Kinetics of Lithium Insertion into Silicon Anodes

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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

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

Understand limitations and provide guidance to improve performance

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

Discharge Power (W/kg)

Available Energy (Wh/kg)

HEV goal

2.7 V, 3x capacitance

P/E=83.3

2.7 V

3.7 V

P/E=13

Gr./LiMnPO₄

Gr./LiMn₂O₄

Gr./LiFePO₄

Gr./NMC

PHEV-10

New Battery Developed for use in a PHEV
Use model to optimize battery design and evaluate ability to satisfy vehicular needs.

**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

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%)
- 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-cm²! Typical resistance of electrodes = 15 Ω-cm²
   Has impact on VT **power goals**.

**Film behavior**

- Large 1\textsuperscript{st} 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 (\textit{i.e.}, single phase region).
Is this voltage offset rate dependent?

Note that Li metal also known to have polarization losses.

Increasing current.

C/30 to ~C/2.
Open-circuit experiments on the Si electrode

Cell was discharged to ~50% SOC at C/8, then kept under open circuit for 48 hours.
Voltage decreases, then increases during delithiation. Side reaction makes it impossible to confirm that voltage (V) potentials will indeed collapse even after 48 hours. Is there a phenomenon that shows a voltage offset at small currents, no voltage dependence on current, and a large time constant on open circuit?
Tafel kinetics with double-layer charging

- A reaction with poor kinetics (small $i_0$) would show an offset even at low rates.

- And would show little change in overvoltage with current, for large $i/i_0$.

- On open-circuit, double layer discharges the faradaic reaction.
  
  - Time constant $\propto \frac{RTC_{dl}}{Fi_o}$
  
  - If $i_0$ 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: 
\[
\frac{dV}{dt} = i_o \exp \left( -\frac{\alpha_c F}{RT} (V - U) \right)
\]

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

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
From an OCV experiment, \( i_o \) and \( C_{DL} \) are not separable.

Assuming \( C_{dl}=10 \, \mu F/cm^2 \), \( i_o \sim O(10^{-13} \, A/cm^2) \)

Estimates on graphite suggest \( i_o \sim O(10^{-3} \, A/cm^2) \) (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 $I/aL_i$.

From Simulations

- 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 delithiation

• 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 LiMnPO₄ cathodes
  • Better description of the phase evolution and transport
Summary

Energy (W/HEV goal)

37 V
2.7 V, 3x capacitance

e
3

V

gage

V

Discharge Power (W/kg)

0.1
1
100

0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0

Capacity (As)

0.0
0.5

Normalized Capacity

0.0 0.2 0.4 0.6 0.8 1.0

0.0 0.1 0.2 0.3 0.4 0.5

Voltage

Voltagel/log Li

Energy Efficiency (%)

0.0 1x10^6 2x10^6 3x10^6 4x10^6 5x10^6 6x10^6

I/(a.L.i_0)

P/E=83.3

Available E

Discharge Power (W/kg)

0.0 0.1 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0

0.0 0.2 0.4 0.6 0.8 1.0

Capacity (As)

0.0 0.1 0.2 0.3 0.4 0.5

Voltage

C/2

Simulations provide insights into barriers.
Publications and Presentations


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.