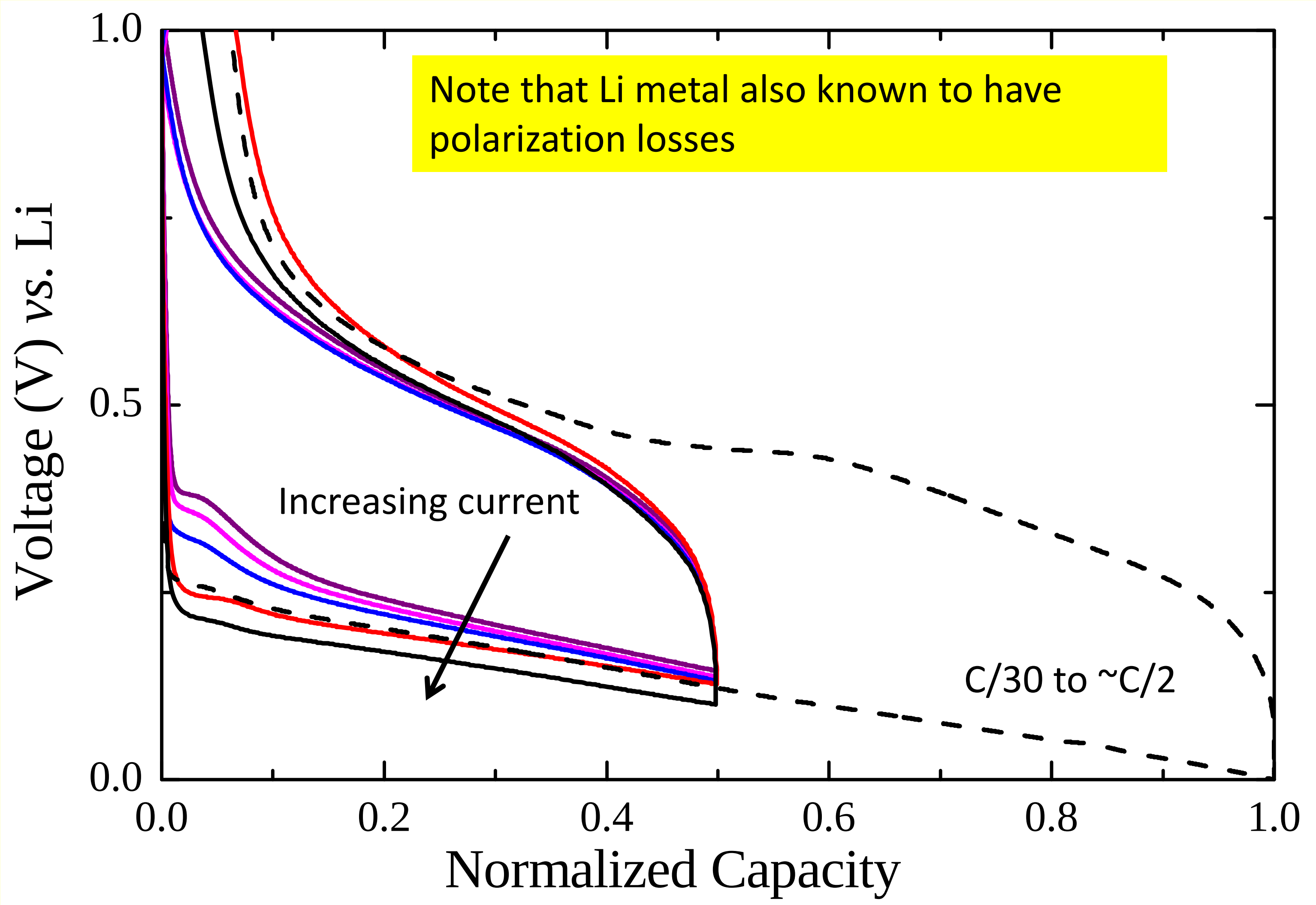


- Large 1st cycle loss
- Good cycleability for many cycles
- Evidence of a side reaction

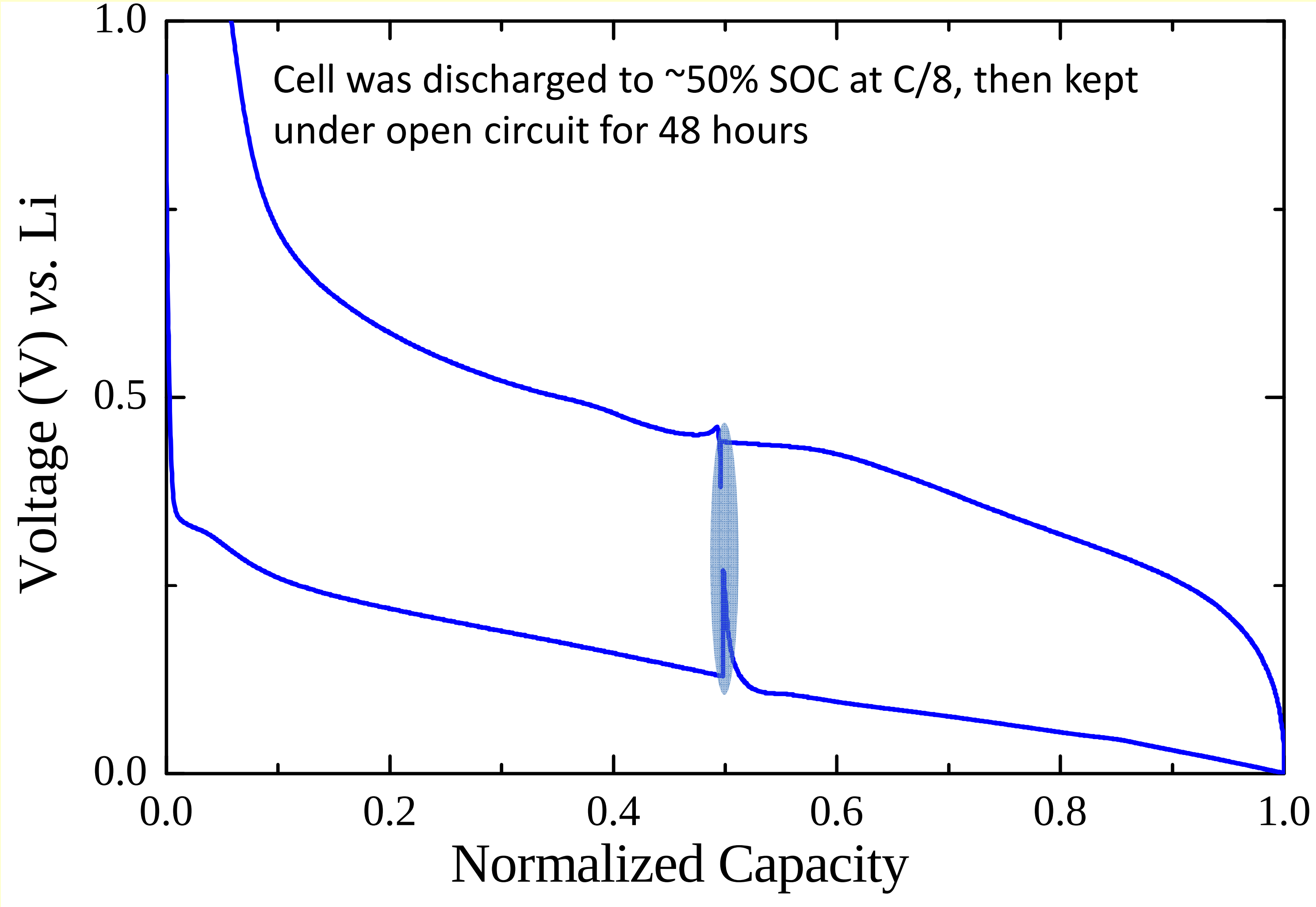
- As-made films are crystalline (based on Raman spectroscopy)
- Electrochemical data suggests that films have features similar to porous electrodes made with silicon powders
- Based on literature data, we believe that we are cycling in the amorphous Si region (*i.e.*, single phase region).



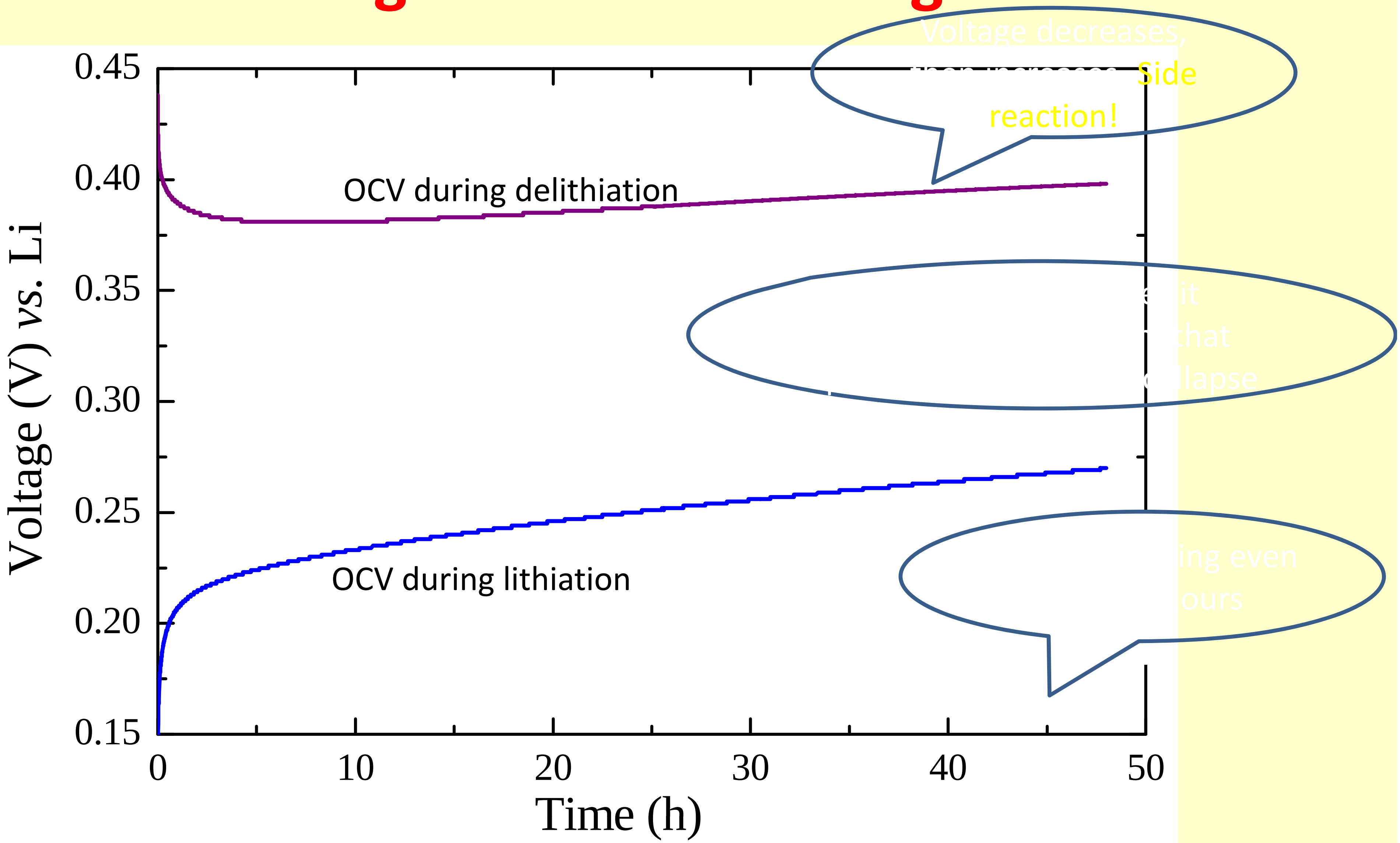
Is this voltage offset rate dependent?



Open-circuit experiments on the Si electrode



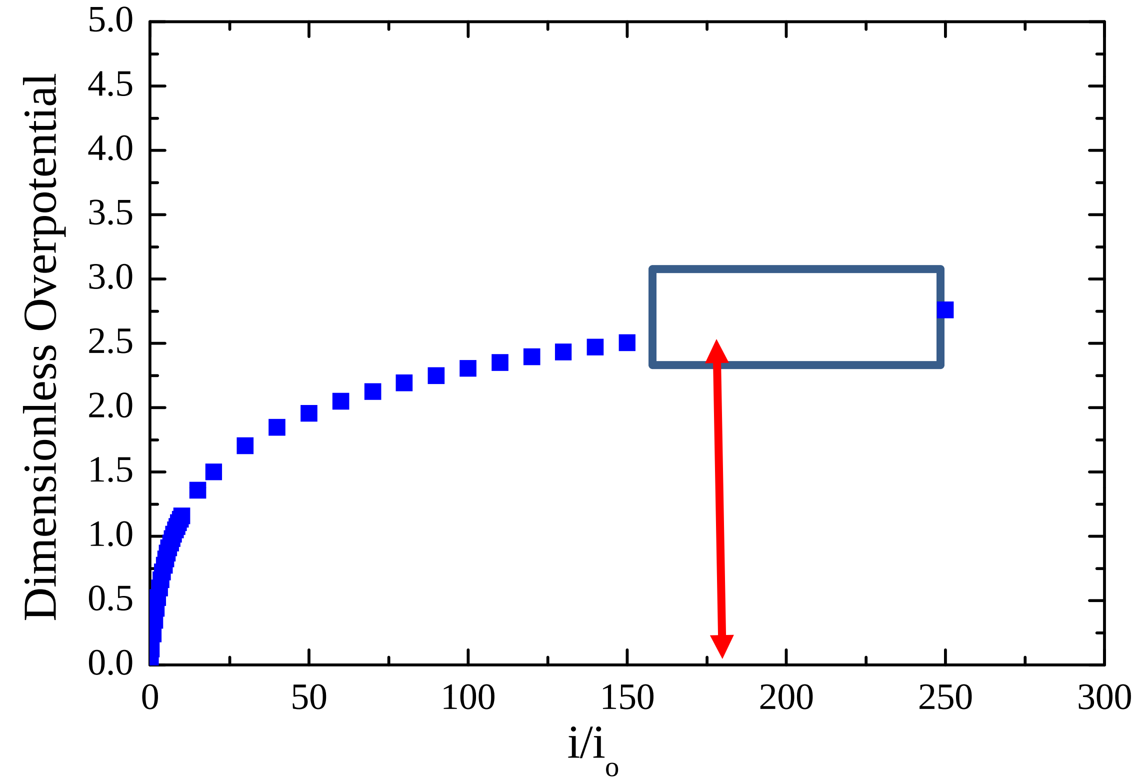
Voltage evolution during OCV



Tafel kinetics with double-layer charging

- A reaction with poor kinetics (small i_o) would show an offset even at low rates

- And would show little change in overvoltage with current, for large i/i_o



- On open-circuit, double layer discharges the faradaic reaction
  - Time constant $\propto \dfrac{RTC_{dl}}{Fi_o}$
  - If i_o is small, time constant can be very large

Estimating the kinetics of the reaction

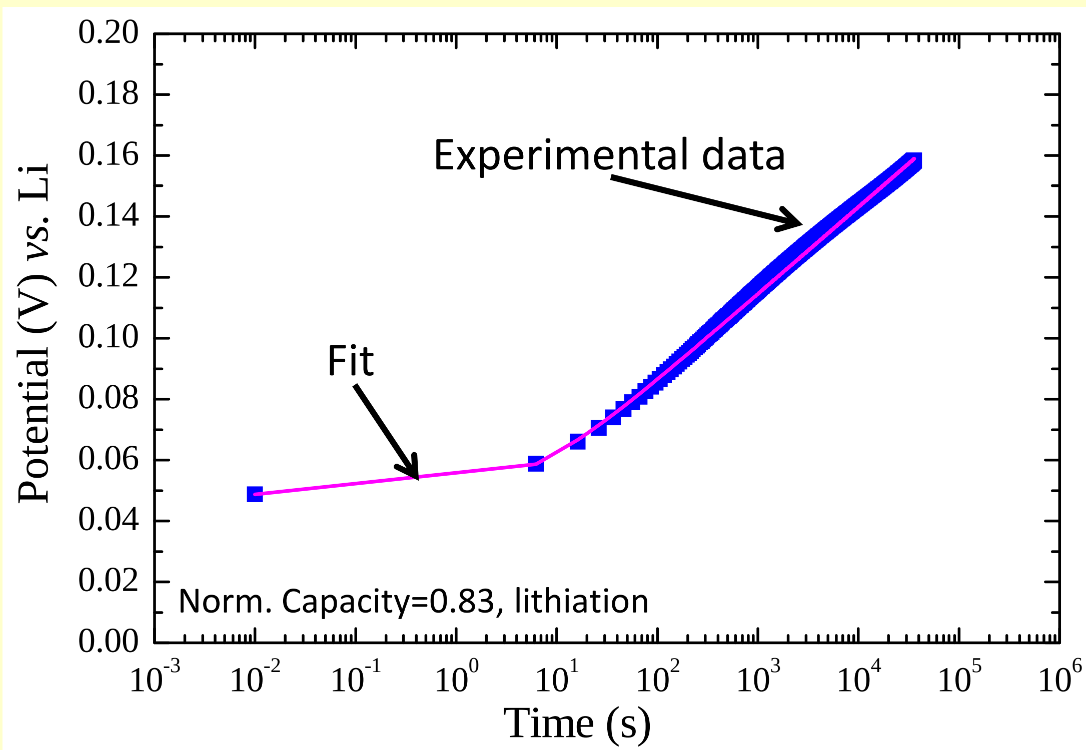
Assumptions:

1. Ignore porous electrode effects- thin film
2. Ignore the side reaction- only important at very long times
3. Use tafel to represent kinetics- very small i_o
4. Current small enough to ignore diffusion losses

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

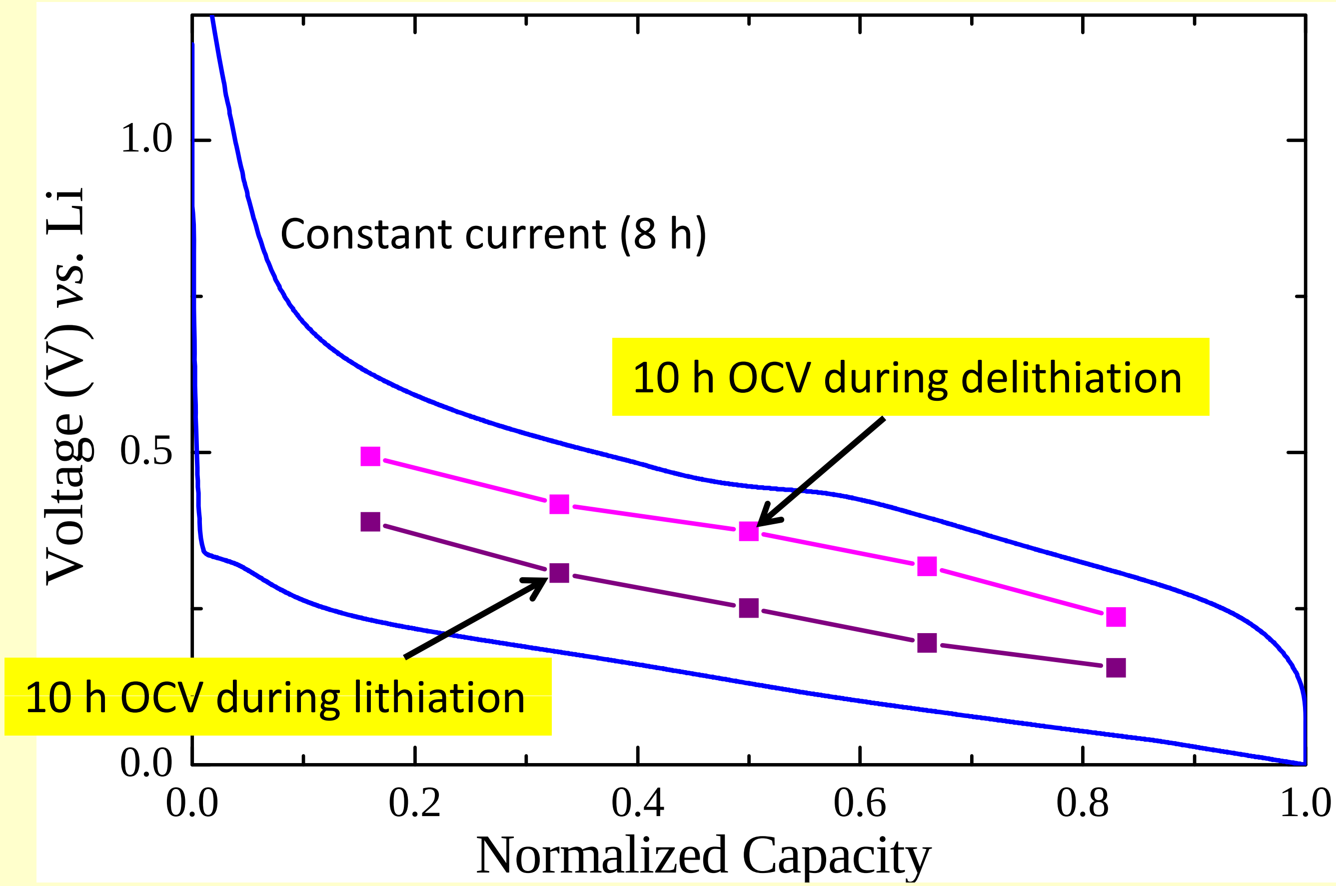
In Tafel kinetics, i_o and U are connected

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



* Davis *et al.*, J. Electrochem. Soc., **154,** A477 (2007)

Voltage offset *vs.* SOC

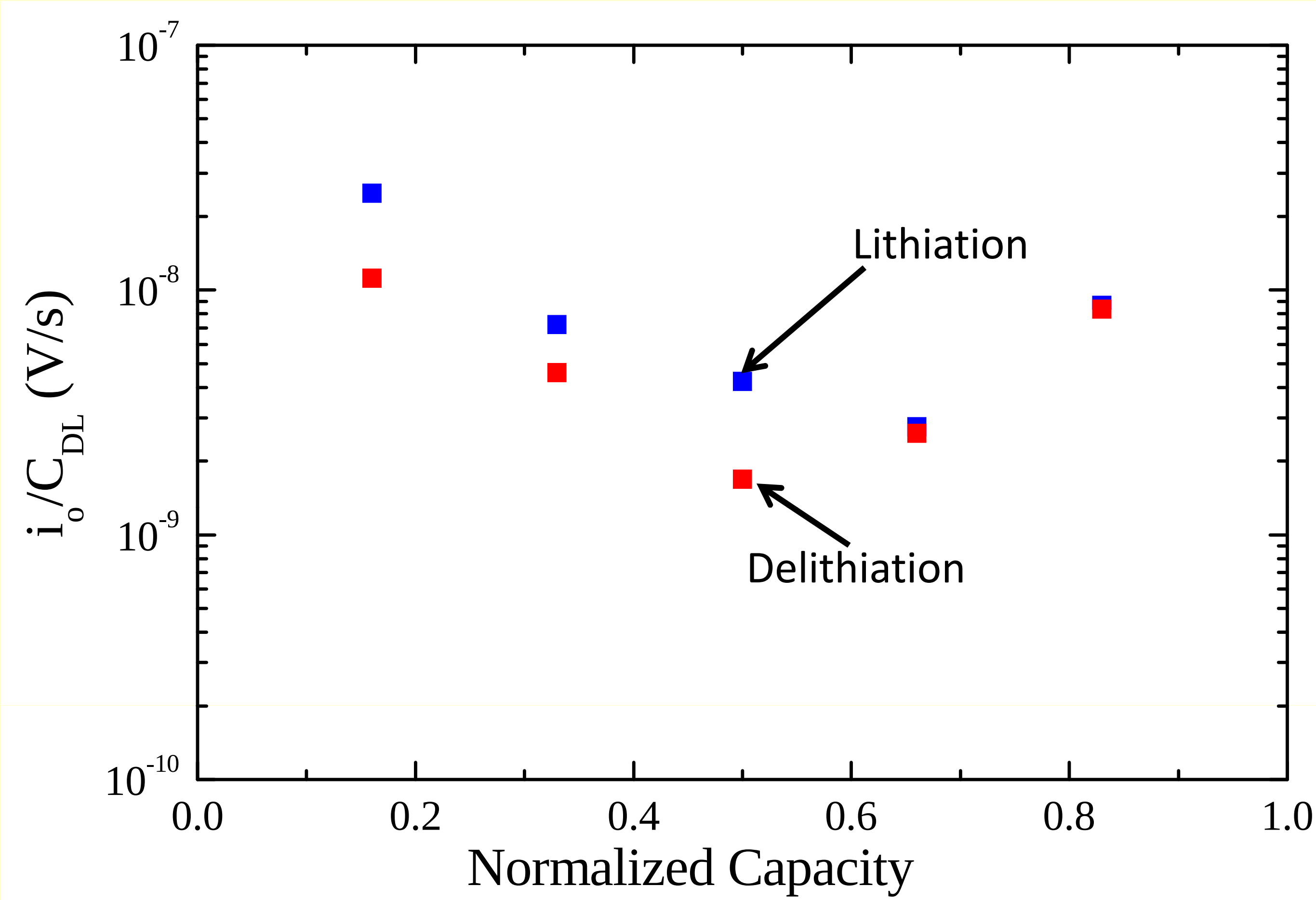


• Note that OCVs don't collapse to same potential because of side reaction

• Similar experiment on silicon-powder porous electrodes performed at low SOC showed that the curves *almost* collapse

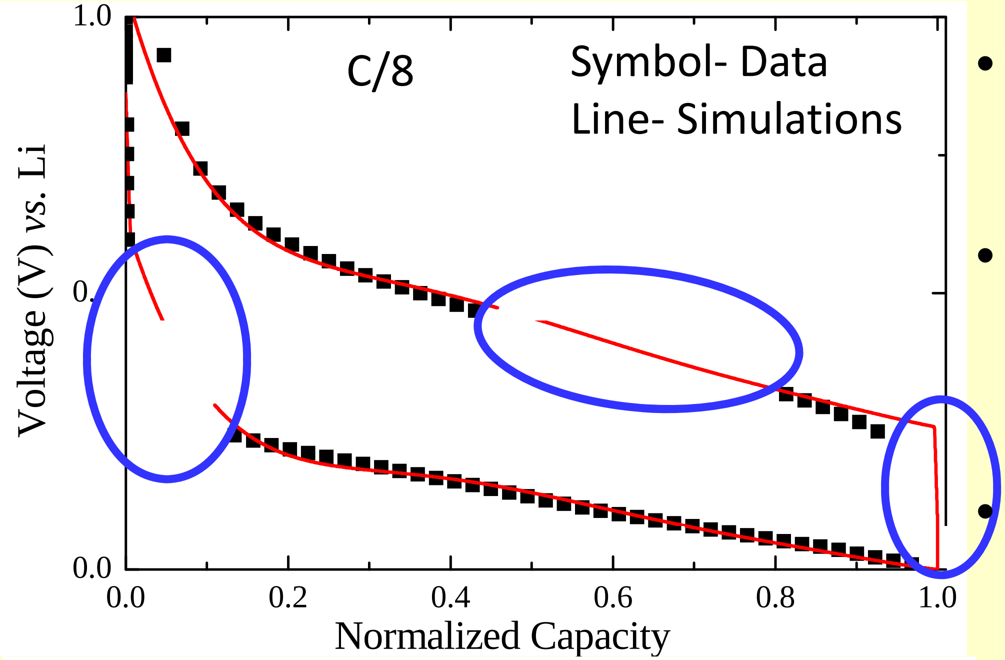
OCV data for these 10 points were used to estimate kinetic parameters across SOC range

Parameter estimation

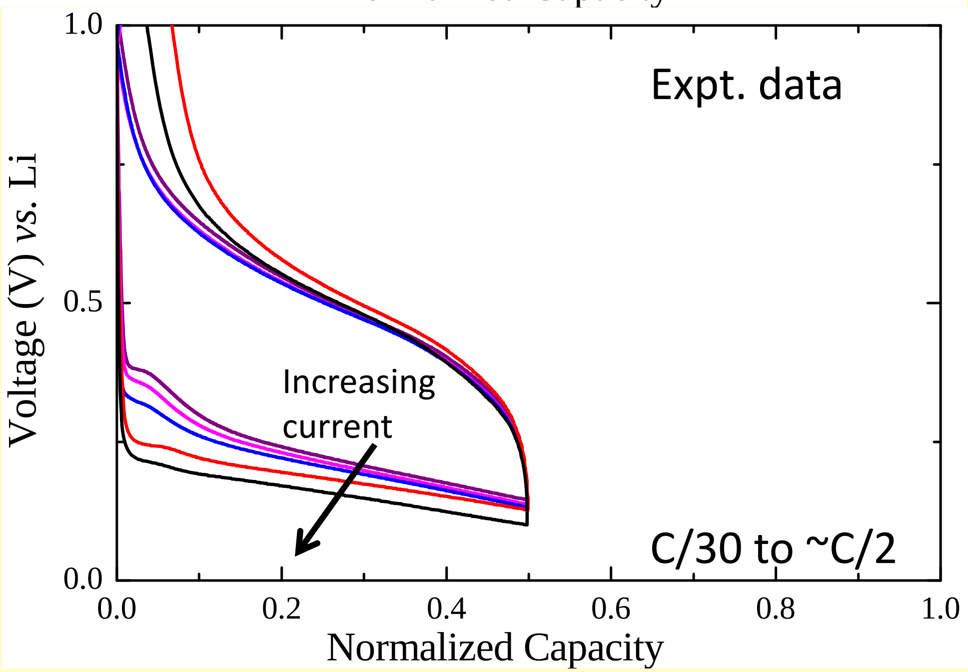


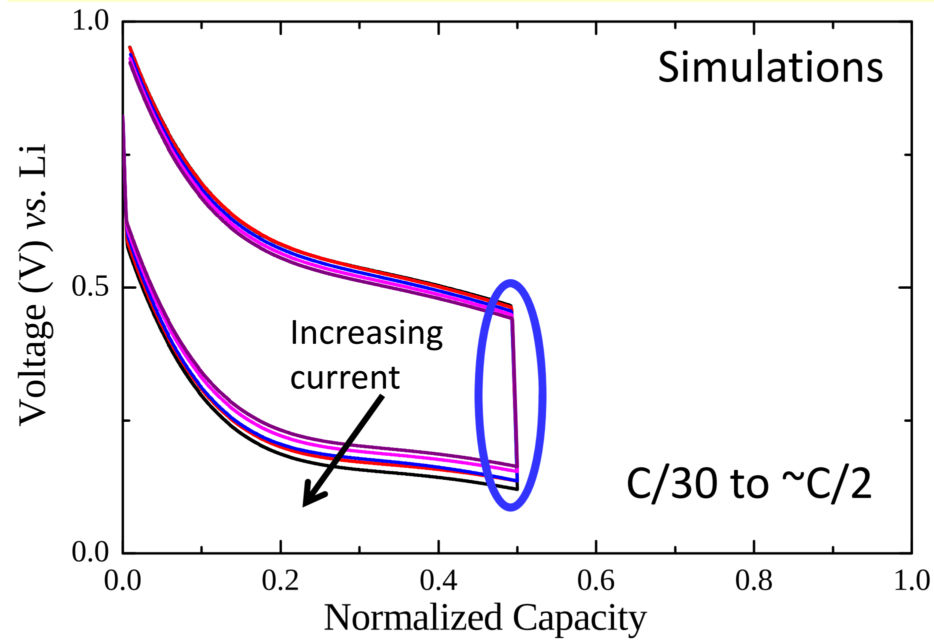
- From an OCV experiment, i_o and C_{DL} are not separable
- Assuming C_{dl}=10 μF/cm^2, i_o O(10^{-13} A/cm^2)
  - Estimates on graphite suggest i_o O(10^{-3} A/cm^2) (see J. *Electrochem*. Soc, **150**, A706, 2003)

Simulation results



- Model does an excellent job of predicting constant current data
- However, voltage evolution on change in current not predicted
  - Related to capacitance and/or area
- Better OCV needed to predict features at 0 and 0.6

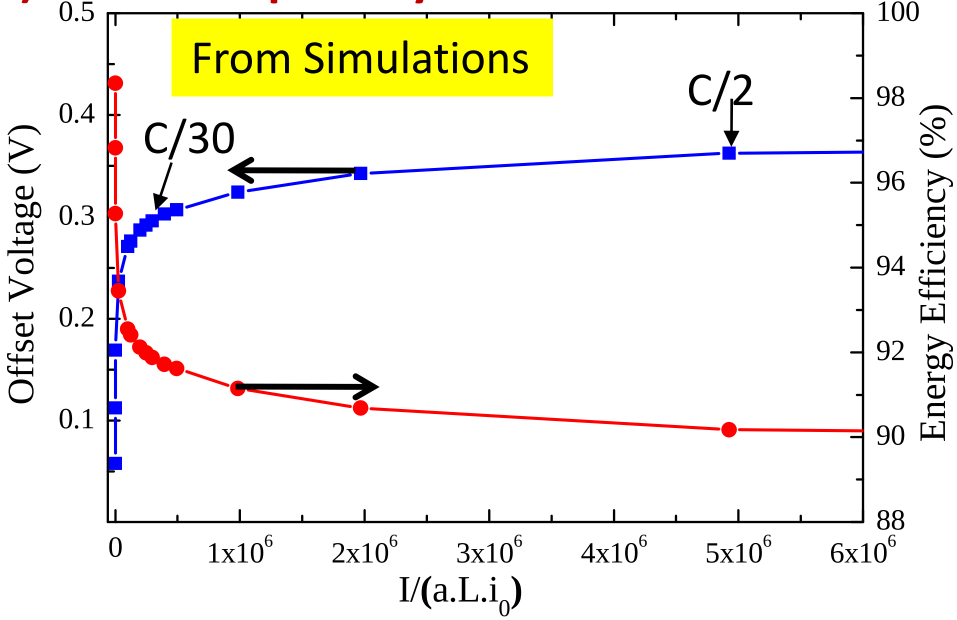


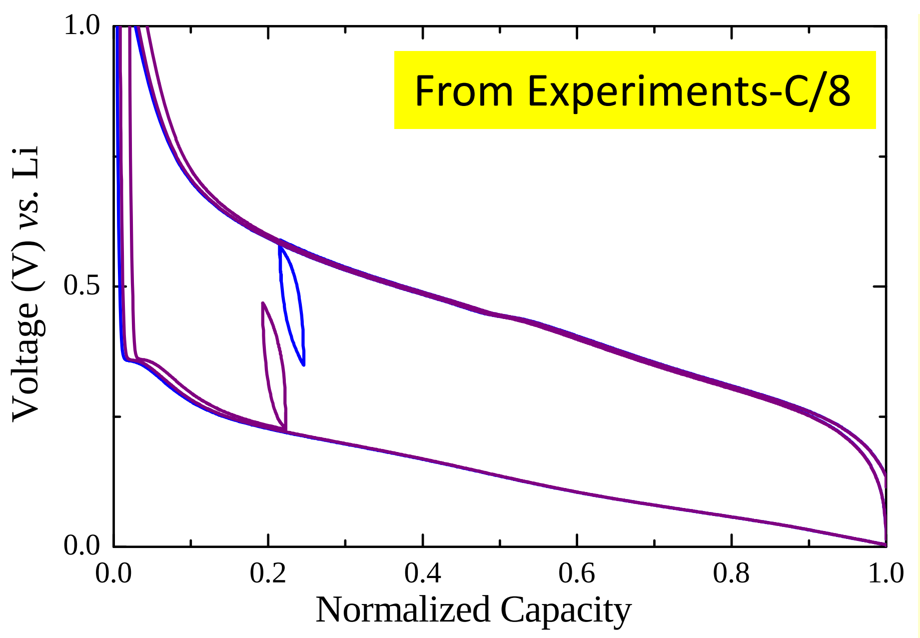


Connection to the barriers

Barriers: (i) Round trip energy efficiency (ii) Power Capability

- Model predicts that high energy efficiency can only be obtained by 5 orders of magnitude decrease in I/aLi_o

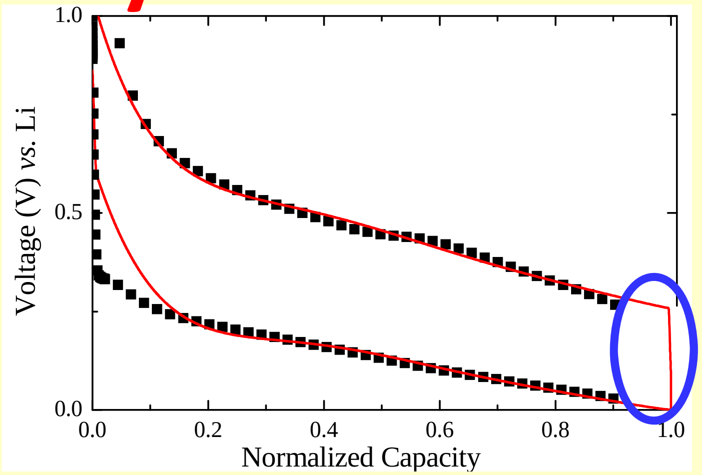


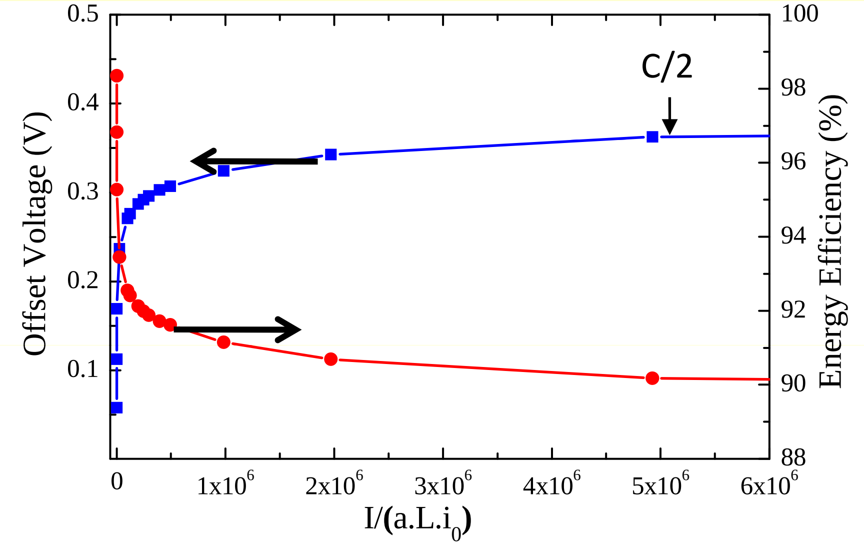


- However, double-layer can sustain currents during short periods allowing lower resistance than predicted by the offset voltage
- Energy efficiency=98.2%

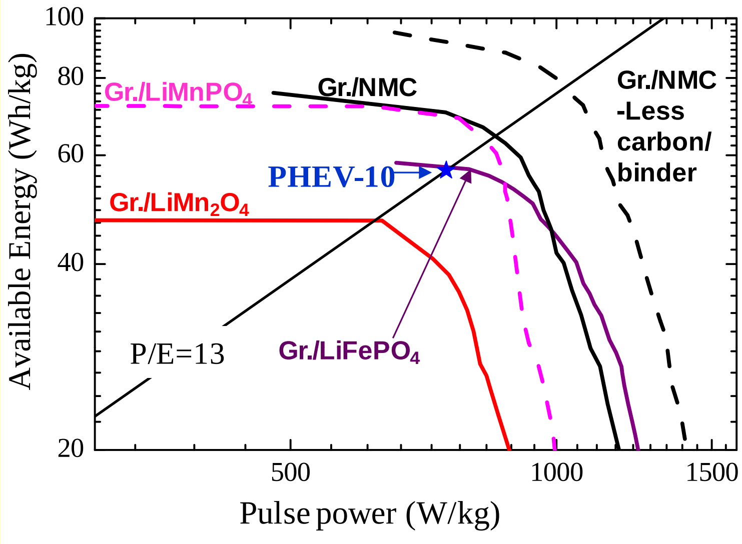
Plans for next fiscal year

- More quantitative predictions of voltage evolution
  - Impedance spectroscopy for capacitance
  - Structural changes between lithiation and delithation



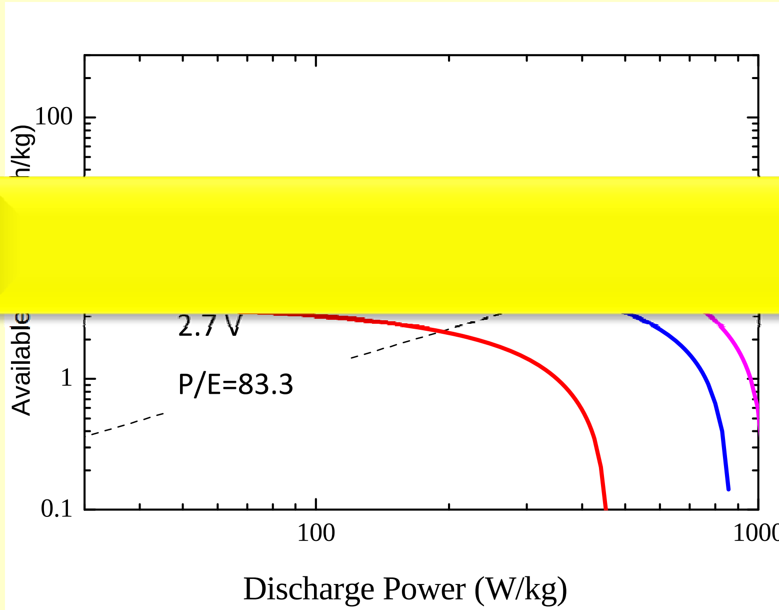


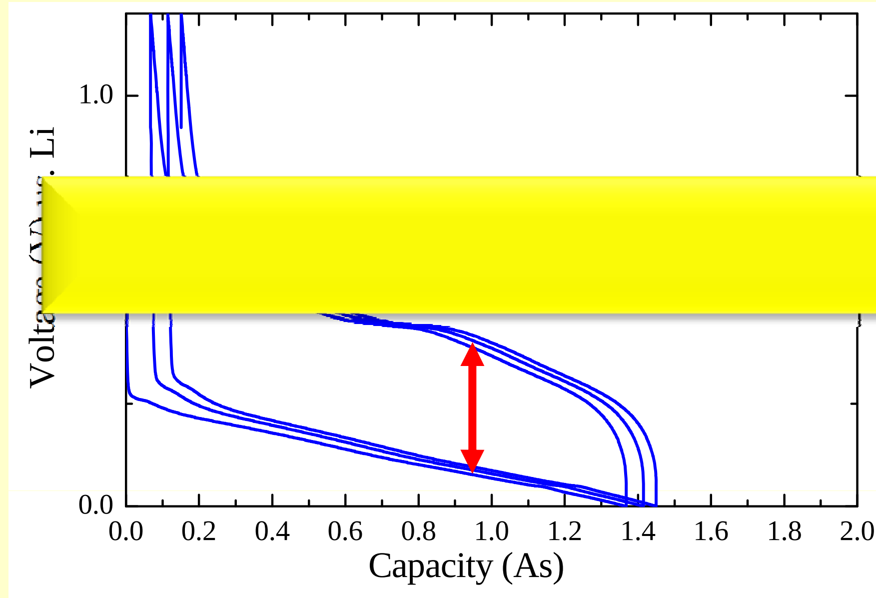
- Estimate transport properties to predict behavior at rates greater than 2 C
  - Develop model with slow kinetics
  - Need electrodes with well defined diffusion lengths

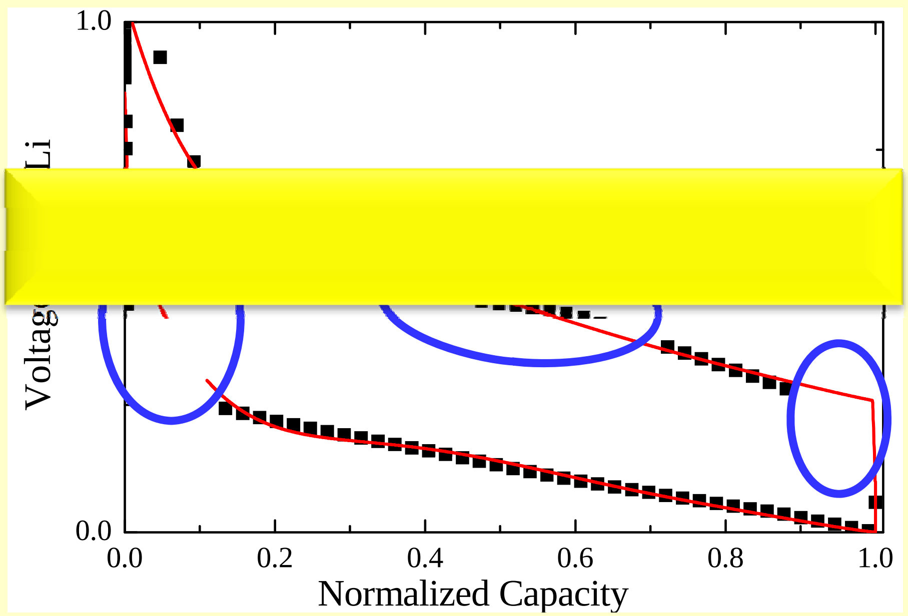


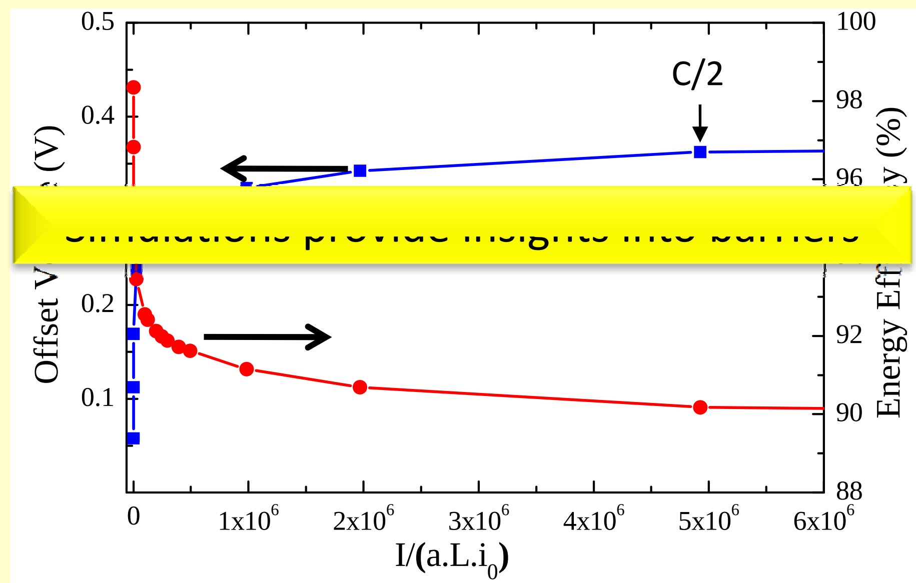
- Develop a comprehensive model for $LiMnPO_4$ cathodes
  - Better description of the phase evolution and transport

Summary


100
1
0.1
2.7 V
P/E=83.3
100
1000
Discharge Power (W/kg)


1.0
0.0
0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0
Capacity (As)


1.0
0.0
0.0 0.2 0.4 0.6 0.8 1.0
Normalized Capacity


0.5
0.4
0.2
0.1
100
98
96
92
90
88
C/2
0 1x10^6 2x10^6 3x10^6 4x10^6 5x10^6 6x10^6
I/(a.L.i0)

Publications and Presentations

1. Sarah Stewart, Paul Albertus, Venkat Srinivasan, Irene Plitz, Nathalie Pereira, Glenn Amatucci, and John Newman "Optimizing the Performance of Lithium Titanate Spinel Paired with Activated Carbon or Iron Phosphate", *J. Electrochem. Soc.*, **155**, A253 (2008)

2. Venkat Srinivasan and John Newman, "Li-ion Batteries for Plug-in Hybrid Applications; A Combined Model-Experimental Study", Presented at the 48th Battery Symposium of Japan, November 2007, abstract number 3F02.

3. Sarah Stewart, Venkat Srinivasan, and John Newman "Meeting FreedomCAR goals for power assist HEVs using batteries and capacitors", *J. Electrochem. Soc., to be* submitted, Feb. 2008.