Screen Electrode Materials and Cell Chemistries

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Overview

Timeline
- Start – Oct. 2008
- Finish – Sep. 2014
- < 8% Complete

Barriers
- An overwhelming number of materials are being marketed by vendors for Lithium-ion batteries.
  - How to select and screen these materials within the effort allocated to this project?
- No commercially available high energy material to meet the 40 mile PHEV application established by the FreedomCAR and Fuels Partnership.
- The impact of formulation and fabrication on performance of electrode materials with a broad variation of chemical and physical properties.

Budget
- Total project funding in FY2009
  - DOE: $350K
Objectives of This Study

- To identify and evaluate low-cost cell chemistries that can simultaneously meet the life, performance, and abuse tolerance goals for Plug-in HEV application.

- To enhance the understanding of advanced cell components on the electrochemical performance and safety of lithium-ion batteries.
**Approach**

- Focus of the investigations will be shifted to high energy materials
  - Avoid materials based on rare elements, expensive precursors, or elaborate processing
  - Search battery material suppliers for new materials
- Material screening process will include
  - Test protocol development for lab scale cells
  - Evaluate materials for PHEV use by testing their
    - *Rate capability*,
    - *HPPC impedance*,
    - *Cycle life*, and
    - *Thermal properties (DSC)*
  - Use laboratory scale cells – coin cell, fixture cell, and pouch cell.
- Recommend promising materials for further thermal abuse evaluation and consider for use in longer-term aging studies.
Test Protocol Development for material screening

- LiFePO$_4$: Mitsui Engineering Shipbuilding (MES), Japan
  - Carbon coated nano size particle
  - Electrochemical enhanced by engineering

- Li$_{1+w}$[Ni$_x$Co$_y$Mn$_z$]$_{1-w}$O$_2$ (NCM): Toda Kogyo, Japan
  - High tap density
  - Surface fluorination

- LiMn$_2$O$_4$: Tronox, USA - Domestic supplier
  - Doping
  - Fluorination

- LiNi$_x$Co$_y$Mn$_z$O$_2$: SoBright, China

Other materials tested, but not shown here, include
- Graphite
- Separator
## USABC Requirements of Energy Storage Systems for PHEV

<table>
<thead>
<tr>
<th>Characteristics at EOL (End of Life)</th>
<th>High Power/Energy Ratio</th>
<th>High Energy/Power Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Equivalent Electric Range</td>
<td>miles</td>
<td>10</td>
</tr>
<tr>
<td>Peak Pulse Discharge Power (10 sec)</td>
<td>kW</td>
<td>45</td>
</tr>
<tr>
<td>Peak Regen Pulse Power (10 sec)</td>
<td>kW</td>
<td>30</td>
</tr>
<tr>
<td>Available Energy for CD (Charge Depleting) Mode, 10 kW Rate</td>
<td>kWh</td>
<td>3.4</td>
</tr>
<tr>
<td>Available Energy for CS (Charge Sustaining) Mode</td>
<td>kWh</td>
<td>0.5</td>
</tr>
<tr>
<td>Maximum System Weight</td>
<td>kg</td>
<td>60</td>
</tr>
<tr>
<td>Maximum System Volume</td>
<td>Liter</td>
<td>40</td>
</tr>
</tbody>
</table>

- Test procedure and method have been defined in “Battery Test Manual for Plug-in Hybrid Electric Vehicles” by INL 2008.
- The energy requirement is a challenge for PHEV success.

<table>
<thead>
<tr>
<th>C-rate calculation for PHEV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Available Energy*</td>
</tr>
<tr>
<td>-------------------</td>
</tr>
<tr>
<td>50%</td>
</tr>
<tr>
<td>60%</td>
</tr>
<tr>
<td>70%</td>
</tr>
</tbody>
</table>

* The calculation includes 30% energy margin.

- The discharge pulse rate is equal to 2C using 60% energy in the battery.
- The charge depleting (CD) rate is equal to C/3 when 50% of battery energy will be used.
The specific capacities of anode and cathode materials should be above 350 and 170 mAh/g, respectively, to meet the PHEV goal with weight and volume requirements.
Battery Cost Analysis

- The unit cost of 20 kWh battery is more than $4500, according to Battery Design Model by Paul Nelson (ANL).

- Material cost makes the major contribution to the battery cost.
  - Active materials, positive and negative, take half of material cost.
  - Electrolyte and separator are the next major contributors.

- Manganese and Iron base materials have the potential to reduce the cost.

- New high energy density anode will significantly reduce the cost.

- New electrolyte and separator should be investigated.
LiFePO$_4$: Mitsui Engineering Shipbuilding (MES)

**Advantage of MES LiFePO$_4$**
- Low cost
- Thermal stability
- High specific capacity
- High power capability
  - Carbon coating
  - Nano size Particle

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Current target value</th>
<th>Measured value</th>
<th>Measurement method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon content</td>
<td>5.3 ~ 6.1 wt.%</td>
<td>6.0wt%</td>
<td>High-frequency furnace method</td>
</tr>
<tr>
<td></td>
<td>(target: 5.6 wt%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific surface area</td>
<td>18~26 m$^2$/g</td>
<td>23.9 m$^2$/g</td>
<td>BET method</td>
</tr>
<tr>
<td>Bulk density</td>
<td>0.18~0.28 g/cm$^3$</td>
<td>0.21g/cm$^3$</td>
<td>-</td>
</tr>
<tr>
<td>Tap density</td>
<td>0.40~0.52 g/cm$^3$</td>
<td>0.44g/cm$^3$</td>
<td>-</td>
</tr>
<tr>
<td>Particle size (D50)</td>
<td>1.1~1.5μm</td>
<td>1.4μm</td>
<td>Laser scattering method</td>
</tr>
</tbody>
</table>
Specific capacity of LiFePO₄ is determined to be 160 mAh/g with about 5% irreversible capacity loss during the 1st cycle between 3.8 V and 3.0 V at C/10 rate.
**High Rate Performance of MES LiFePO₄**

- The Graphite/LiFePO₄ cell can deliver more than 80% capacity at 10C rate.
- ASI results of HPPC is comparable to Graphite/LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂ lithium ion battery.
**Engineering Effect on MES LiFePO₄ Performance**

- The ASI increases with increasing electrode porosity.
- According to SEM image, much better contact between the particles are obtained after calendering.
- The carbon/carbon matrix is likely to be the major cause for the high resistance of the cell with high porosity.
**Toda Li$_{1+w}$[Ni$_x$Co$_y$Mn$_z$]$_{1-w}$O$_2$ (NCM):**

Serial of lithium rich NCM materials with various Ni, Co, and Mn ratios

Advantages of Toda materials:

- High energy density
  - High specific capacity,
  - High tap density,
  - More capacity with nickel rich material
  - High electrode loading density
- Better stability with surface fluorination

![Voltage Profile of Toda NCM](image)

<table>
<thead>
<tr>
<th>Sample producer</th>
<th>ID</th>
<th>BET m2/g</th>
<th>D50 µm</th>
<th>Tap density g/cm³</th>
<th>Capacity, mAh charg-1</th>
<th>Capacity, mAh disch-1</th>
<th>coulombic %</th>
<th>ASI cm³/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Japan</td>
<td>NCM111</td>
<td>0.39</td>
<td>6</td>
<td>2.43</td>
<td>169.72</td>
<td>148.65</td>
<td>87.59</td>
<td>43.8</td>
</tr>
<tr>
<td></td>
<td>NCM523</td>
<td>0.23</td>
<td>10.2</td>
<td>2.37</td>
<td>191.26</td>
<td>162.53</td>
<td>84.98</td>
<td>28.5</td>
</tr>
<tr>
<td></td>
<td>NCM622</td>
<td>0.22</td>
<td>10.8</td>
<td>2.61</td>
<td>201.18</td>
<td>166.76</td>
<td>82.85</td>
<td>28.5</td>
</tr>
<tr>
<td>Germany</td>
<td>NCM111</td>
<td>0.59</td>
<td>8</td>
<td>2.4</td>
<td>177.88</td>
<td>156.66</td>
<td>88.07</td>
<td>34.8</td>
</tr>
<tr>
<td></td>
<td>NCM111/F</td>
<td>0.36</td>
<td>8.2</td>
<td>2.3</td>
<td>181.70</td>
<td>159.88</td>
<td>87.99</td>
<td>35.8</td>
</tr>
<tr>
<td></td>
<td>NCM111/HD</td>
<td>0.26</td>
<td>8.5</td>
<td>2.8</td>
<td>170.00</td>
<td>147.33</td>
<td>86.66</td>
<td>36.2</td>
</tr>
</tbody>
</table>
NCM523 and NCM622 have comparable ASI (30 ohm-cm²) to NCA cell (Gen2), which is lower than that of NCM111 electrode.

The pulse ASI of fluorinated NCM and high tap density NCM are similar to each other.
Fluorination Effect on Toda Li$_{1+w}$[Ni$_x$Co$_y$Mn$_z$]$_{1-w}$O$_2$

Advantages of fluorinated NCM

- Improve the cycle life under 1C rate continuous charge and discharge at room temperature.
- Reduce the heat generation at fully charged state with electrolyte.
Fluorination Effect on Tronox LiMn$_2$O$_4$

The thermal stability of LiMn$_2$O$_4$ can also be improved by fluorination.

Tronox is domestic manganese spinel supplier.

The Tronox spinel with following characteristics:
- Aluminum doped
- Chromium doped
- Surface fluorinated

DSC of LiMn$_2$O$_4$
SoBright NCM Material \((LiNi_xCo_yMn_zO_2)\)

- The NCM might provide
  - Higher energy density
  - Higher power

Physical Properties

<table>
<thead>
<tr>
<th>Item</th>
<th>Typical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni+Co+Mn (wt%)</td>
<td>58.6</td>
</tr>
<tr>
<td>PSD ((\mu)m)</td>
<td></td>
</tr>
<tr>
<td>D10</td>
<td>6.08</td>
</tr>
<tr>
<td>D50</td>
<td>11.13</td>
</tr>
<tr>
<td>D90</td>
<td>22.73</td>
</tr>
<tr>
<td>Tap Density (g/cm(^3))</td>
<td>2.38</td>
</tr>
<tr>
<td>SSA (m(^2)/g)</td>
<td>0.25</td>
</tr>
<tr>
<td>Morphology</td>
<td>Spherical particle</td>
</tr>
<tr>
<td>pH value</td>
<td>11.08</td>
</tr>
</tbody>
</table>
High Capacity of SoBright Material

- The reversible capacity between 4.3 V and 3.0 V is about 162 mAh/g with 14% capacity loss during first cycle.
- The cutoff voltage can be extended to 4.5 V and 4.7 V with more than 170 and 180 mAh/g reversible specific capacity, respectively.
Power Capability and Thermal Stability

- The ASI is about 30 ohm-cm², which is comparable to NCM material.
- The thermal stability of SB blend is comparable to NCA material.
**Plans for Next Fiscal Year**

- Investigate materials from different suppliers for high energy (PHEV) and high power (HEV) application
  - Hitachi Chemical’s anode materials
  - Nano-size LiMnPO$_4$ from HPL
- New binder study
- New electrolyte study – Fluorinated solvent (Daikin)
- New anode materials search and evaluation
  - High energy density
  - Stable material
- Continue to evaluate advanced cathode, anode, binder, separator, and electrolyte systems as they become available from various sources.
Summary

- MES olivine can be used for high power applications. Electrode optimization is needed to achieve its best performance.

- Variations of Toda Li$_{1+w}$[Ni$_x$Co$_y$Mn$_{1-w}$]$_{1-w}$O$_2$ (NCM) materials indicate that the nickel rich material can deliver high energy density. The surface fluorination can further improve its thermal and cycleability.

- Tronox spinel can supply high power capability. The surface fluorination improves the thermal stability.

- SoBright NCM material has high power and high energy density. Its thermal stability is comparable to NCA (Gen2) electrode.
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