Investigations of electrode interface and architecture

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Overview

• Timeline
  – Start July, 2007

• Budget
  – $300k FY08
  – $300k FY09

• Technical barriers for PHEV
  – Cycle and calendar life (5000 cycles EV; 300,000 cycles HEV; 15 yr.)
  – Abuse tolerance
  – Much higher energy density (40 mile system: 11.6 kWh; 120 kg; 80 liter)

• Partners
  – Oak Ridge National Laboratory
  – High Temperature Materials Lab, ORNL
    • In situ SEM, TEM
  – Collaboration
    • LBNL independent cathode testing
Objectives

• Investigate the use of highly-conductive graphite as the current collector for Li-ion battery cathodes.

• Study the properties of the SEI formed between Li or graphite anodes in aprotic electrolytes. Use these fundamental studies to identify new strategies to stabilize the interface.
## Milestones

- Condensed from FY08 and FY09 AOP

<table>
<thead>
<tr>
<th>Milestones</th>
<th>Target Date</th>
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</thead>
<tbody>
<tr>
<td>1. Project the energy and power densities for batteries with graphite current collectors</td>
<td>Sept 08</td>
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<tr>
<td>2. Improve the microstructure characterization and control of LiFePO$_4$-graphite cathodes, correlating properties with simulation.</td>
<td>May 09</td>
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<tr>
<td>3. Evaluate cycling performance of selected cathodes at ORNL and LBNL.</td>
<td>May 09</td>
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<tr>
<td>4. Address issues of thermal conduction, mechanical robustness, and cost.</td>
<td>Sept 09</td>
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<tr>
<td>5. Continue in situ studies revealing the nature and transport of SEI at the Li-electrolyte interface</td>
<td>Sept 09</td>
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</table>
Approach - *graphite current collector*

- A conductive carbon skeleton will improve uniformity of current and temperature in cathode - extending lifetimes and safety.

<table>
<thead>
<tr>
<th>advantages</th>
<th>concerns</th>
<th>evaluate</th>
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<tbody>
<tr>
<td>shorter path for electrons and heat,</td>
<td>cost</td>
<td>half-cell cycle</td>
</tr>
<tr>
<td>more conductive particle contacts,</td>
<td>manufacturing</td>
<td>thermal</td>
</tr>
<tr>
<td>less aging from binder &amp; corrosion</td>
<td></td>
<td>mechanical</td>
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LiFePO$_4$ + PVDF + C-black on Al foil

Replace coating with composite

LiFePO$_4$ + C (AR-pitch) + C fibers (5-10µm)
Technical Progress – choosing material

- Many new graphite and carbon nanotube products are being developed.
- Materials are still too expensive, but prices have dropped dramatically. This is expected to continue.
- Estimated cost of carbon for 1.4 Ah battery is $0.40 to $1.70
- Some fiber papers and mats can be rolled for coating. (100µm and up)

<table>
<thead>
<tr>
<th>foams</th>
<th>bonded fibers</th>
<th>unbonded fibers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Koppers foam $0.44/g</td>
<td>Calcarb CBCF $0.16/g</td>
<td>Hollingsworth and Vose, $0.16/g PAN-based</td>
</tr>
<tr>
<td></td>
<td>Toray paper $3/g (10x dec. proj.) pitch-based</td>
<td>10µm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10µm</td>
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</table>
Technical progress – cost effective materials

• Lower cost MWCNTs by CVD “Cratos V Nano-Wool” an ORNL R&D 100 award
• Small (1-5%) addition of CNT greatly enhance properties of less costly carbon fibers and foams
• Cost of CNT-reinforced lignin fibers may approach 2 to 7 ¢/g


> Li-ion batteries will be 2nd major commercial success for CNTs.
> Showa Denko, Japan producing >100 tons/yr, mainly for battery application.
Technical Progress – control of microstructure and composition

• Coating from solution of finely ground LiFePO₄ + AR pitch. Pitch forms conductive graphitic bonds when treated at 500-700°C.

• Carbon analysis larger than expected. 3-5% residual from solvents and precursors.

• Solution dries as web rather than coated fibers. Geometry complex.

• Challenge to increase density without pressing. Slurry 0.2 to 1.3 g/cc solids.

![Image of microstructure analysis](image1)

![Graph of carbon analysis](image2)

by EDX and combustion infrared analysis
Technical Progress – cycling and rate performance

- Rate performance
  - Better for carbon fibers than foams
  - 1mm-thick CBCF with transverse fibers equals thinner paper composites
  - Have not identified maximum loading, where density impedes cycling

- Energy density
  - Up to 30 mWh/cm² for 5mm CBCF
  - Only 120 mWh/cm³
  - Improvement requires much higher LiFePO₄ loading

- Cycle life
  - Better for thin composites
  - Limited by Li degradation.

** Normalized by total weight of cathode: LiFePO₄ + carbon skeleton

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** Specific Energy (mWh/g) vs. Specific Power (mW/g) for various composites:

- 1 mm graphite foam (LQI)
- 1 mm CBCF
- 0.1 mm Toray paper (2x slurry)

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** Toray composite
- 0.11mm thick

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** Graph showing discharge capacity vs. cycle number for Toray composite (C/2 and C/30 rates)

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Managed by UT-Battelle
for the U.S. Department of Energy
**Technical Progress – evaluate by V. Battaglia**

- Samples prepared matching dimensions and capacity of typical LBNL samples*
  - 9/16” diameter, 1-2.5 mAh/cm² (1.6-4 mAh)
  - LiFePO₄ composites with Toray paper, 0.37mm and 0.11mm thick

- Results LBNL are TBD

- Sister cells at ORNL (1 cm diameter)

<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>LBNL samples</th>
<th>Projection high loading</th>
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</thead>
<tbody>
<tr>
<td>0.37 mm</td>
<td>0.37 mm</td>
<td>0.37 mm</td>
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<tr>
<td>0.11 mm</td>
<td>0.11 mm</td>
<td>0.11 mm</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Loading (wt.% LFPO)</th>
<th>LBNL samples</th>
<th>Projection high loading</th>
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<tbody>
<tr>
<td>35 %</td>
<td>35 %</td>
<td>70 %</td>
</tr>
<tr>
<td>45 %</td>
<td>45 %</td>
<td>70 %</td>
</tr>
<tr>
<td>70 %</td>
<td>70 %</td>
<td>~30%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Capacity (mAh)</th>
<th>LBNL samples</th>
<th>Projection high loading</th>
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<tbody>
<tr>
<td>2.5 mAh</td>
<td>2.5 mAh</td>
<td>~12 mAh</td>
</tr>
<tr>
<td>0.6 mAh</td>
<td>0.6 mAh</td>
<td>~12 mAh</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Vol.% Porosity</th>
<th>LBNL samples</th>
<th>Projection high loading</th>
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<tbody>
<tr>
<td>62 %</td>
<td>62 %</td>
<td>~70 %</td>
</tr>
<tr>
<td>70 %</td>
<td>70 %</td>
<td>~70 %</td>
</tr>
<tr>
<td>~30%</td>
<td>70 %</td>
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Technical Progress – initial thermal testing

• Thermography:
  – flash diffusivity system: through thickness measurement of thermal diffusivity
    • comparison of through-thickness thermal diffusivity of carbon supported cathodes and conventional cathodes
  – In-plane diffusivity using continuous (laser) point-source heating
    • comparison of in-plane thermal diffusivity of carbon supported cathodes and conventional cathodes
    • clear demonstration of heat dissipation due to point source heating, which is representative of localized thermal failure in lithium ion cells
Future work - carbon skeleton current collectors

• Immediate
  – Thermal conductivity study
  – Wrap up study with commercial foams and fiber papers, publish results

• Continuing effort - for much higher LiFePO$_4$ loading & dense structure, (also lower cost & better control)
  – Use loose carbon fibers. Cast dispersion of fibers with AR-pitch + LiFePO$_4$ powders; bond with one step heating (poss. microwave).

• Vision for a future project
  – Coated continuous carbon fibers for interwoven battery architecture
    • LiFePO$_4$-coated graphitized fibers
    • Si-plated or bare graphitized fibers
    • Need highly conductive skeleton for 3D architecture with high aspect ratio electrodes
    • Potential for multifunctional use, another route to system mass and volume efficiency
      – (J. Snyder, Army Research Lab, JECS 156 (2009) A215.)
**Approach – Studies of SEI at Li metal anode**

- Why do we need further work on SEI layer?  Is a Li anode possible?

**Background:**

No Li dendrites for thin film battery with ORNL electrolyte (Lipon ~1µm).

But unsupported Lipon barrier on Li → cracks if volume change is uneven.

Polyplus’s study of Lipon on Li anode → improvement, but flaws develop leading to dendrites.

**Approaches for engineering solution:**

- Reinforce thin Lipon film
- Engineer SEI layer
  - promote uniform Li plate/removal
  - enhanced mobility for smoothing interface.

Understanding is lacking. What is transport path for Li across SEI? How is SEI growth passivated?
Technical Progress – SEI formation

- Characterization by Electrochemical Impedance Spectroscopy (5 or 10mV signal) to minimize perturbation of the interface
- SEI forms rapidly but continues to age and become more resistive for many hours
- Results of side-by-side tests show vinylene carbonate addition to LiPF$_6$ (EC+EMC) electrolyte contributed another dispersion (layer of SEI), but did not reduce resistivity or non-linear behavior.
Technical Progress – transport properties of SEI

- DC chronopotentiometry reveals highly non-linear electrical response
Future work – *Li transport at SEI in relation to surface roughening*

- Expand investigation of non-linear electrical response
  - Goal is to understand mechanism, gain new insight
  - Evaluate distribution of current
    - (IR thermography, electrochemical scanning probe)
  - Evaluate alternative electrolytes, additives, or anodes (Si, C)
    - silane (Song) or chlorosilane derivatives (Dunn, Wudl),
    - dioxolane (Aurbach) or propylene carbonate
    - roughened Li surface or carbon

- Reevaluate – what is promising route to stabilize Li interface?
Summary

- Composites of carbon fibers + LiFePO$_4$ form effective cathodes. Advantages include more uniform current and temperature distribution. The remaining challenge is to increase the density and LiFePO$_4$ loading in the composite by alternative processing routes. Continued reduction in the cost of carbon fibers will make this cost effective.

- Non-uniform transport due to the morphological and compositional heterogeneity of the SEI may cause degradation of interface for both lithium and lithium-ion electrodes. A non-linear electrical response of the SEI formed in a carbonate electrolyte has been observed for the first time. Understanding the creation and distribution of high current paths will suggest new strategies to engineer protective barriers and stabilize the interface.