Olivines and Substituted Layered Materials

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Overview

Timeline

- ongoing

Barriers

- Barriers addressed
  - Cost
  - Power/Energy Density
  - Cycle Life

Budget

- Total project funding
  - 100% DOE
- FY08 505k
- FY09 525k

Partners/Collaborations

- E. Rodriguez (LANL)
- T. Hollenkamp (CSIRO, Australia)
- S. Patoux (CNRS, France)
- H. Gabrisch (UNO)
- S. Whittingham (SUNY), C. Grey (magnetic measurements)
- E. Cairns (LBNL), A. Deb (U. Michigan) EXAFS, S. Cramer (UC Davis)
Objectives

• To develop low-cost benign cathode materials having electrochemical characteristics (e.g., cycle life, energy and power densities) consistent with the goals of the USABC and/or FreedomCAR.

• Recent and ongoing work:
  – Lower cost of Li[\(\text{Ni}_x\text{Co}_y\text{Mn}_z\)]O_2 electrodes by full or partial replacement of Co with other metals—maintain or improve electrochemical performance
  – Investigate feasibility of using LiMnPO_4 and related compounds in batteries for vehicular applications
  – New materials
Milestones

• FY2008
  – 4.3a Complete characterization of best-performing substituted transition metal oxides. (9/08). Postponed to 12/09 due to large amounts of data.
  – 4.3b Determine feasibility of synthesizing electrochemically active nano-
    LiMnPO$_4$ and/or Li(Mn,Fe)PO$_4$ and other polyanionic compounds for
    use in the BATT program. (9/08). A go decision has been made, with
    plans to reassess during FY2009.
• FY2009
  – Finish characterization of Li[\(Ni_xAl_yCo_{1-y}Mn_z\)]O$_2$ \(x+y+z=1\) compounds
    (3/09) on schedule, decision is to continue investigating these materials
  – Develop spray pyrolysis method for synthesis of LiMnPO$_4$ and other
    polyanionic compounds (6/09). on schedule
Approach

• Cathode materials are synthesized and characterized electrochemically. Relevant physical properties are measured in conjunction with the diagnostics teams. Emphasis is placed on reducing cost and improving electrochemical properties. Some work is directed towards surveying new materials with potential for increased energy density.
  – Li[Ni$_x$Co$_y$Mn$_z$]O$_2$ (started in FY2007)
    • Synthesized Li[Ni$_{1/3}$Co$_{1/3}$+yM$_y$Mn$_{1/3}$]O$_2$; M=Al, Ti, Fe and Li[Ni$_{0.4}$Co$_{0.2}$-yM$_y$Mn$_{0.4}$]O$_2$; M=Al, Fe (FY2007-2008)
    • Electrochemical and preliminary structural characterization (FY2007-2008)
    • In-depth structural and spectroscopic characterization of Li[Ni$_{0.4}$Co$_{0.2}$-yM$_y$Mn$_{0.4}$]O$_2$; M=Al, Fe (FY2008-2009)
  – LiMnPO$_4$ and variants (started in FY2008)
    • Synthesis of nanostructured LiMnPO$_4$/C composites
    • Electrochemical characterization
    • Evaluation of feasibility in batteries for vehicular applications
  – Application of synthesis techniques for LiMnPO$_4$ to new materials (start in latter half of FY2009).
Technical Accomplishments/Progress/Results

nano-LiMnPO₄/C composites and variants

Raman of carbon coating
(R. Kostecki, LBNL)

Mg substitution reduces unit cell volume—relieves strain

Mg substitution raises discharge potential
Summary and Future Work-LiMnPO₄

- Lack of sample homogeneity leads to lower than expected utilization at low rates
- Develop spray pyrolysis method to improve homogeneity (FY 2009)
- Reasonable rates can be achieved, but they come at the expense of energy density (Mg substitution, C coating)
- Go/no go decision on LiMnPO₄ for vehicular applications (FY 2009)
  - Most likely “no go” (LiFePO₄ and oxides are much better)
  - BUT apply synthesis knowledge to materials that don’t work right now
  - Example: LiMnBO₃ 221 mAh/g-no electrochemical activity
  - compare LiFeBO₃ ~3Vvs Li (electroactive at low rates)

Technical Accomplishments/Progress/Results

Li[Ni$_x$Co$_{y-w}$M$_w$Mn$_z$]O$_2$

- FY2007-2008: Li[Ni$_{0.4}$Co$_{0.2-y}$Al$_y$Mn$_{0.4}$]O$_2$ and other systems
- Reduce materials cost by replacing some or all Co

Co electroactive above 4.3V vs Li
Practical capacity not affected by replacing with inactive Al

Particle morphology unaffected by substitution

Solid solutions are formed for 0≤y≤0.2
Electrochemical Results

Li[Ni_{0.4}Co_{0.2-y}Al_{y}Mn_{0.4}]O_2

Al substitution reduces capacity below 4.3V

Higher capacities upon cycling to 4.7V, but increased fade rate

Better cycling with Al substituted compounds

Al substitution raises charge/discharge potentials

Better rate capability with Al-substituted compounds

Best overall results with Li[Ni_{0.4}Co_{0.15}Al_{0.05}Mn_{0.4}]O_2

Goal this year - understand effect of Al on structure and electrochemistry
Cycling profiles of Li/Li$_{[\text{Ni}_{0.4}\text{Co}_{0.2-y}\text{Al}_y\text{Mn}_{0.4}]\text{O}_2}$ cells

Increased polarization at end of charge-overcharge protection
Increased first cycle irreversible capacity to 4.3V, no effect to 4.7V
Characterization of Li[Ni$_{0.4}$Co$_{0.2-y}$Al$_y$Mn$_{0.4}$]O$_2$ conductivity and FTIR

Pressed pellet conductivities
\( \sigma \) decreases as Al content increases
- \( y=0 \): \( 1.1 \times 10^{-5} \) S/cm at 75°C
- \( y=0.05 \): \( 1.2 \times 10^{-6} \) S/cm at 75°C
(compare to LiCoO$_2$: \( 10^{-3} \) S/cm at RT)
activation energies rise with higher Al content—increased ionicity

FTIR: M-O vibration/bending region
3 modes are predicted
M-O stretch shifts to higher \( \text{cm}^{-1} \) as Al content increases
O-M-O bends intensify consistent with changes in unit cell and decreased bond covalency
Combined XRD/Neutron Rietveld Refinements

Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2
Neutron work aided by E. Rodriguez, LANL
### Structural Parameters

Li[Ni$_{0.4}$Co$_{0.2-y}$Al$_{y}$Mn$_{0.4}$]O$_2$

<table>
<thead>
<tr>
<th>Al Content (y)</th>
<th>Unit Cell Parameters</th>
<th>$z_{Ox}$</th>
<th>Unit Cell Volume ($\text{Å}^3$)</th>
<th>$N_{i3a}$</th>
<th>$I$ (LiO$_2$) (Å)</th>
<th>$R_{wp}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>a (Å) 2.87238(2)</td>
<td>c (Å) 14.2688(2)</td>
<td>0.24165(3)</td>
<td>101.954(2)</td>
<td>0.066(1)</td>
<td>2.616(1)</td>
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<td>2.621(1)</td>
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<td>c (Å) 14.2896(3)</td>
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<td>0.074(1)</td>
<td>2.622(1)</td>
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<td>c (Å) 14.2993(2)</td>
<td>0.24159(3)</td>
<td>101.932(2)</td>
<td>0.074(1)</td>
<td>2.624(1)</td>
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- Slight decrease in a lattice parameter
- Slight increase in c lattice parameter
- Slight increase in anti-site mixing
- Increase in LiO$_2$ slab spacing
- Decreased covalency in T.M plane with Al substitution—shortens M-M distances, weakens LiO bonds, increases c and I(LiO$_2$)
Relative Diffusion Coefficients (GITT)

Li/Li[Ni_{0.4}Co_{0.2-y}Al_{y}Mn_{0.4}]O_{2} cells

- Experiments are ONLY to compare diffusion behavior as function of state-of-charge (x) in Li\(_{x}[\text{Ni}_{0.4}\text{Co}_{0.2-y}\text{Al}_{y}\text{Mn}_{0.4}]\text{O}_{2}\)
  - Absolute diffusion coefficients not possible to determine with composite electrodes
  - Data normalized w.r.t. parent material, Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_{2}

- Materials all exhibit similar behavior
  - Decrease in diffusion rates at low x
  - GITT experiments are slow, deintercalation proceeds further than in constant i charging to 4.3V for Al substituted materials
  - In constant i experiments, Al substitution causes discharge to be limited to compositions with fast Li diffusion
Li[Ni$_{0.4}$Co$_{0.15}$Fe$_{0.05}$Mn$_{0.4}$]O$_2$

Fe substitution decreases conductivity, reduces capacity, does not improve rate capability, increases first cycle irreversible capacity, has negative impact on cycling behavior.

<table>
<thead>
<tr>
<th></th>
<th>Ni (3a)</th>
<th>I (LiO$_2$), Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li[Ni$<em>{0.4}$Co$</em>{0.2}$Mn$_{0.4}$]O$_2$</td>
<td>0.066(1)</td>
<td>2.616</td>
</tr>
<tr>
<td>Li[Ni$<em>{0.4}$Co$</em>{0.15}$Fe$<em>{0.05}$Mn$</em>{0.4}$]O$_2$</td>
<td>0.072(1)</td>
<td>2.617</td>
</tr>
</tbody>
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Increase in antisite defects
Li slab dimension unchanged
Li[\text{Ni}_{1/3}\text{Co}_{1/3-y}\text{Al}_y\text{Mn}_{1/3}]\text{O}_2

Solid solutions below about y=1/4

- Al substitution reduces capacity
- Al shifts potentials positive
- Modest improvement in rate capability
  (rate capability of 3x1/3 is better than 442)

<table>
<thead>
<tr>
<th>y</th>
<th>I(\text{LiO}_2), \text{Å}</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>2.59</td>
</tr>
<tr>
<td>1/12</td>
<td>2.66</td>
</tr>
<tr>
<td>1/6</td>
<td>2.65</td>
</tr>
<tr>
<td>1/4</td>
<td>2.64</td>
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</table>
Li[Ni_{1/3}Co_{1/4}M_{1/12}Mn_{1/3}]O_2; M=Al, Ti, Fe

Capacity to 4.7V: Ti>Co>Al>Fe; Capacity to 4.3V: Co≈Ti>Al>Fe
Rate: Ti>Al>Co>Fe; capacity retention: Fe is inferior
Ti^{4+} aliovalent substitution → electroactive Mn^{3+} adds capacity back in

c/3a is a measure of lamellarity:
- contributions from Ni(3a) and other structural effects
- Increase for Ti, Al
- Decrease for Fe

<table>
<thead>
<tr>
<th>M</th>
<th>c/3a</th>
</tr>
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<tbody>
<tr>
<td>Co</td>
<td>1.660</td>
</tr>
<tr>
<td>Ti</td>
<td>1.661</td>
</tr>
<tr>
<td>Al</td>
<td>1.663</td>
</tr>
<tr>
<td>Fe</td>
<td>1.656</td>
</tr>
</tbody>
</table>
Computational work on Al substitution in LiMO$_2$ systems (K. Persson, M. Kocher)

Density of States Calculations

LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$

As Al is substituted for Co...

- The number of occupied states near the Fermi level decreases.
- This decreases the electrical conductivity...
- and decreases the covalency of the bonding
- The pDOS show no Al occupied states, suggesting ionic Al$^{3+}$.
- The Bader analysis reveals an increase in the number of electrons associated with O in LiMn$_{1/3}$Ni$_{1/3}$Al$_{1/3}$O$_2$, relative to LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$.
- Oxygen is becoming more ionic (i.e., closer to O$^{2-}$)
Summary and Future Work

Li[Ni\textsubscript{x}Co\textsubscript{y-w}M\textsubscript{w}Mn\textsubscript{z}]O\textsubscript{2}

- Co content in mixed transition metal oxides can be reduced through judicious substitution (Al, Ti)
  - Substituent need not be electroactive (Fe made things worse!)
  - Changes in electrostatic landscape are influential for structure and diffusivity
    - \(I(\text{LiO}_2)\) is affected by Ni(3a) amount as well as bonding (degree of covalency)
    - It may not always be necessary to minimize anti-site defects below a certain level
    - Theoretical work by K. Persson and M. Kocher corroborates these results
- Many unanswered questions
  - Effect of state-of-charge on conductivity, \(I(\text{LiO}_2)\), does Al migrate?
  - How are metals arranged in the transition metal layer?
  - Effect of synthesis parameters
  - Is low level Ti substitution worth pursuing?
- Plan is to continue work on these materials-goal is to reduce Co as much as possible and to achieve an understanding of how best to do that
- Collaborations planned or underway
  - Magnetic measurements (Whittingham, Grey), computation K. Persson
  - NMR (Cabana, Grey), EXAFS (Cairns, Deb, Cramer)