Analysis and Simulation of Electrochemical Energy Systems

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June 8, 2010

This presentation does not contain any proprietary or confidential information

Project ID: ES083

Overview

Timeline

- Start: October 1, 2009
- End: September 30, 2010
- Percent complete: 70%

Barriers

- 750 deep discharge cycles
- 10 year calendar life
- 30-40 kWh available energy

Budget

- Total project funding
  - DOE share: 100%
  - Contractor share: 0%
- Funding received:
  - FY09: $830k
  - FY10: $430k
- Personnel: 2 students, PI in summer

Partners

- Collaboration with Bosch on shape change in lithium anodes
- Sion Power
- Informal collaborations with Vince Battaglia, John Kerr, and Venkat Srinivasan (LBNL-BATT)

Objectives

I. Understand interactions between redox shuttles and solid electrolyte interphase (SEI)
   - How are the shuttle reduction and a passivating film consistent?
   - What does the reduction mechanism tell us about the SEI?

II. Shape change in Li-metal anodes
   - How does cycling affect the morphology of Li metal?
   - How will the morphology affect anode protection layers?

Milestones

- Characterize $Li_{4+3x}Ti_5O_{12}$ interface (April 2009) *Complete*
- 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) *Complete*
- Measure kinetics of ferrocenium reduction through passivating films on an inert electrode surface. (Dec. 09)- *Delayed to April 2010 due to experimental difficulties*
- Identify key components and reactions to model. (Feb. 10)- *Cancelled due to change in direction to concentrate on modeling shape changes in lithium electrodes*
- Compare reduction kinetics of different redox shuttles on inert surfaces. (Apr. 10) *On schedule*
- Initiate kinetic studies using either highly-ordered-pyrolytic-graphite or composite graphite electrodes to approximate more closely conditions in a real cell. (Jul. 10) *On schedule*
- Determine effects of added impurities to Gr/LiFePO4 system. (Sep. 10)- *Cancelled due to change in direction to concentrate on modeling shape changes in lithium electrodes*
- Construct 2-D model of Li-metal redistribution. (Aug 10) *Added- on schedule*

Approach

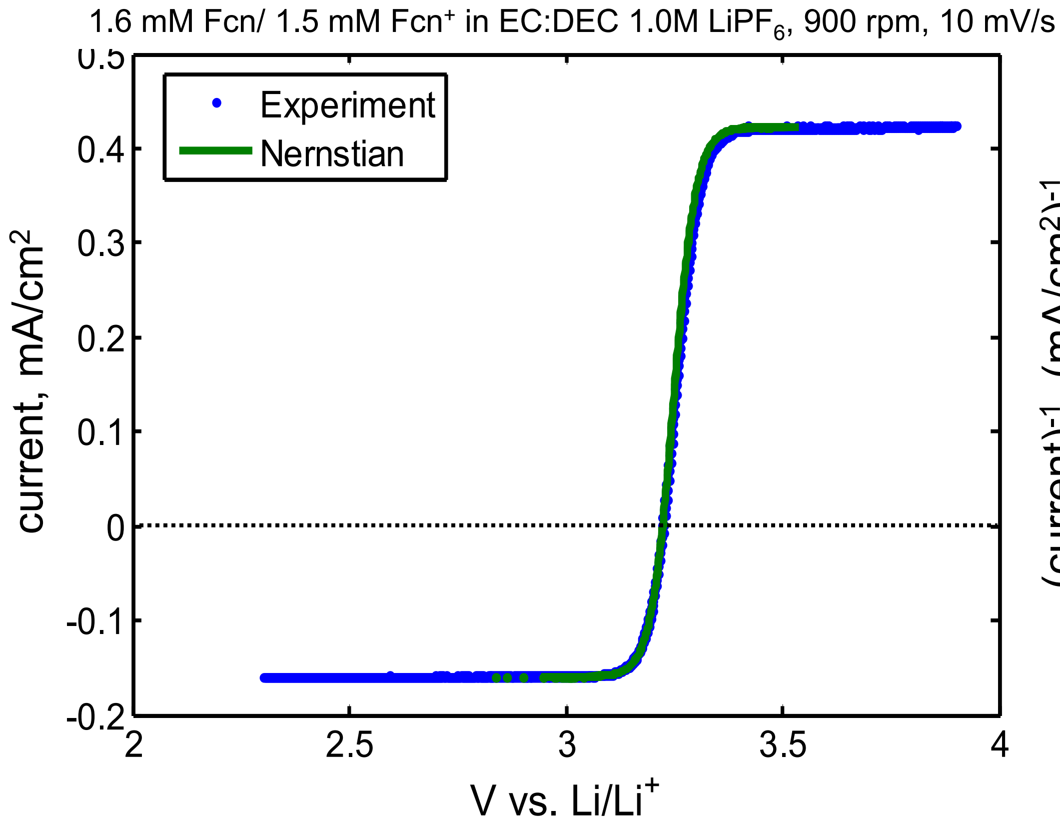
I. Rotating-disk-electrode experiments to study interaction of redox shuttles and SEI

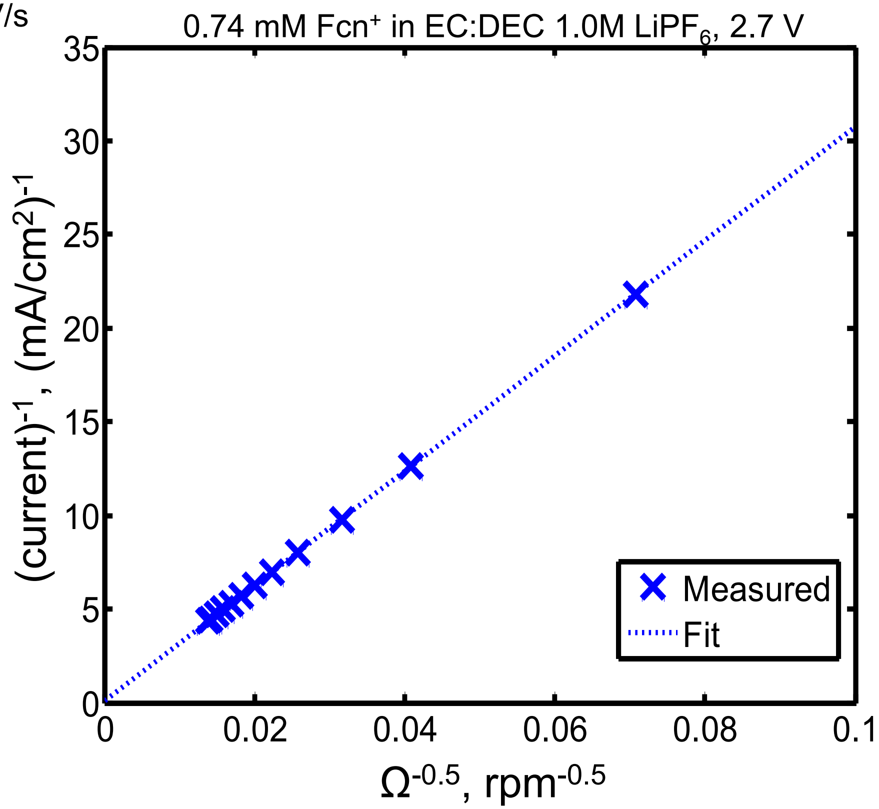
- Goal: determine kinetic mechanism of shuttle reduction in presence and absence of passivating films

II. Li shape change

- Goal: elucidate the effects of extended deep-discharge cycling on a lithium-metal electrode in the absence of dendrite formation

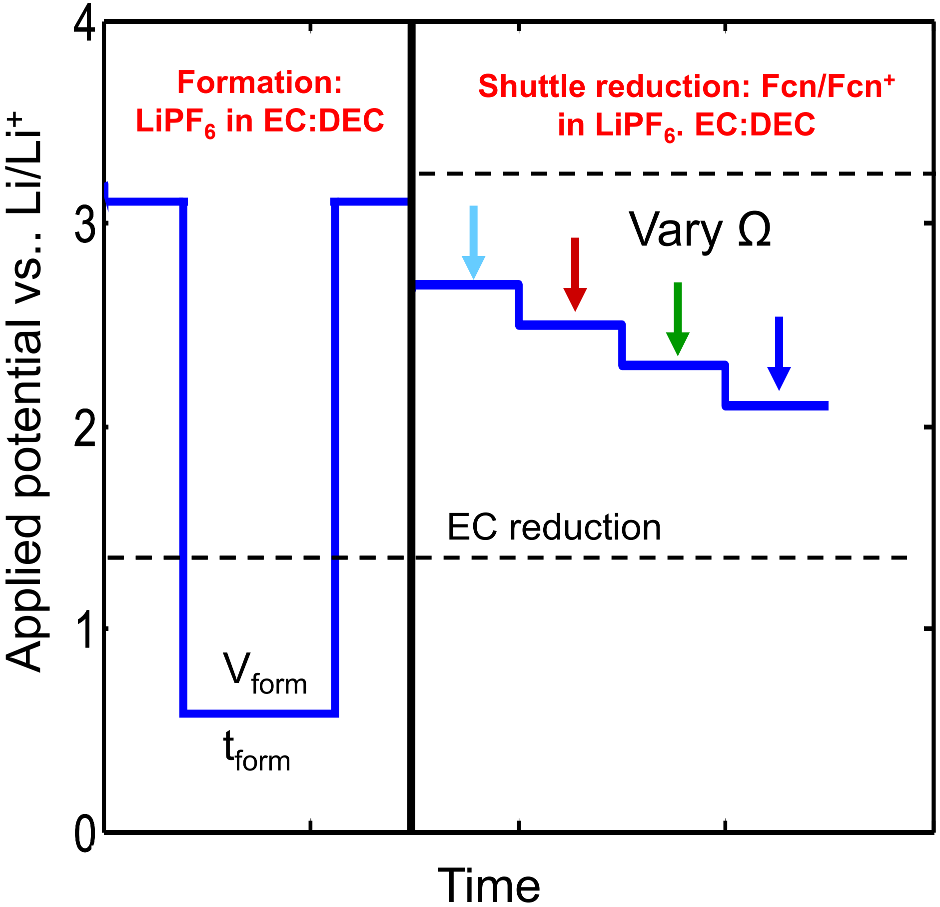
I. Ferrocene as a model redox shuttle

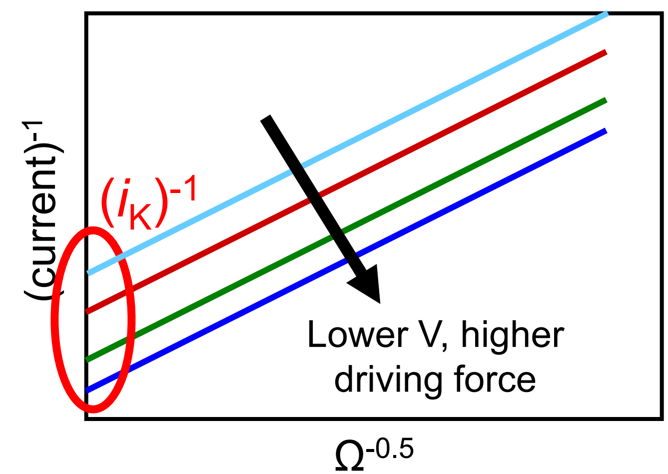


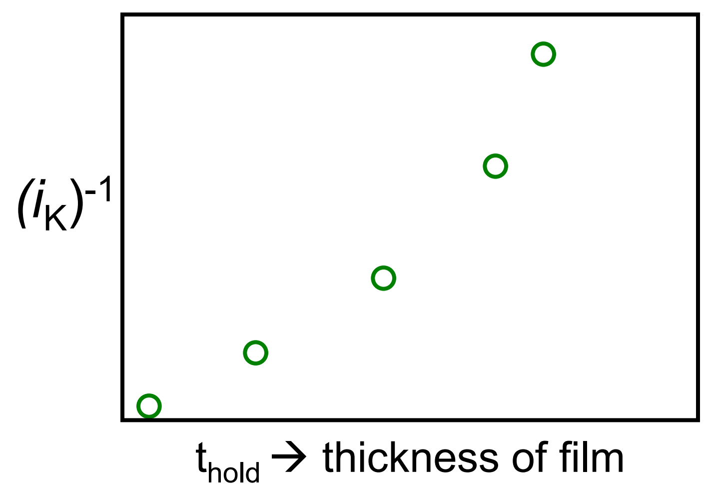


On a pristine electrode, ferrocene reduction is entirely reversible

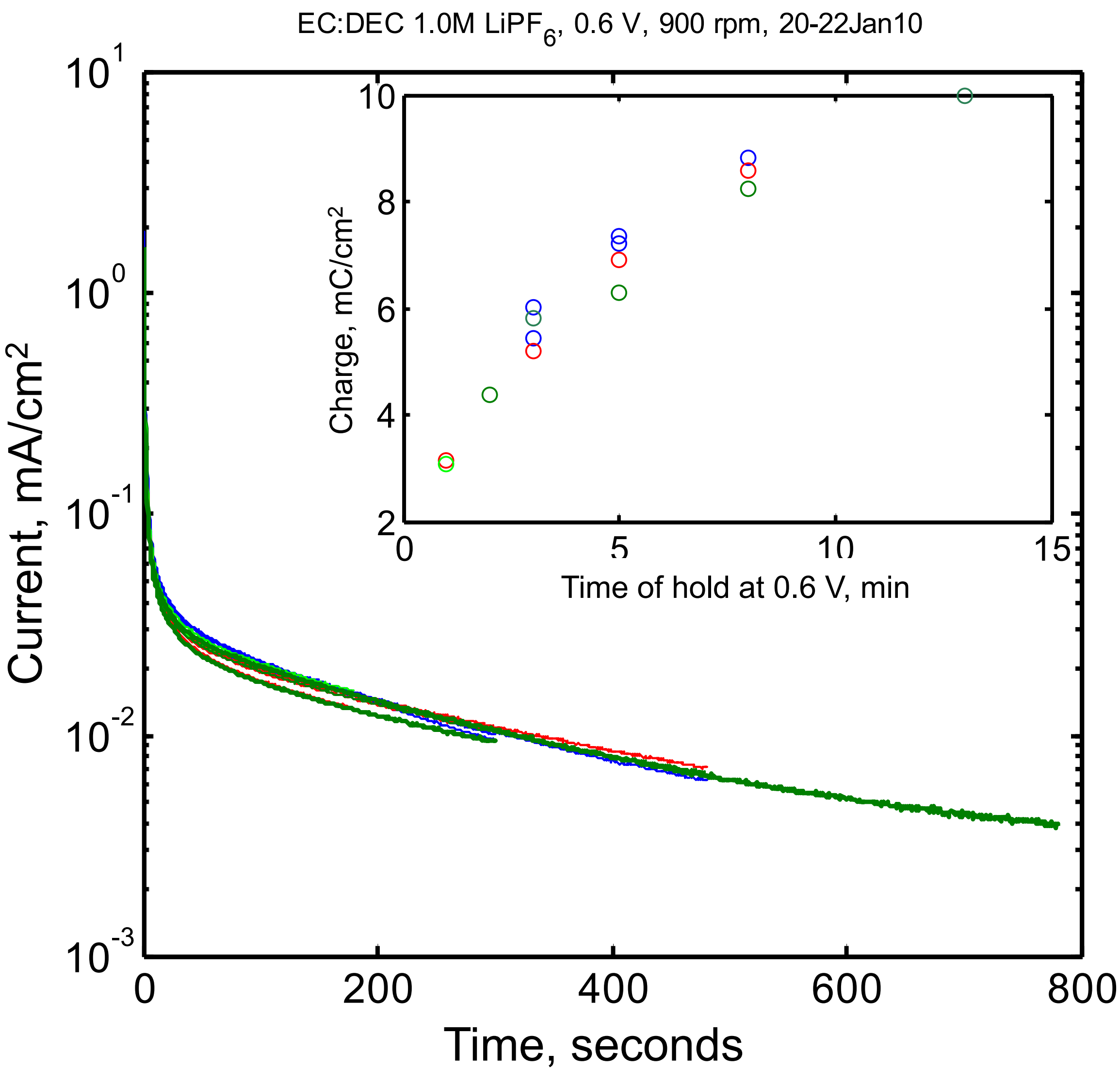
Form film at low voltage, then measure shuttle reduction kinetics

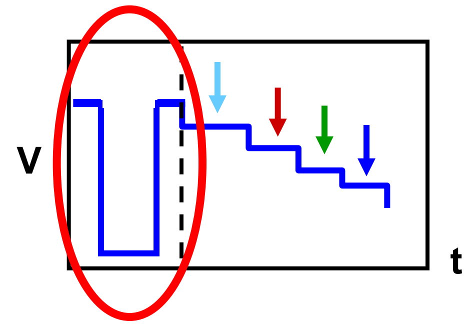






Formation of surface films at 0.6 V

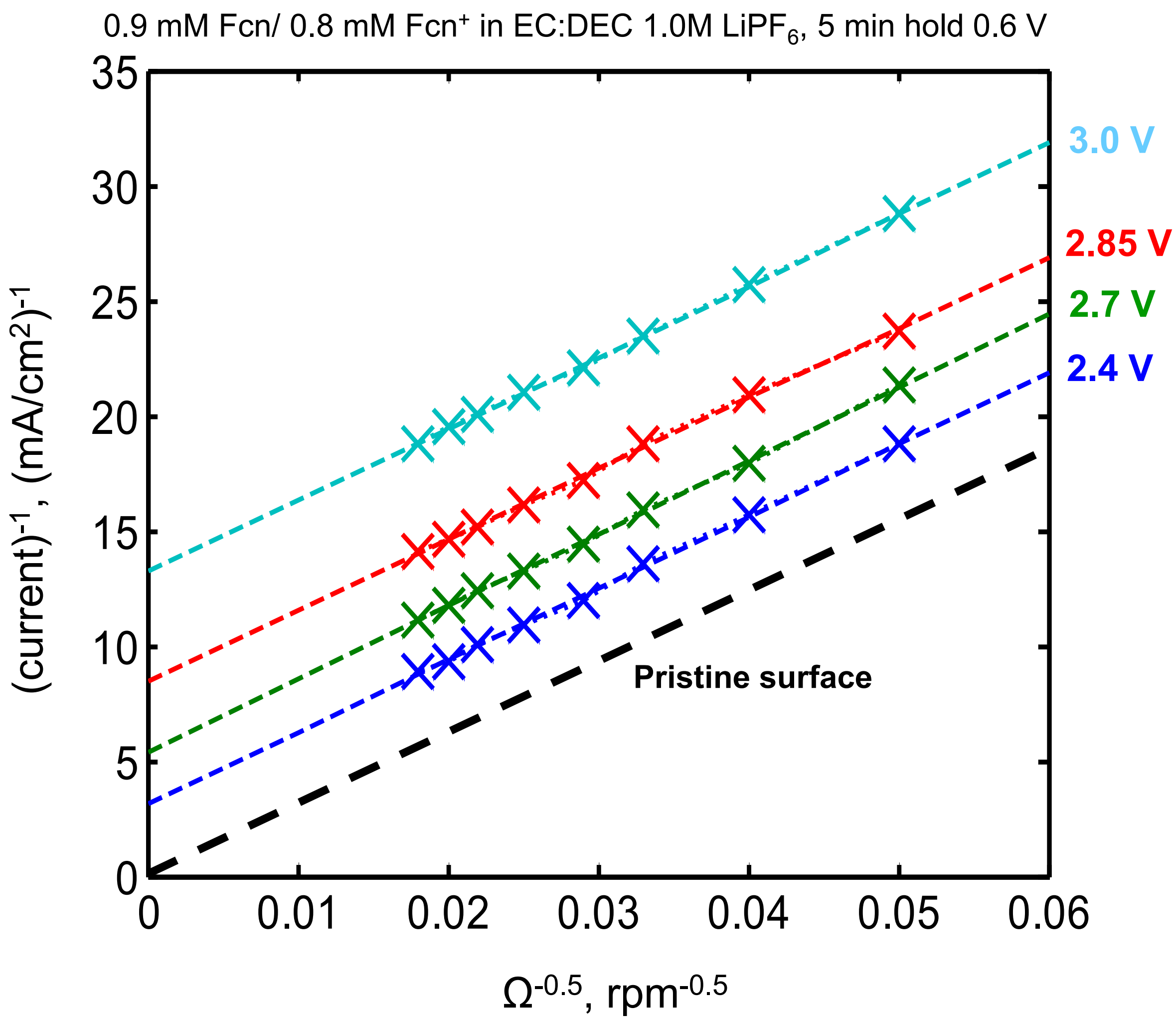


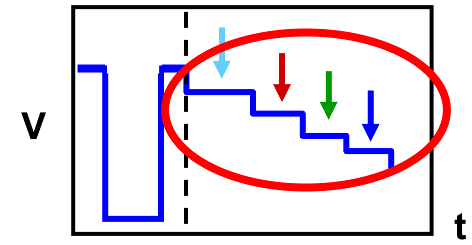


Holding a glassy carbon electrode at 0.6 V vs.. Li/Li^+ produces a current that decays with time because electrolyte reduction products passivate the surface.

This solution does not contain the redox couple.

Surface films increase kinetic intercept of ferrocenium reduction

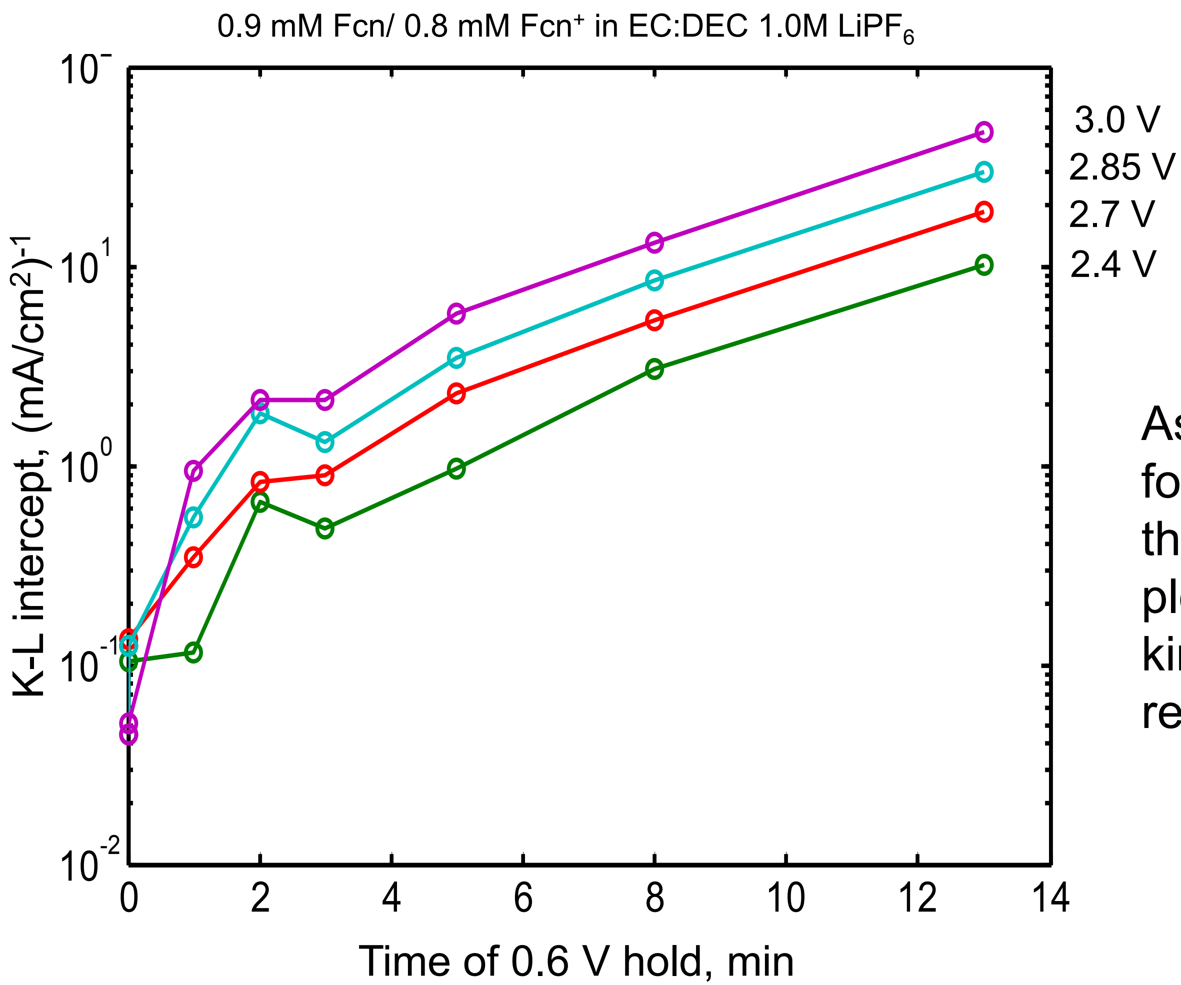




After film formation holds at 0.6 V, the Koutecký-Levich plots show kinetic inhibitions to ferrocenium reduction (non-zero intercepts)

Parallel curves show that changes have occurred to the surface, not to transport in the bulk solution.

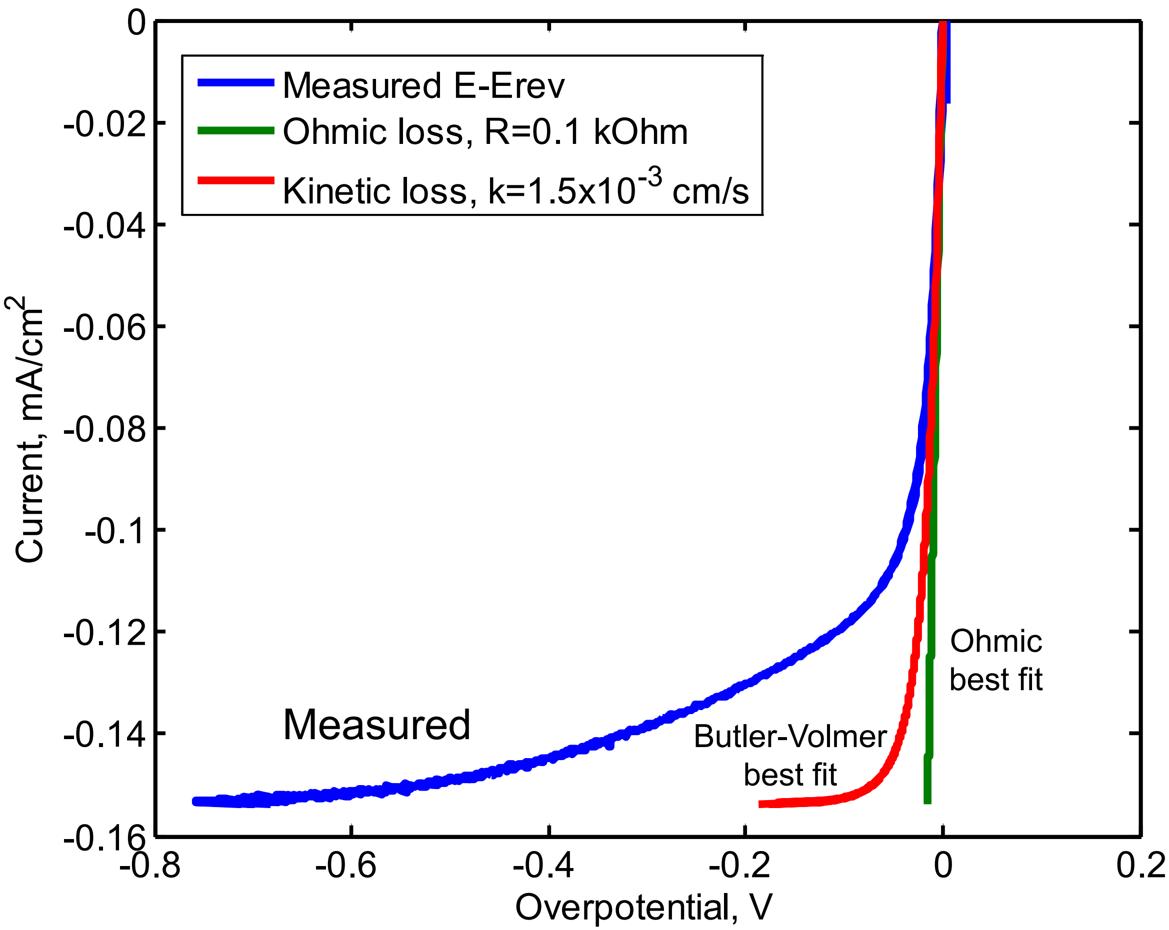
Kinetic intercepts increase with time of film formation hold



As the time of the formation hold increases, the intercept of the KL plot rises, showing more kinetic inhibition to shuttle reduction.

Standard kinetic models cannot describe ferrocene reduction through film

1.6 mM Fcn/ 1.5 mM Fcn⁺, 900 rpm, 10 mV/s, 3 min hold at 0.6 V

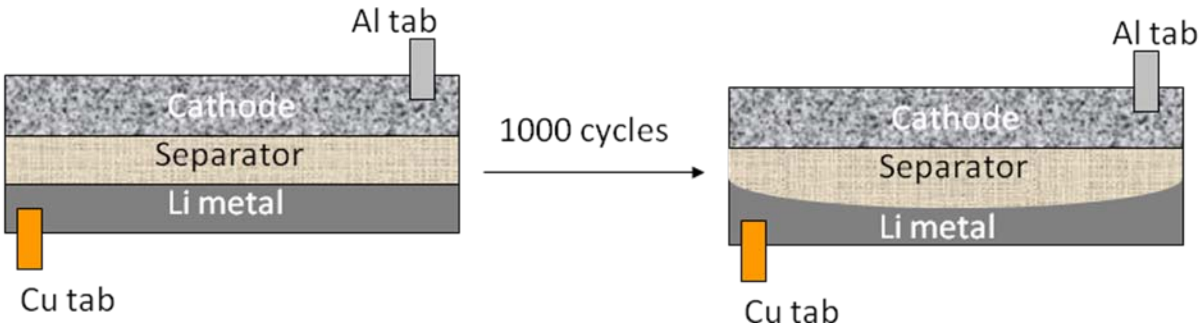


A simple model considering transport, Butler-Volmer kinetics, and ohmic resistance cannot match the measured i-V curve.

We are currently searching for alternate mechanisms to explain this behavior.

II. Li Morphology in a Li-Metal Battery

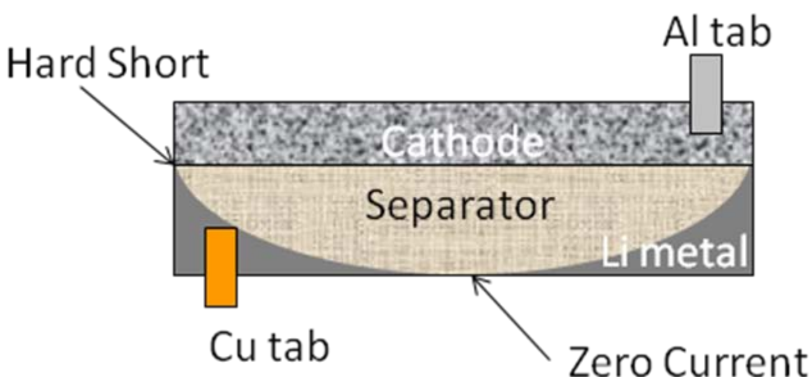
Even if dendrites can be prevented, extended deep cycling could cause gradual redistribution over long length scales (cm)



Current density distributions could cause an increase in thickness near the tabs.

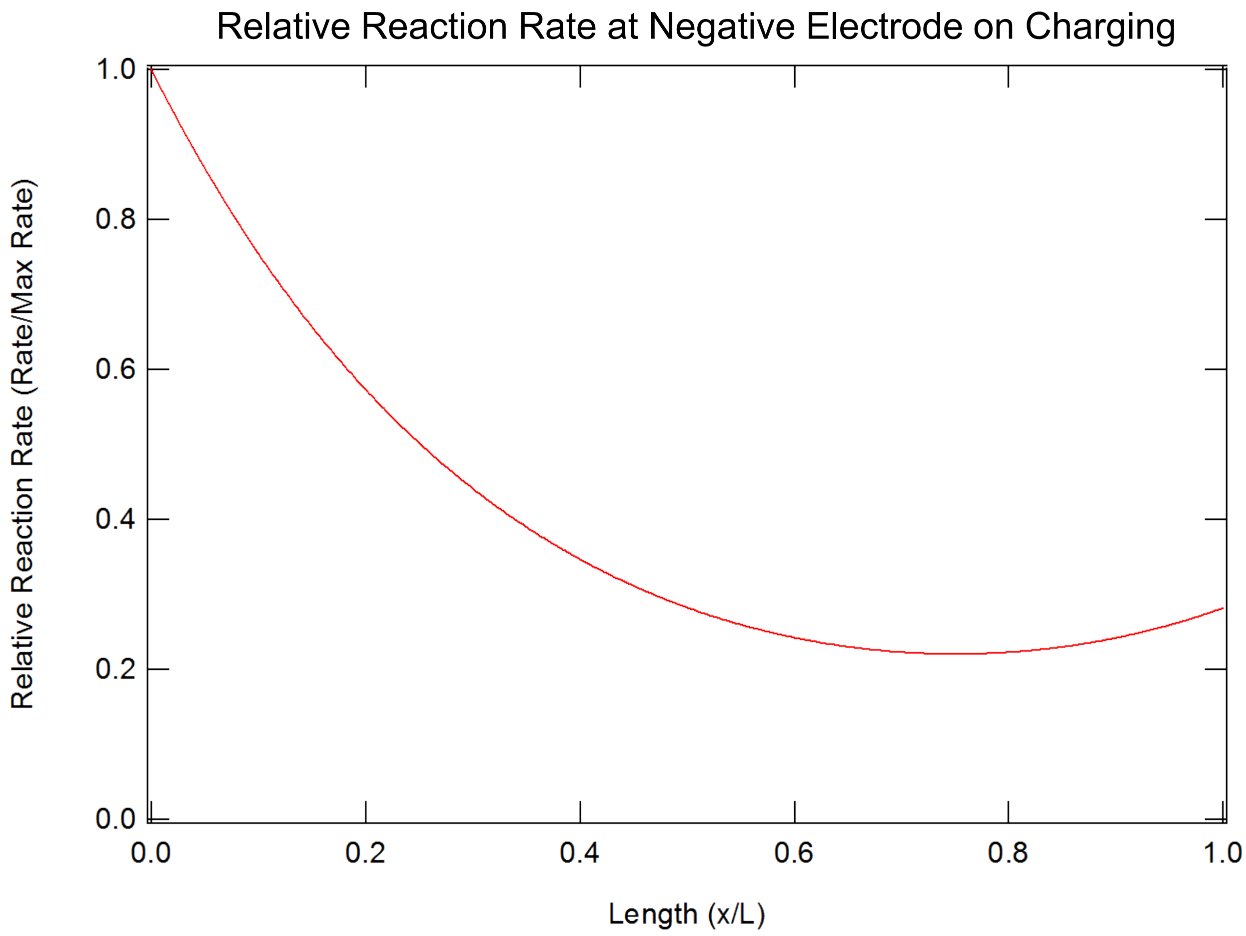
Severe redistribution could cause significant safety and life cycle concerns

Significant current density distributions could cause severe redistribution, resulting in several failure mechanisms including hard shorting and areas of zero current



Changes in Li morphology could affect protective layers implemented to stop dendrite formation

Initial order of magnitude analysis suggests that a reaction rate distribution could occur



Model assumes constant concentration and simplified reaction kinetics

Shows a significant reaction rate distribution along the length of the negative electrode

Future Work

- Develop model that explains kinetic behavior of ferrocene reduction through SEI
- Measure and fit behavior of different shuttle molecules
  - Redox potential
  - Molecule size and shape
- Develop a realistic 2-D model of a Li-metal battery
  - Pressure effects
  - Hot spots
  - Mechanical strength required of protective layers

Summary

- Redox shuttles used as electrochemical probes to understand behavior of passivating films
- Reduction of ferrocenium shows unusual behavior not explained by standard kinetic models
- Begun work on modeling long-term shape changes in lithium anodes