ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY

FreedomCAR

Analysis and Simulation of Electrochemical Energy Systems

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This presentation does not contain any proprietary or confidential information

Project ID: es_18_newman

Overview

Timeline

- Start: October 1, 2008
- End: September 30, 2009
- Percent complete: 70%

Barriers

- Enhance abuse tolerance (EEST Roadmap 3.4.2.3)
- Diagnose and model cell behavior (EEST 3.4.3.4)

Budget

- Total project funding
  - DOE share: 100%
  - Contractor share: 0%
- Funding received:
  - FY08: $410k
  - FY09: $830k
- Personnel: 2 students, PI in summer

Partners

- Nitash Balsara (LBNL-BATT)
- Vince Battaglia (LBNL-BATT)
- John Kerr (LBNL-BATT)
- Venkat Srinivisan (LBNL-BATT)

Objectives

I. Explain why lithium deposits preferentially at edges during cell charging

II. Investigate use of redox shuttles for overcharge protection
   - What properties does a redox shuttle need in order to protect the cell during overcharge?
   - How is the existence of an SEI compatible with the successful operation of a shuttle?

Milestones

- Complete study of capacity usage in HEVs and PHEVs (April 2008) *Complete*

- Complete two-dimensional modeling of lithium deposition (August 2008) *Complete*

- Characterize $Li_{4+3x}Ti_5O_{12}$ interface (April 2009) *In progress*

- Identify shuttle and electrolyte systems and initiate experimental studies in $Li_{4+3x}Ti_5O_{12}$ /Li_yFePO_4 and Li_xC_6/ Li_yFePO_4 cells (September 2009) *In progress*

Approach

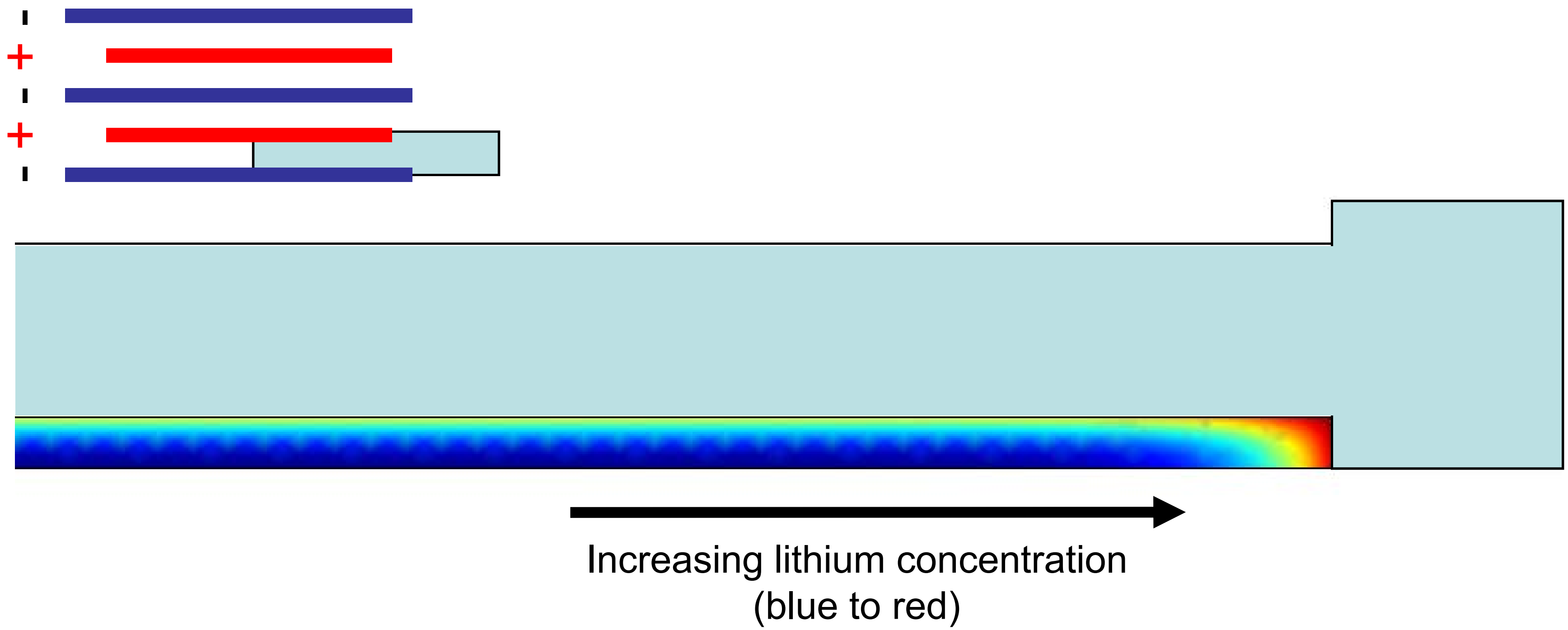
I. Develop two-dimensional model that explains edge effects on lithium deposition during charging

- Physical properties (conductivity, rate constants)
- Design parameters (geometry, capacity ratio)

II. Use combination of experiments and simulations to study interaction of redox shuttles and SEI

- Simplified zero-dimensional model, for basic insights
- Detailed battery model to examine complexities
- Classical electrochemistry experiments to determine physical constants

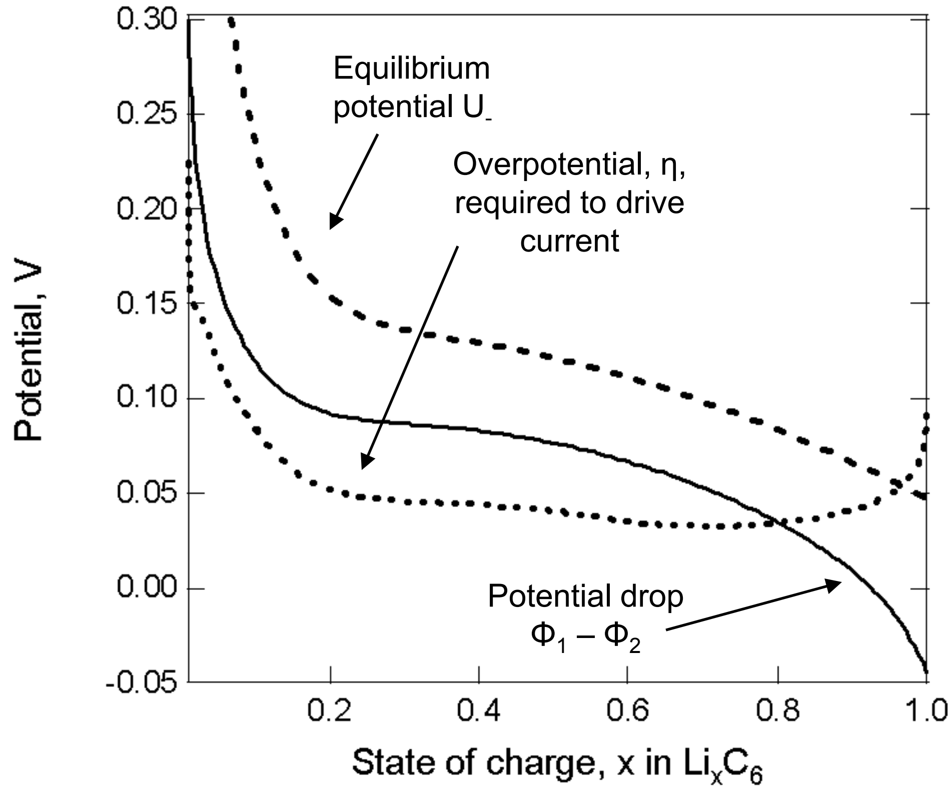
I: Modeling Li deposition



- Highest lithium concentration at edge of electrode
- Liquid-phase potential gradient means overpotential variation along electrode

Why does lithium deposit at the edge of the electrode?

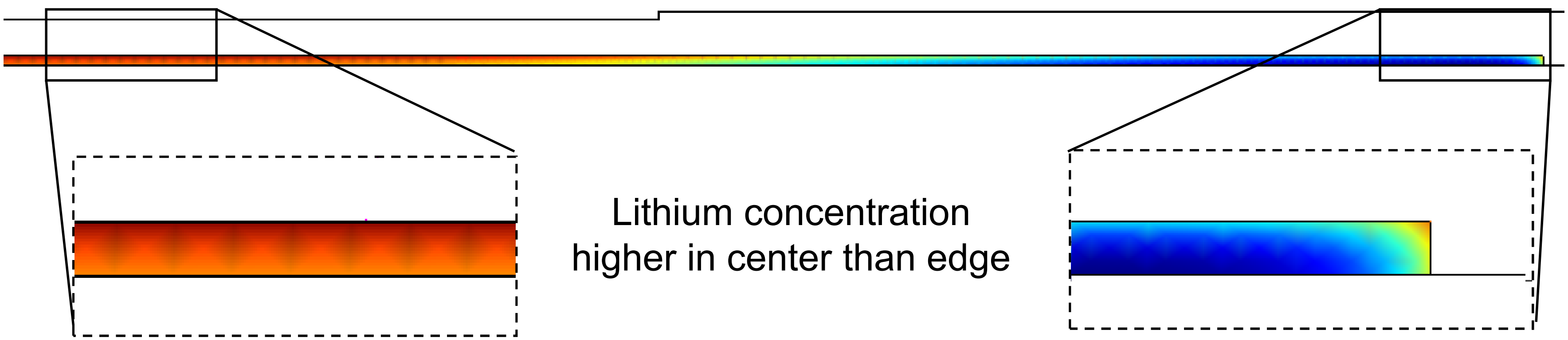
- Two factors determine current distribution:
  - Geometry: favors current at edge
  - Concentration: kinetics, OCP depend on state of charge
- Higher overpotential required as electrode saturates
- Higher concentration at edge means earlier deposition



Electrode extension prevents deposition

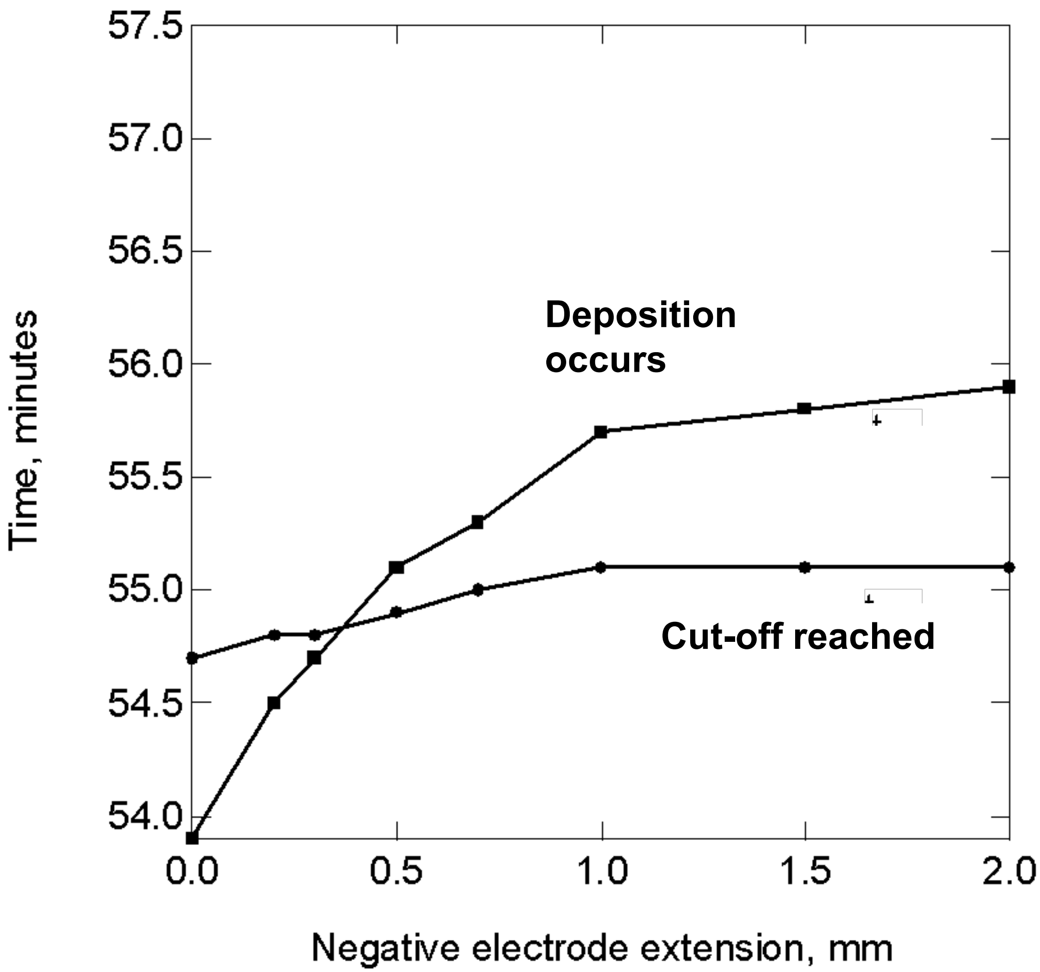
Negative electrode extension of 0.5 mm

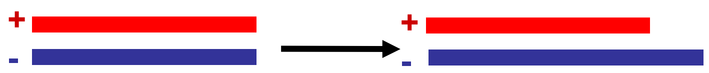
t ~ 60 min (1C charge)



- Capacity added at edge, where most needed to prevent saturation of lithium
- Can postpone deposition until after cell reaches cutoff potential

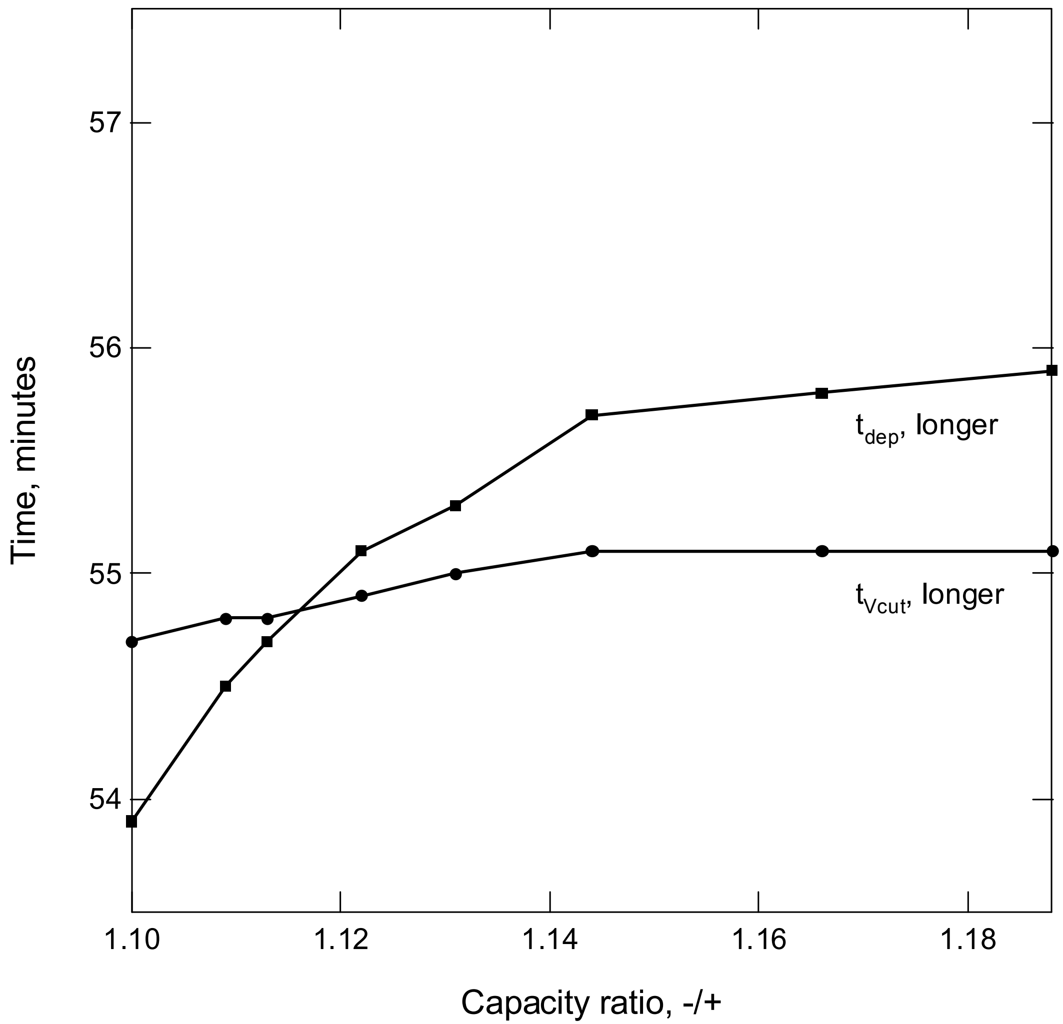
Effect of electrode extension on time to reach cutoff potential and deposition conditions

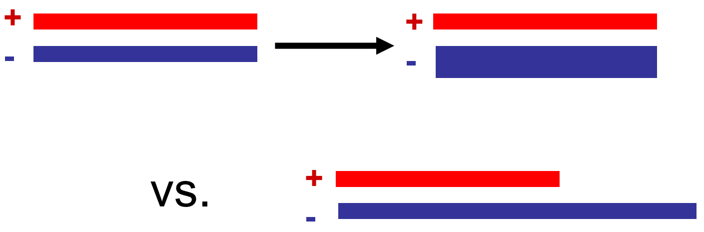




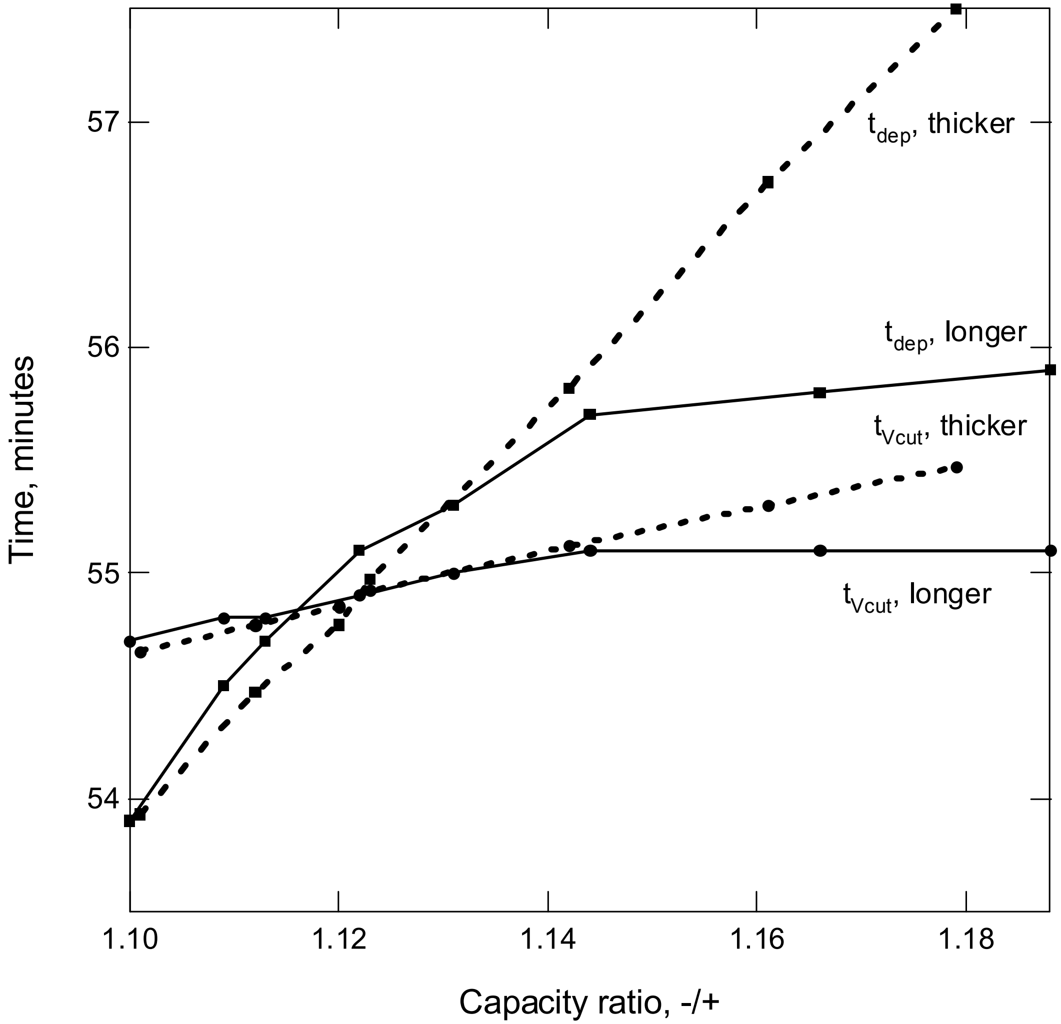
0.5 mm extension sufficient to delay deposition past time of cutoff potential

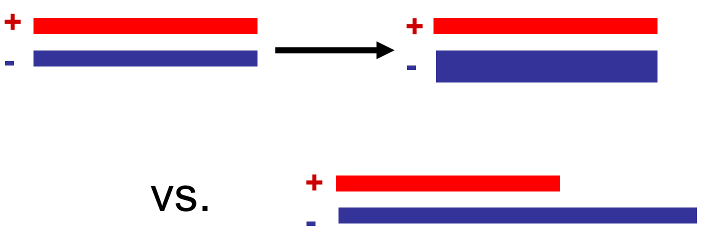
Comparison between thicker and longer negative electrodes





Comparison between thicker and longer negative electrodes



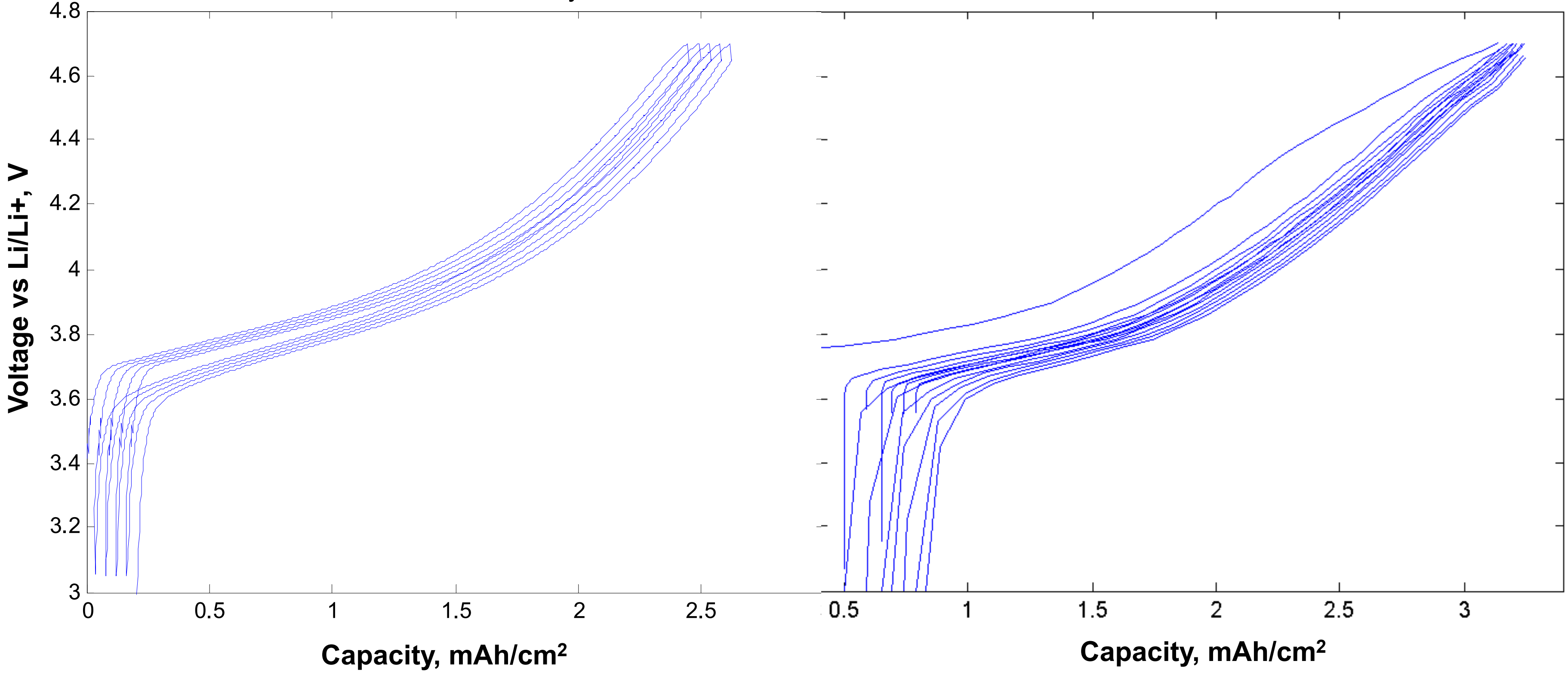


At lower capacity ratios, extending the negative electrode delays t_{dep} more effectively than making it thicker.

The location of added capacity does not affect t_{Vcut}.

II. Simple model for overcharge protection

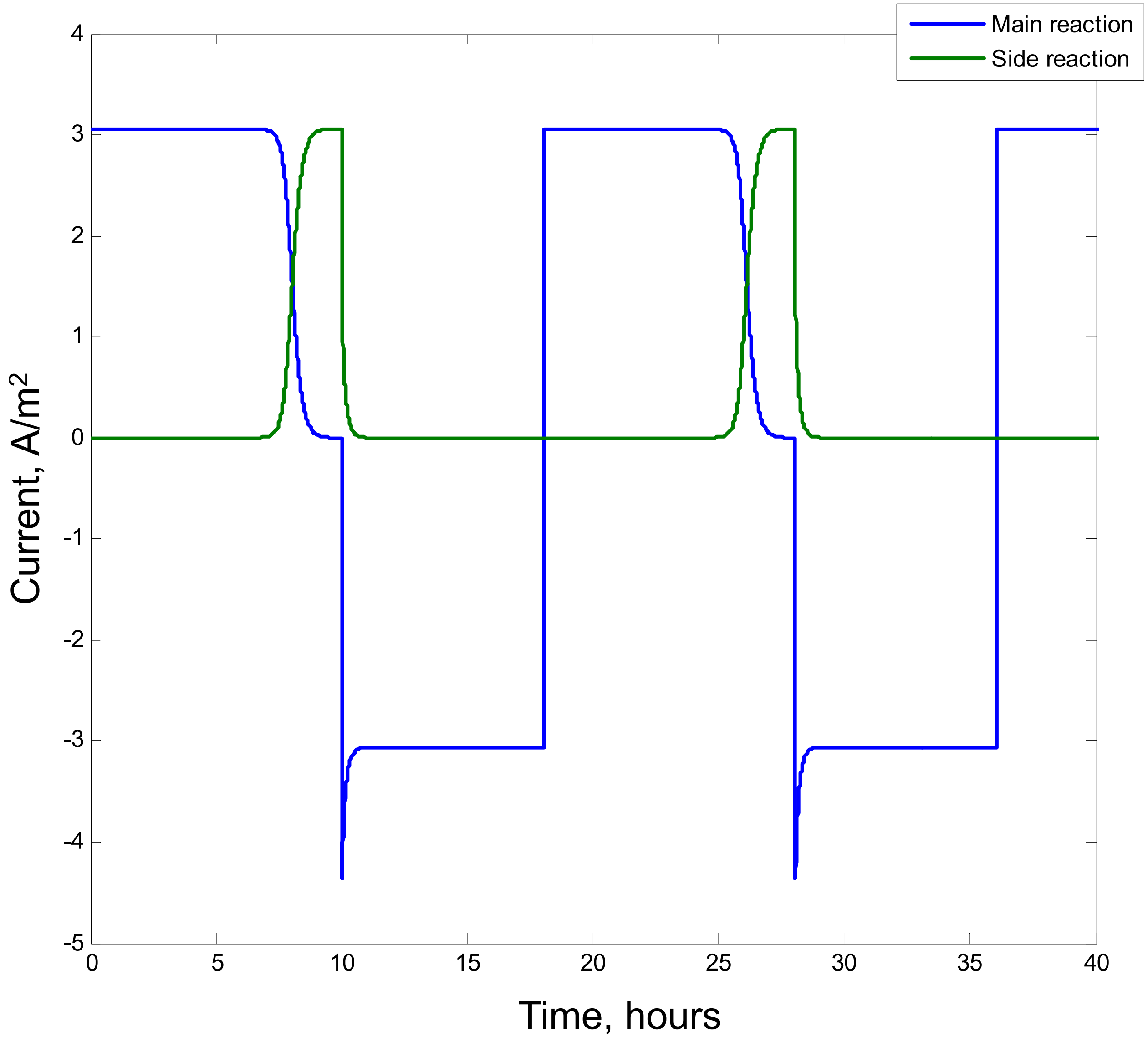
Cell is $Li/Li_yNi_{1/3}Co_{1/3}Mn_{1/3}$, cycling from 3.5-4.7 V



Model

Experiment

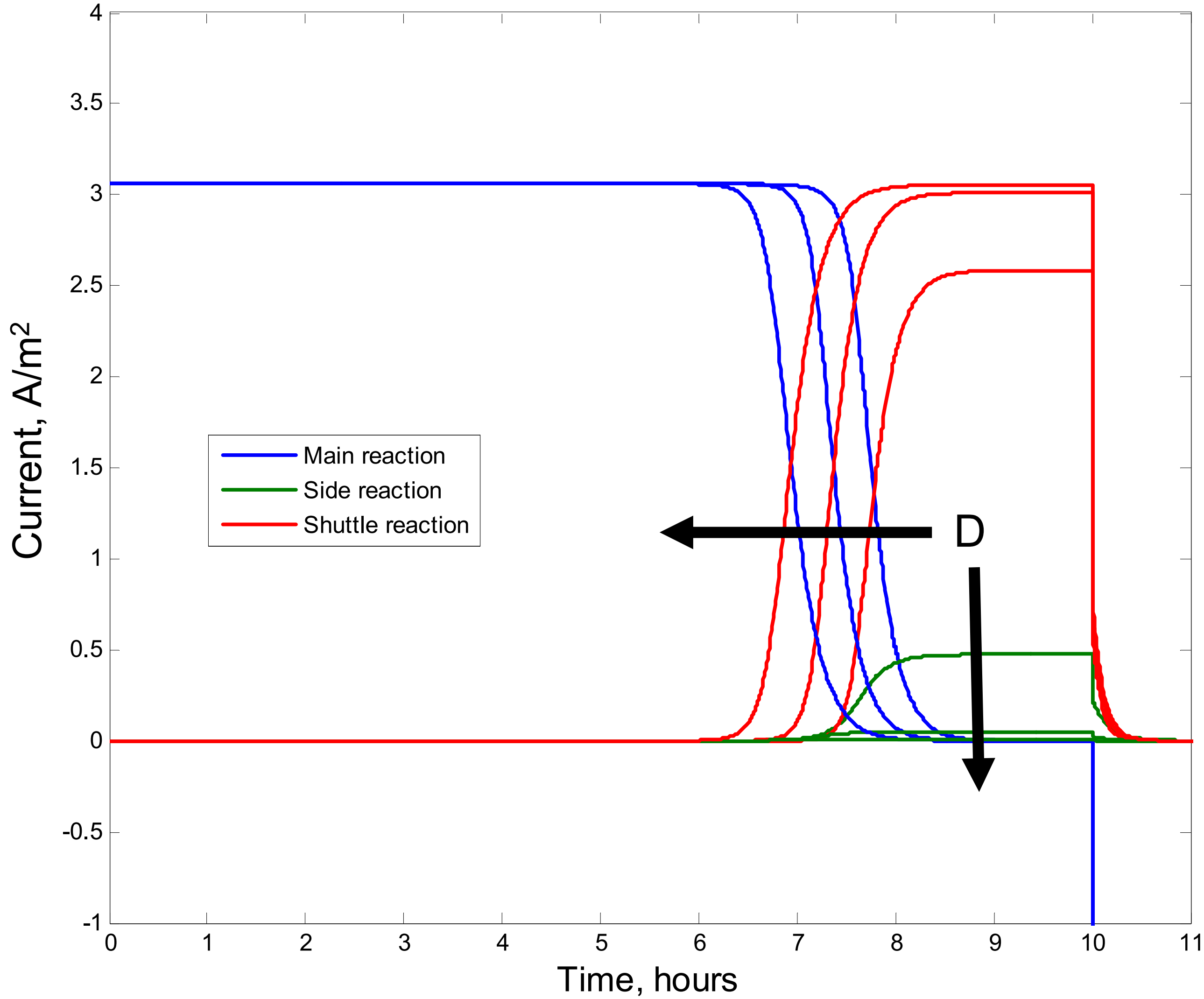
Main and side reaction currents vs time



Charging cell at a rate of C/10 for ten hours

Side reaction (green) will consume electrolyte and lead to capacity fade

Tradeoff between current efficiency and ability of shuttle to prevent side reactions



Future Work

- Modeling:
  - Develop more complicated model to capture transport properties of redox shuttles (May 2009)
  - Validate model by building and cycling cells containing shuttle molecules (August 2009)
  - New project on transport properties of block copolymer electrolytes
- Experimental
  - Compare shuttle kinetics in presence and absence of films (December 2009)

Summary

- A two-dimensional model explains why lithium deposits preferentially at edge of electrodes and provides guidance for electrode design
- Simple model may be useful for fitting rate constants at very slow rates, but needs to include transport in order to capture shuttle behavior
- Tradeoffs between energy storage and overcharge protection