ELECTROCHEMISTRY DIAGNOSTICS AT LBNL

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presented by
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OVERVIEW

Timeline

• LBNL participated in the ATD Program since its inception in 1999
• ABRT Program began October 2008

Barriers Addressed

• Inadequate Li-ion battery energy, durability and safety for PHEV applications
• High irreversible capacity loss during first cycle

Budget

• Total budget since ATD Program inception $4900K
• FY08 funding $300K
• FY09 funding $600K
• FY10 funding TBD

Partners

• ANL, BNL, INL, and SNL
• Dan Abraham is the ABRT Program diagnostic lead
• John Newman (LBNL/UCB) is the Berkeley electrochemistry program lead
OBJECTIVES

• **Diagnostic Evaluation of ABRT Program Lithium Battery Chemistries**
  - Carry out post-test characterization of components from ABRT test cells
  - Understand factors that can enhance the stability of SEI layers
  - Establish and investigate degradation mechanisms of PHEV cells

• **Minimization of Irreversible Capacity Losses**
  - Synthesis and diagnostic evaluation of novel C/Me composites
  - Investigation of reactive impurities in anodes
MILESTONES

• Completed work on ATD Program cells in FY 2008
  ➢ Detailed characterization of Gen-2 and Gen-3 electrode composition, structure, and SEIs
  ➢ Provided key information on anode SEI characteristics, and demonstrated important differences between Gen-2 and Gen-3 cathodes
  ➢ Identified new surface processing method to enhance SEI stability

• Initiated new ABRT Program task in FY 2009
  ➢ Evaluation and development of new approaches to minimize first-cycle electrode capacity losses
BARRIERS ADDRESSED

• HEV and PHV battery durability and safety, as well as the need for efficient cell-formation processes, are the major barriers addressed by LBNL diagnostic work.

• The primary LBNL role in the ABRT Program is to carry out specific diagnostic evaluations to determine the changes in cell components that accompany battery power fade, capacity fade, and/or catastrophic failure.

• LBNL also seeks to identify the electrode and electrolyte processes that are significantly influenced by various cell-formation protocols.
APPROACH

• Strategies to minimize irreversible capacity losses
  - Synthesis and diagnostic evaluation of C/Me composites
  - Investigation of reactive impurities in anodes

• Diagnostic evaluation of ABRT Program lithium-ion battery chemistries
  - Carry out post-mortem diagnostic evaluations of components from ABRT test cells and model thin-film cells
    - Spectroscopic, microscopic, X-ray, chromatographic, and related techniques
  - Understand factors that can enhance the stability of SEI layers
  - Establish and investigate degradation mechanisms of PHEV cells
GRAPHITE ANODE SURFACE STRUCTURE
D/G Band Intensity Ratio Mapping

- Structure of graphite in the anode breaks down slowly upon cycling at relatively high rates
- Substantial surface disorder was observed in the anode cycled at 60°C
- Continuous change of anode surface reactivity vs. the electrolyte can be expected

Average spectra from 40-60 μm area
DIAGNOSTICS OF GRAPHITIC ANODES

Summary of Work Completed in FY 2008

- The surface of the graphite anode undergoes gradual structural degradation upon cycling.

- This phenomenon has been reported in the literature and appears to occur generally in all graphitic carbons. Kostecki et al., J. Power Sources (2003), Markevich et al., J. Power Sources (2005), Hardwick et al., J. Electrochem. Soc. (2008)

- The carbon structure and morphology determines the properties of the SEI layer. S. K. Jeong et al., J. Power Sources (2003), P. Novák et al., J. Power Sources, (2007)

What are the possible implications for Li-ion cell electrochemical performance and degradation mechanism?
• High Li$^+$ concentration gradients upon charging/discharging may cause the surface crystallites to breakdown

• What magnitude of force is needed to achieve this?
MODELS OF INTERCALATION INTO GRAPHITE

(a) Rüdorff model

(b) Daumus-Hérol model

~10% local expansion upon Li+ intercalation
DIAGNOSTICS OF CYCLED ANODES

Mag-10/1M LiPF$_6$, EC:DMC/Li cells were cycled 200 times at 25$^\circ$C between various potential limits at the C/5 rate.

- The initial phase of lithium intercalation into graphite (ca. Li$_{0.05}$C$_6$) is responsible for most of the structural damage.

- Avoid complete de-lithiation of graphite to minimize graphite disordering!

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Cycling Potential Range</th>
<th>Li$_x$C$_6$ limits</th>
<th>$I_d/I_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>-</td>
<td>$x=0$</td>
<td>0.25 ± 0.03</td>
</tr>
<tr>
<td>Anode 1</td>
<td>1.0 &lt;-&gt; 0.18 V</td>
<td>0$\leq x &lt; 0.05$</td>
<td>0.61 ± 0.04</td>
</tr>
<tr>
<td>Anode 2</td>
<td>0.23 &lt;-&gt; 0.098 V</td>
<td>0.1$&lt; x &lt; 0.5$</td>
<td>0.58 ± 0.03</td>
</tr>
<tr>
<td>Anode 3</td>
<td>0.15 &lt;-&gt; 0.005 V</td>
<td>0.5$&lt; x \leq 1$</td>
<td>0.45 ± 0.06</td>
</tr>
</tbody>
</table>
1 nm films of Mn and Fe were deposited onto MAG10 composite anodes.

**Cyclic Voltammetry**

- Thick layers (~50 nm) of Ni, Co, Mn on graphite accelerate degradation of graphitic composite anodes.
- 1 nm layers of Fe or Mn on composite MAG-10 anodes affect slightly the kinetics of SEI layer formation and Li\(^+\) intercalation/deintercalation.
- Fe, Mn thin films covered only a small fraction of the total graphite surface area in the composite electrode.
• Mn thin film (1 nm) on the HOPG basal plane affects the electrochemical response of graphite in 1M LiPF₆, EC:DEC electrolyte.
  ➢ Formation of the SEI at 0.8V is suppressed.
  ➢ Kinetics of lithium intercalation at low potentials are inhibited.
• A thicker (10 nm) Mn layer completely blocks the HOPG surface.
GEN-3 CATHODE DIAGNOSTICS

Cell G3A.60L45.I105.23.64.54.G.T

- Cycle Life tested at 45°C
- 20% capacity fade and 54% power fade @ 64 weeks
- Received Dec 2008, cell ID #A-05

Results

- C/25 capacity after disassembly was 100% of initial (1.29 mAh/cm²)
- No evidence for particle isolation by XRD after rapid charging
- Active material morphology and composition like new
GEN-3 ANODE DIAGNOSTICS
Cell G3A.60L45.I105.23.64.54.G.T

Results

• No visible damage
• No transition metals in most areas
• Very small number of small deposits with variable metal ratios
• Most likely fade mechanisms:
  ➢ Loss of available lithium
  ➢ Electrolyte starvation (separator was dry upon opening the cell)

EDX Metals Analysis

<table>
<thead>
<tr>
<th>Deposit</th>
<th>Mn</th>
<th>Ni</th>
<th>Co</th>
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<tbody>
<tr>
<td>1</td>
<td>47.5</td>
<td>35.2</td>
<td>17.3</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>78.5</td>
<td>21.5</td>
<td>-</td>
</tr>
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</table>
FUTURE WORK

• Studies of SEI layer formation/stabilization
  ➢ Continue studies of the effect of surface poisoning by transition metals on anode processes and cell performance
  ➢ Conduct spectroelectrochemical experiments on the edge planes of model HOPG electrodes

• Diagnostics of ABRT Program cell components
  ➢ Examine electrode composition, structure, and surface films
  ➢ Compare degradation mechanisms in ATD vs. ABRT cells

• Overcharge Protection
  ➢ Develop a reliable, inexpensive, self-actuating mechanism for overcharge protection in Li-ion batteries for PHEVs

• Material Scale-up
  ➢ Carry out property-consistent scale-up of promising new materials developed in the Batteries for Advanced Transportation Technologies (BATT) Program and test the materials according to PHEV protocols
SUMMARY

• **Supporting research for improved lithium-ion batteries:**
  - Carbon disordering increases anode surface reactivity and causes SEI layer reformation, which shifts the cathode to a higher SOC and accelerates cathode degradation.
  - Complete delithiation of graphitic anodes accelerates structural disordering and must be avoided in order to extend Li-ion cell lifetimes.
  - Diagnostic analyses showed little electrode degradation of a Gen-3 cell with significant capacity and power loss.
    - Loss of available Li and/or electrolyte starvation are likely cell fade mechanisms.

• **Approach:**
  - Advanced spectroscopic, microscopic, X-ray, chromatographic, and related techniques to characterize cell components
  - Development of new surface-processing methods

• **Accomplishments:**
  - Completed systematic study of graphite anode structural degradation in FY 08, and extended study in FY 09 to identify approach to anode stabilization
  - Identified likely fade mechanisms in Gen-3 cells

• **Plans:**
  - Continue studies of cell components and anode SEI stabilization
  - Initiate new work on cell overcharge protection and BATT Program materials scale up.