STABILIZED SPINELS AND NANO OLIVINES

ARUMUGAM MANTHIRAM
Electrochemical Energy Laboratory (ECEL)
Materials Science and Engineering Program
The University of Texas at Austin

May 20, 2009

Project ID #: es_23_manthiram

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OVERVIEW

Timeline
- Project start date: April 2004
- Project end date: May 2010
- 75% complete

Budget
- Total project funding
  - DOE: $871K
- Funding for FY08
  - $165K
- Funding for FY09
  - $260K

Barriers
- Barriers
  - Cost
  - Cycle life
  - Energy and power densities
- Targets
  - Acceptable cycle life for spinel cathodes
  - Low manufacturing cost for olivine cathodes
  - Increased energy and power densities with spinel cathodes
OBJECTIVES

• To develop high performance cathodes for lithium ion batteries and a fundamental understanding of their structure-composition-performance relationships

- To develop low cost spinel manganese oxide compositions exhibiting improved capacity retention at elevated temperatures

- To develop spinel-layered oxide composite cathodes offering a combination of high power and energy

- To develop low cost manufacturing processes for olivine cathodes with controlled size and nanomorphologies
<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone</th>
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<tbody>
<tr>
<td>March 2008</td>
<td>Optimization of the 4 V spinel to layered oxide ratios and microstructures in the spinel-layered oxide composite cathodes</td>
</tr>
<tr>
<td>September 2008</td>
<td>Optimization and surface modification of the 5 V spinel cathodes based on LiMn_{1.5}Ni_{0.5}O_{4}</td>
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<tr>
<td>March 2009</td>
<td>Rapid synthesis and characterization of various phospho-olivines with controlled size and nanomorphologies</td>
</tr>
<tr>
<td>June 2009</td>
<td>Optimization of stabilized spinel-layered oxide composite cathodes</td>
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<tr>
<td>September 2009</td>
<td>New cathode materials based on polyanions</td>
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</table>
• Develop a firm understanding of the factors controlling the electrochemical performances of cathode materials and utilize the understanding to develop high performance cathodes

- Cationic and anionic substitutions in 4 V spinel cathodes
- Cationic substitutions in 5 V spinel cathodes
- Surface modifications of 5 V spinel cathodes
- Composites consisting of high power spinel & high energy layered oxides
- Olivine cathodes with controlled particle size & unique nanomorphologies

- Solid state and solution-based synthesis approaches
- Advanced chemical and structural characterizations
- In-depth electrochemical evaluation including impedance analysis
- Understanding of the structure-property-performance relationships
STABILIZED HIGH POWER 4 V SPINEL CATHODES

High temperature cyclability

Voltage vs. Li/Li⁺ (V)

LiMn$_2$O$_4$

LiMn$_{1.85}$Li$_{0.075}$Co$_{0.075}$O$_4$

LiMn$_{1.85}$Li$_{0.075}$Co$_{0.075}$O$_{3.94}$F$_{0.06}$

LiMn$_{1.75}$Li$_{0.125}$Co$_{0.125}$O$_4$

LiMn$_{1.75}$Li$_{0.125}$Co$_{0.125}$O$_{3.88}$F$_{0.12}$

LiMn$_{1.7}$Li$_{0.15}$Co$_{0.15}$O$_4$

LiMn$_{1.7}$Li$_{0.15}$Co$_{0.15}$O$_{3.83}$F$_{0.17}$

LiMn$_{1.7}$Li$_{0.15}$Co$_{0.15}$O$_{3.76}$F$_{0.24}$

- Stabilized spinels with optimized cationic and anionic substitutions offer superior capacity retention at elevated temperatures with high rate capability.
• Surface modifying $\text{Al}_2\text{O}_3$, ZnO, and $\text{Bi}_2\text{O}_3$ layers are continuous on the layered oxide
• Surface modifying $\text{AlPO}_4$ layer is crystalline, but not continuous
- Surface modification improves the rate capability and rate capability retention due to the suppression of thick SEI layer formation.
  - \( \text{Bi}_2\text{O}_3 \) coating gives the best rate capability.
  - \( \text{Al}_2\text{O}_3 \) coating gives the best rate capability retention.
SURFACE (XPS) CHARACTERIZATION OF 5 V SPINELS

- LiAlO$_2$ formed on Al$_2$O$_3$ coated sample surface during sintering
- Bi formed on Bi$_2$O$_3$ coated sample surface during cycling
- Formation of Li$^+$-conducting LiAlO$_2$ and metallic Bi improves rate capability
COMPARISON OF THE POLARIZATION RESISTANCE, $R_p$

- $R_p$ values are obtained from the slope of the voltage vs current curves after 3 and 50 cycles

$$R_p = R_{ohm} + R_{ct} + R_{diff}$$

- $\text{Bi}_2\text{O}_3$ coating shows the smallest $R_p$, resulting in the best rate capability

- $\text{Al}_2\text{O}_3$ coating shows the smallest $\Delta R_p$, resulting in the best rate capability retention
• Al₂O₃ is the most effective and AlPO₄ is the least effective in preventing the growth of SEI layer as revealed by the XPS analysis of LiF concentration at various depths.

• XPS data are consistent with the $\Delta R_s$ values.

• The differences in $R_p$ and $\Delta R_p$ are due to the differences in $R_{ct}$ and $\Delta R_{ct}$, and $\Delta R_{ct}$ originates from $\Delta R_s$. 
RAPID SYNTHESIS OF OLIVINE LiMPO₄ (M = Mn, Fe, Co, Ni)

- Microwave-assisted solvothermal (MW-ST) process to produce LiMPO₄ (M = Mn, Fe, Co, Ni) within a short reaction time of 5 – 15 minutes at < 300 °C, followed by ambient-temperature networking with multi-walled carbon nanotubes (MWCNT).
**XRD PATTERNS OF OLIVINE LiMPO$_4$ (M = Mn, Fe, Co, Ni)**

- Highly crystalline, phase pure LiMPO$_4$ (M = Mn, Fe, Co, Ni) are formed by the MW-ST method without requiring any post heat treatment in reducing gas atmospheres.
- The lattice parameters and unit cell volume decrease as we go from M = Mn to Ni in LiMPO$_4$ due to the decreasing ionic radius of the M$^{2+}$ ions.

### Table: Crystallographic Unit cell Parameters of LiMPO$_4$

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V, (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMnPO$_4$</td>
<td>10.446</td>
<td>6.106</td>
<td>4.746</td>
<td>302.71</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>10.321</td>
<td>6.000</td>
<td>4.695</td>
<td>290.74</td>
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<tr>
<td>LiCoPO$_4$</td>
<td>10.216</td>
<td>5.923</td>
<td>4.704</td>
<td>284.64</td>
</tr>
<tr>
<td>LiNiPO$_4$</td>
<td>10.047</td>
<td>5.862</td>
<td>4.681</td>
<td>275.69</td>
</tr>
</tbody>
</table>
TEM IMAGES OF LiMPO₄ (M = Mn, Fe, Co, Ni)

- Single crystalline LiMPO₄ (M = Mn, Fe, Co, Ni) with nanothumb-like shapes are formed by the microwave-solvothermal method.
- The LiMPO₄ nanocrystals exhibit a preferential growth along the [001] direction with the easy lithium diffusion direction (b axis) perpendicular to the long axis.
Nano networking with MWCNT increases the rate capability due to the enhancement in electronic conductivity.
Performances of LiMnPO_4 and LiCoPO_4 are inferior compared to that of LiFePO_4.
RAPID SYNTHESIS OF LiFePO$_4$/C NANOCOMPOSITES

**MW-ST method – *Ex situ* carbon coating**

- **Fe(CH$_3$COO)$_2$**
- **H$_3$PO$_4$**
- **LiOH**
- **HOC$_2$H$_4$O$_4$H**

Microwave

Solvothermal nucleation and crystal growth

LiFePO$_4$ nanorods

Mixed with sucrose and heated at 700 °C, 1 h, H$_2$/Ar atm

LiFePO$_4$/C nanocomposite

**MW-HT method – *In situ* carbon coating**

- **FeSO$_4$**
- **H$_3$PO$_4$**
- **LiOH**
- **H$_2$O**

Microwave

(i) Nucleation and crystal growth

Nanoclusters

Fe$_3$(PO$_4$)$_2$(OH)$_2$

(ii) Hydrothermal carbonization

Glucose, Li$^+$

(iii) *In situ* carbon coating

LiFePO$_4$/C nanocomposite

700 °C, 1 h, H$_2$/Ar atm

LiFePO$_4$/C nanocomposite
SEM AND TEM IMAGES OF LiFePO$_4$/C NANOCOMPOSITES

- MW-HT method gives larger particle size than the MW-ST method
- The easy lithium diffusion direction (\(b\) axis) is perpendicular to the long axis, providing an advantage to enhance lithium diffusion and rate capability
ELECTROCHEMICAL PERFORMANCES OF LiFePO$_4$/C

- Carbon coating improves rate capability due to enhanced electronic conductivity
- MW-ST sample shows higher rate capability due to smaller particle size
FUTURE WORK

• Continue on the optimization of 4 V and 5 V spinel cathodes by cationic and anionic substitutions and surface modifications

• Investigate the electrochemical performances of composites consisting of a high power stabilized spinel and a high energy layered oxide

• Understand the role and effectiveness of various surface coatings in controlling the growth of undesired SEI layer on high voltage (> 4.5 V) cathodes by employing various characterization techniques (XPS, FTIR, Raman, & impedance analysis)

• Understand the influence of crystallite size/shape and defect chemistry on the charge-discharge mechanisms of olivine LiMPO₄ by making use of the novel microwave-solvothermal (MW-ST) and microwave-hydrothermal (MW-HT) methods

• Synthesize solid solutions between various olivine LiMPO₄ (M = Mn, Fe, Co, and Ni) by MW-ST and MW-HT approaches and understand their structure-composition-performance relationships

• Synthesize and characterize new cathode compositions containing polyanions, employing the microwave-assisted processes
SUMMARY

• Stabilized spinel compositions with appropriate cationic and anionic substitutions exhibit superior cyclability compared to the conventional spinel cathode

• Surface modified 5 V spinel cathodes exhibit better cyclability, rate capability, and rate capability retention due to the suppression of SEI layer growth during cycling and lower polarization and charge transfer resistances

• Microwave-assisted solvothermal and hydrothermal approaches give olivine cathodes in 5 – 15 minutes at < 300 °C without requiring any reducing gas atmospheres, offering the potential to lower the manufacturing cost

• Building on the fundamental understanding gained, the future work will continue focusing on developing high performance cathode compositions

• IP developed through the BATT program has led to the founding of a startup (ActaCell) in Austin, TX