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

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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
- Gerd Ceder (MIT)
- Pradeep Guduru (Brown U.)
- UC-Berkeley Microlab
- Enovix Inc. (formerly microAzure)
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
Approach

Develop continuum model for an electrode

Obtain material parameters (equilibrium, transport etc.)

Compare model to data
- Extract unknown parameters

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

- $D_v = 3.8 \times 10^{-15} \text{ cm}^2 / \text{s}; 75 \text{ nm}$
- $D_v = 1 \times 10^{-14} \text{ cm}^2 / \text{s}$

**Silicon simulation**
Gao Liu, LBNL

**Stress Effects**
Pradeep Guduru, Brown U.

**Reaction distributions**
Tom Richardson, LBNL

**Electrode Failure**
Vince Battaglia, LBNL
Ultra-high Rate LiFePO$_4$

Why are some LiFePO$_4$ particles capable of such high discharge rates?

Methodology

Single particle model with double layer charging

LiFePO$_4$

Porous electrode model

LiFePO$_4$

Lithium Foil

Separator

Al Current Collector

Particle size=75 nm

Particle size=50 nm

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

- FePO₄ 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 LiFePO₄ material?
Porous Electrode Model Results

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.

Collaboration: G. Ceder

Baseline data

- Kang and Ceder (low rate)
- Kang and Ceder (high rate)
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

Simulations of reaction distribution

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

![Graph showing comparison of model to data](image)

- 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

- 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.

- Wafer curvature is related to the stress via the Stoney equation.
- Stress is monitored *in situ* during lithiation/delithiation.
- 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

Present focus

Failure of active material: fracture

Failure of binder: fracture/yield

De-lamination from current collector

De-bonding of binder-active material

Failure of composite electrode

What is the predominant mode of failure?

Data: H. Zheng and V. Battaglia, LBNL
Simulations of Stress Effects

**Graphite/PvDF**
- 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

**Graphite/SBR:CMC**
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 LiFePO₄ 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 Li₁₅Si₄ 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