Develop & evaluate materials & additives that enhance thermal & overcharge abuse

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Overview

Timeline
- Start: 10/01/2008
- End: 09/30/2014
- 30% completed

Budget
- Total project funding
  - DOE - $880K
  - Contractor - $0
- Funding received in FY09
  - $440K
- Funding for FY10
  - DOE - $440K

Barriers
- Barriers addressed
  - Cell safety
  - Cell flammability

Partners
- Sandia National Laboratory
- EnerDel
- Hitachi Chemicals
- ECPRO
Objectives of the work

- Identify the role of each cell components in the abuse characteristics of different cell chemistries.

- Identify and develop more stable cell materials that will lead to more inherently abuse tolerant cell chemistries.

- Secure sufficient quantities of these advanced materials (and electrodes) & supply them to SNL for validation of safety benefits in 18650 cells.
Approach

Current targets: a) Safer electrode materials – cathode and anode  
b) additives for stable SEI on anode  
c) surface modification for safer cathode  
d) safer electrolyte components – solvent and salt  
e) redox shuttles for overcharge protection

- Commercial source  
- Partners  
- In-house synthesis

Impact on safety at component level
- Thermal analysis  
- Electrochemical analysis

Validation at cell level
- SNL  
- Industrial partners
Recent Accomplishments and Progress

- SEI formation on different carbon anodes
  - Material investigated: MCMB-1028, 3 types of surface modified graphite from Hitachi, and Hard carbon
  - 18650 cells using LiFePO$_4$ and different carbons were secured and sent to SNL for ARC study.
  - Both DSC (ANL) and ARC (SNL) data agreed that the type of carbon anode significantly impact the safety of lithiated carbon.

- Electrolyte additive for stable SEI layer
  - Three electrolyte additives were identified to provide stable SEI on graphite and hence improve the safety of lithium ion cells.
  - Better capacity retention with the electrolyte additives.
  - SNL is quantifying the impact of LiDFOB at the 18650 cell level.

LiDFOB
Recent Accomplishments and Progress (cont’d)

- **Role of LiPF$_6$ for the thermal reactivity of cathodes**
  - The reaction of delithiated NMC with electrolyte components studied with DSC.
  - LiPF$_6$ was investigated against pure solvents, LiBF$_4$, LiTFSI and Li$_2$B$_{12}$F$_{12}$.
  - LiPF$_6$ has negative impact on safety of cathode by reducing the onset temperature from ~310°C to about ~230°C.

- **Surface coating of cathode materials**
  - Al$_2$O$_3$ coating was shown to be beneficial to the electrochemical performance of NCA.
  - 18650-cells using NCA and Al$_2$O$_3$ coated NCA were secured from industrial partner to verify the impact of coating at the cell level.
    - Some cells were provided to INL/ANL for life test.
    - 10 cells were shipped to SNL for abuse tests.
    - 10 cells were shipped to EnerDel for overcharge and nail penetration test.
Redox shuttles for overcharge protection

- Three new aromatic redox shuttles with a redox potential of 4.17, 4.2 and 4.85 V vs. Li⁺/Li were synthesized at ANL.
- Their overcharge protection functionality was confirmed in coin cells.
- The structures of redox shuttle are in the process of being patented, and might be disclosed at the merit review.

Only 2 of 5 areas are selected for oral discussion today.

(1) SEI decomposition reaction on different carbons.
(2) Redox shuttles for overcharge protection.
• Thermal runaway of LIB can be triggered at about 140-180°C.

• SEI decomposition is the only exothermal reaction below 200°C.

• The continuous SEI decomposition plays a critic role in triggering the major reaction of cathode with electrolyte at above 200°C.

• A good SEI is expected to decompose at high temperature and generate low exothermal heat flow.
**Carbon anodes used for the safety study**

<table>
<thead>
<tr>
<th>Description</th>
<th>MCMB-1028</th>
<th>SMG-N-7b</th>
<th>SMG-N-20</th>
<th>SMG-Ns-15f</th>
<th>HC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>D$_{50}$ (μm)</strong></td>
<td>11.8</td>
<td>11.1</td>
<td>19.5</td>
<td>21.6</td>
<td>TBD</td>
</tr>
<tr>
<td><strong>BET (m$^2$/g)</strong></td>
<td>2.01</td>
<td>5.0</td>
<td>5.1</td>
<td>0.7</td>
<td>TBD</td>
</tr>
</tbody>
</table>

- Physical parameters investigated: bulk structure, particle size, surface area
- Physical characterization of hard carbon is ongoing.
Reaction of lithiated carbons with electrolyte

1.2M LiPF₆ in EC/EMC (3:7)

- Major exothermal reaction was observed above 220°C for all carbons.

- The focus is the SEI decomposition that trigger thermal runaway at low temperature.

  - At temperature below 200°C, MCMB generated more heat than surface modified graphite (SMG series). Hard carbon generate the least heat.

  - Heat flow of SMG-N-20 is lower than SMG-N-7b, and SMG-Ns-15f.

  - Kinetics of the SEI decomposition is another key parameter.
**SEI Decomposition kinetics on different carbons**

Lithiated MCMB-1028 with 1.2M LiPF$_6$ in EC/EMC(3:7)

Model free kinetics determination:

\[
\ln\left(\frac{\phi}{T_p^2}\right) = k - \frac{E_a}{RT}
\]

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</tr>
</thead>
<tbody>
<tr>
<td>Ea (kJ/mol)</td>
<td>53.54</td>
<td>88.08</td>
<td><strong>92.66</strong></td>
<td>78.46</td>
<td>87.34</td>
</tr>
</tbody>
</table>

• **Kinetics:** SMG-N-20 > SNG-N-7b ~ Hard carbon > SMGNs-15f > MCMB-1028
• **How about the response at cell level?**
LiFePO$_4$ was used as cathode to minimize the exothermal reaction on cathode side.

Three carbons were examined: SMG-N-7b, SMG-N-20, and SMG-Ns-15f.

SMG-N-20 > SMG-N-7b > SMG-Ns-15f

Cell safety data is similar to components level safety data.
Overcharge abuse of lithium ion batteries

Possible consequences:
- Accelerate capacity/power fade; shortening life.
- Decomposition of cathode electrode.
- Lithium plating on anode.
- Heat generation; possibly triggering thermal runaway.
- Electrolyte decomposition and gassing; potential leakage.
- Internal short.

The cell voltage can be properly capped with a stable redox shuttle.
- The redox potential of redox shuttle is required to be at least 0.2 V higher than the working potential of the cathode.
- Possible cell balancing with a shuttle
Unmatched long term overcharge protection

ANL-RS-1 mixed with proprietary redox shuttle
MNC vs. MCMB-2528 25°C.

- Cathode: Li$_{1.1}$[Mn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$]$_{0.9}$O$_2$
- Anode: MCMB-1028
- Current: C/3
New redox shuttles synthesized at ANL

- Three new redox shuttles were synthesized at ANL (IP in the process of being generated)

- ANL-RS-2 and ANL-RS-4 are good candidates for 4 V class materials.

- ANL-RS-3 is promising for high voltage materials such us Composite electrode material.
Long term electrochemical performance of new redox shuttle (ANL-RS-4)

LiFePO$_4$/LTO; 1.2 M LiPF$_6$ in EC/EMC (3:7); 2.3 wt% of redox shuttle

- ANL-RS-4 showed excellent electrochemical performance in LiFePO$_4$/LTO cell. More study is needed for other lithium ion chemistry like oxides cathode and carbon anodes.
- Electrochemical study of ANL-RS-2 and ANL-RS-3 is ongoing, and will be reported later.
Collaborations

• **Partners**
  - Sandia National Laboratory: cell level verification of safety improvement using components identified at ANL.
  - EnerDel: overcharge abuse and nail penetration test of 18650 cells.
  - Hitachi Chemical: collaboration on the safety characteristics of carbon anodes and 18650 cell fabrication.
  - ECPRO: collaboration on 18650 cell fabrication using NCA based 18650 cells (Coated & non–coated NCA)

• **Technology transfer:**
  Collaboration with EnerDel & JCI to validate ANL’s redox shuttles.
  - overcharge protection
  - cell capacity balancing
Proposed Future work

- Continue exploring electrolyte additive to reduce heat flow from SEI decomposition at low temperature.

- Investigate the safety of anode that doesn’t require SEI

- Quantify the impact of LiPF$_6$ on the thermal stability of delithiated cathode and explore the possible safety mitigation techniques.

- Investigate the role of none flammable electrolyte & ionic liquid on the safety of lithium battery

- Investigate the effect of cathode composition, morphology and surface area on safety

- Systemic characterization of ANL’s new redox shuttles, and continue exploring new shuttle structures.

- Work with SNL and industrial partner to validate new shuttles in a full cell configuration (focus on overcharge & cell balancing)

- Work with industrial partner to make 18650 cell using ANL composite electrode & investigate the safety performance of this high energy material in collaboration with SNL
Summary

• Several components were investigated for safety improvement:
  (a) carbon anodes; Role of SEI
  (b) electrolyte additives for more stable SEI layer;
  (c) electrolyte components;
  (d) redox shuttles for overcharge protection;
  (e) oxide (LiNi_{0.8}Co_{0.15}Al_{0.05}O_2) coated with Al_2O_3

• SMG-N-20 and a hard carbon were identified as potentially safer anode than MCMB-1028.

• Three new stable redox shuttles discovered at ANL are promising for overcharge protection for 4 V class cathode materials.
Collaborations

- P. Roth (SNL) (provide materials and cells for cell level safety studies)
- Hitachi chemical (make 18650 cells based on LiFePO4 and several carbon made from the same process but have different surface area)
- ECPRO (make 18650 cells with Al$_2$O$_3$ coated and non coated NCA)
- EnerDel (Overcharge test, nail penetration of 18650 cells)
- EnerDel and JCI (shuttle validation and effect on cell monitoring)
- Daikin (provide new non flammable solvent and flame retardant)
- 3M (provided new shuttle for ANL for screening purpose)
- Many Japanese and Korean companies (supplied material that impact the safety of lithium batteries)