Fundamental Approach to Electrode Fabrication and Failure Analysis

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LBNL
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Overview

Timeline
- October 2008
- September 2012
- 65 % Complete

Barriers
- Barriers addressed
  - A. Cost
  - C. Performance
  - E. Life

- Targets
  - 205 $/kWh
  - 207 Wh/l
  - 15 years

Budget
- Total project funding
  - DOE share = 100%
  - Contractor share = 0%
- Funding received in FY10
  - $865 k
- Funding for FY11
  - $865 k

Partners

<table>
<thead>
<tr>
<th>PIs</th>
<th>Companies</th>
</tr>
</thead>
<tbody>
<tr>
<td>V. Srinivasan</td>
<td>Conoco Phillips</td>
</tr>
<tr>
<td>B. Lucht</td>
<td>Daikin, Japan</td>
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<tr>
<td>M. Doeff</td>
<td>NEI</td>
</tr>
<tr>
<td>J. Cabana</td>
<td>SWeNT</td>
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<tr>
<td>G. Ceder</td>
<td>Nippon Denko</td>
</tr>
<tr>
<td>K. Zaghib</td>
<td>HydroQuebec</td>
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<tr>
<td>A. Manthiram</td>
<td></td>
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<td>A. Angell</td>
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Objectives

To make “good” electrodes.

- What does this entail?
  
  • Correlate electrode performance with the fundamental properties of its constituents.
  
  • Provide fundamental understanding of key electrode processing steps.
  
  • Provide fundamental understanding of electrode failure, i.e. is it a result of the electrode formulation/processing or of the active material properties?
  
  • Test materials to evaluate their full potential.
  
  • Provide quality electrodes to other BATT researchers.
Relevance: 2010 to 11

Objectives

Specific to 2010/11 –

– Develop a sealed cell with a reference electrode that allows long-term cycling outside of a glove box and does not require an additional separator. (Critical to understanding cycle life issues.)

– Understand the electrode performance of an off-stoichiometric material as compared to a carbon-coated material. (A material tested in the ABR Program but moved to the BATT Program for in-depth analysis.)

To meet OVT’s Targets of Cost, Performance, and Life it is essential that we have electrodes that exhibit maximum energy density, adequate pulse-power capability, and long life.
**Approach/Strategy**

- **BATT PIs**
  - Industrial Partners

- **Powders**
  - Physical Characterization
    - BET, PSA, SEM, TEM
  - Chemical Characterization
    - Dissolution
  - Electrode Fabrication
    - Tensile & Peel Strength, Viscosity, 4-pt. Probe
  - Electrode Characterization
    - Side rxns vs. Li, Rev. and Irrev. Capacity, Rate
  - Cell Characterization
    - Side Rxns in Full Cell, Cycling Ability, Impedance

- **Fundamental Understanding of Key Fabrication Steps**
- **Correlations of Electrode Performance to Physical Properties**
- **Fundamental Understanding of Performance Limitations and Cycle Life**
- **Fundamental Understanding of Failure Modes**
- **Modeling**
  - Updated Manuals Publications

**Diagnostics**

**Battaglia Group**
DOE Reportable Milestones
2010 thru 2011

Distribute electrodes cycled to different cut-off voltages to BATT program members. (Apr. 10)

- Complete

Report results of mechanical properties vs. cycling capability of NCM-PVdF-based cells. (Sep. 10)

- Complete

Procure 20 g of high-quality LiNi$_{1/2}$Mn$_{3/2}$O$_4$. (Jan. 11)

- Complete

Supply laminates of LiNi$_{1/2}$Mn$_{3/2}$O$_4$ that survive 100 cycles. (Apr. 11)

- On schedule

Report the solubility of Mn compounds. (Apr. 11) **On schedule**

Report side-reaction rates of NCM vs. Li and vs. Graphite. (Jul. 11)

- On schedule

Report the rate of side reaction of LiNi$_{1/2}$Mn$_{3/2}$O$_4$ vs. Li. (Sep. 11)

- On schedule
Technical Accomplishments and Progress:

1. Battery Fabrication Manual published online Dec. 17, 2010

Following the manual, a visiting researcher was able to achieve this level of performance in 4 months.

More on this system in the poster – es029_battaglia_2011_p
Technical Accomplishments and Progress:
1. Battery Fabrication Manual published online Dec. 17, 2010

88 Downloads as of March 9, 2011
- 14 Countries
- 25 States in the U.S.

http://berc.lbl.gov/vbattaglia/cell-analysis-tools/
Technical Accomplishments and Progress:


Modeling Capacity Fade

- Coulombic efficiency is fairly constant from 50 cycles onward.
- Capacity fade begins at ~ 150 cycles.
- Consider two models for capacity fade:
  - Linear – \( Q = Q_0 - Q_0(1 - \eta)(N_{cycle} - 150) \) where \( \eta = \) cycle efficiency
  - Fractional – \( Q = Q_0\eta^{(N_{cycle} - 150)} \)
- The 2 models are indistinguishable w/ \( \eta = 0.99953 \); under predicts by a factor of 1.7.
- Only 40% of the side reaction is detrimental. Goal is 0.99996 efficient.

It is critical to understand these side reactions.
Technical Accomplishments and Progress:


Side Reactions

- No effect of vinylene carbonate (VC) or formation protocol on graphite side-reaction rates when cycled against Li.

- Coulombic inefficiency of graphite doubled when cycled against NCA, suggesting the presence of a high-voltage shuttle.

- VC appeared to deactivate the shuttle and thereby improve coulombic efficiency.
Technical Accomplishments and Progress:


We have developed a novel 3-electrode coin cell to simultaneously study long-term cycling effects and side reactions of both electrodes.

We expect this cell to be very helpful in assessing cell failure!
Technical Accomplishments and Progress:

3. HQ’s LiFePO$_4$ is as high rate as G. Ceder’s (MIT) with the addition of acetylene black.

The Materials

Three LiFePO$_4$ materials were evaluated:

a) Ceder’s off-stoichiometric, nano-material: LiFe$_{0.9}$P$_{0.95}$O$_{4-\delta}$

b) LBNL’s stoichiometric, nano-material: LiFePO$_4$

c) HQ’s carbon coated material: LiFePO$_4$ / C

X-ray signatures are similar

Amorphous film is visible with HRTEM

Carbon film is visible with HRTEM

The Ceder material was pre-evaluated in the ABR Program.
Technical Accomplishments and Progress:

3. HQ’s LiFePO$_4$ is as high rate as Ceder’s with the addition of acetylene black.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D$_{10}$ (µm)</th>
<th>D$_{50}$ (µm)</th>
<th>D$_{90}$ (µm)</th>
<th>BET (m$^2$.g$^{-1}$)</th>
<th>Eqv. Dia. (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiFe$<em>{0.9}$P$</em>{0.95}$O$_{4-δ}$</td>
<td>0.135</td>
<td>0.333</td>
<td>0.498</td>
<td>33.9551</td>
<td>0.049</td>
</tr>
<tr>
<td>Bare LiFePO$_4$</td>
<td>0.219</td>
<td>0.402</td>
<td>0.651</td>
<td>47.3239</td>
<td>0.035</td>
</tr>
<tr>
<td>LiFePO$_4$ / C</td>
<td>0.252</td>
<td>0.415</td>
<td>0.657</td>
<td>12.9335</td>
<td>0.12</td>
</tr>
</tbody>
</table>

PSA detects secondary particles; BET detects primary particles
Technical Accomplishments and Progress:

3. HQ’s LiFePO$_4$ is as high rate as Ceder’s with the addition of acetylene black.

The MIT and LBNL nano-particles agglomerate into secondary particles.

The HQ carbon-coated material segregates as primary particles.
Technical Accomplishments and Progress:

3. HQ’s LiFePO$_4$ is as high rate as Ceder’s with the addition of acetylene black.

- At 65% carbon, the electrode thickness does not affect the rate performance.
- For the bare material and HQ material, 15% carbon additive is essentially all that is needed.
- With large amounts of conductive additive (65%) the rate is mostly limited by solid-state diffusion of Li in FePO$_4$.
- Solid state diffusion is much slower for the bare material than either the MIT LiPO-coated nanomaterial or the HQ carbon coated material.
Technical Accomplishments and Progress:
3. HQ’s LiFePO$_4$ is as high rate as Ceder’s with the addition of acetylene black.

65% Carbon Additive

With 65% carbon additive, the materials are rate limited by solid-state diffusion.

- The single-crystal HQ material has straight paths to the center of the particles.
- The coating on the MIT primary particles appears to facilitate diffusion to the center of the secondary-particle.
- The LBNL material exhibits slower diffusion through the tortuous secondary particle.
Technical Accomplishments and Progress:

3. HQ's LiFePO$_4$ is as high rate as Ceder's with the addition of acetylene black.

Schematic of Solid State Diffusion Limitation

- Fast but tortuous
- Slow and tortuous
- Slow but non-tortuous

Work in progress.
Collaborations and Coordination with Other Institutions

Companies
- Daikin, Japan will send their newest high-voltage electrolytes
- Conoco Phillips provided baseline graphite and will send CGP-A12 shortly
- NEI will provide a baseline LiNi$_{1/2}$Mn$_{3/2}$O$_4$ spinel material for distribution to BATT PIs through Y.-M. Chiang’s Group
- Daikin, America will provide a baseline electrolyte for distribution to BATT PIs
- HydroQuebec will provide LiNi$_{1/2}$Mn$_{3/2}$O$_4$ spinel material

Principal Investigators
- Receive powders from G. Ceder (MIT)
- Make laminates for the V. Srinivasan Group (LBNL)
- Make laminates for the J. Cabana Group (LBNL)
- Provide TEM for the T. Richardson/G. Chen Groups (LBNL)
- Provide electrodes to the B. Lucht Group (URI)
- Make laminates with the M. Doeff Group (LBNL)
- Receive LTO laminates and new LiNi$_{1/2}$Mn$_{3/2}$O$_4$ materials from the K. Zaghib Group (HQ)
- Provide powders and electrolyte to A. Manthiram Group (UT)
- Provide powders and electrolyte to J. Zhang Group (PNNL)
- Provide powders and electrolyte to A. Angell Group
Proposed Future Work

- Electrode design optimization
- Electrode failure analysis

  - LiNi$_{0.5}$Mn$_{1.5}$O$_4$ has been identified as a focus area; we will use our approach to provide a fundamental understanding of its limitations.

  - Optimize the design of high-energy electrodes, investigate the fabrication of high-loading electrodes that cycle well, and study the roles of inactive material chemistry and material physical structure
  - Study the side reactions of all components, including the binder, conductive additive, and the current collector, and identify reaction products
  - Investigate dissolution as a function of SOC, and determine its mechanism.
  - Compare the performance of active material from various sources, and correlate performance to differences in physical properties such as crystallography, degree of metals disorder, and particle structure.
  - Distribute powders, electrolytes, and laminates of baseline systems to BATT partners.
  - Investigate the effect of Daikin high-voltage electrolyte on rate of side reactions, and identify reaction products with help from Diagnostics team.
Summary

We are an integral part of a comprehensive team to assess electrode materials from a fundamental perspective.

• We have developed a robust methodology for making electrodes that is proven to be transferable to BATT researchers and other institutions.

• Side reactions play a pivotal role in cell lifetime; we have developed a sealed 3-electrode cell that will allow us to rigorously study these effects and decouple the anode and the cathode for long-term studies.

• We conducted a rigorous assessment of two BATT LiFePO₄-based materials and determined mechanisms for their inherent limitations.
Technical Back-Up Slides
Technical Accomplishments and Progress:


Side Reaction and Cell Balancing

Rate of side reaction is a function of cell voltage.

Demonstrates how much capacity a cell can be balanced during an 8 hr trickle charge.

Demonstrates that if Gr./NCM is held at 4.2 V, there is 10.7% capacity available for cell balancing without the need for electronics!
Technical Accomplishments and Progress:

3. HQ’s LiFePO$_4$ is as high rate as Ceder’s with the addition of acetylene black.

Weight of active material vs. weight of conductive additive?

One can derive through geometric arguments the weight ratio of one material needed to cover another material:

$$\frac{w_p}{w_c} = b \left( 1 + \frac{\lambda}{2\lambda} + \frac{1}{\lambda^2} \right)$$

where, $\lambda = \frac{r_p}{r_c}$ and $b = \frac{\rho_p}{\rho_c} \frac{3\sqrt{3}}{8\pi} = \frac{\rho_p}{\rho_c} 0.20675$

If $\lambda = 0.4/0.05$ and $\rho_p/\rho_c = 3.6/(0.4\times2)$ then $w_c/w_p > 0.17$

Gives an electrode of 14% carbon, 81% LiFePO$_4$, and 5% binder.
Technical Accomplishments and Progress:

3. HQ’s LiFePO$_4$ is as high rate as Ceder’s with the addition of acetylene black.

The Addition of Carbon Additive to the 3 Materials

- MIT material requires the least amount of carbon additive to attain high rates.
- Ohmic and kinetic resistance not much improved beyond 15% carbon additive.

The addition of conductive carbon facilitates access to the particles beyond just an improvement in kinetics or ohmic resistance!