Performance and Safety of Olivines and Layered Oxides

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Overview

Timeline
• Start date: October 1, 2009 (new project)
• End date: September 31, 2010
• Complete: 30%

Budget
• Total project funding
  - FY10 $300K

Barriers Addressed
• Energy density
• Cycle life
• Safety

Partners
• Collaborations: Grey (Stony Brook), Ceder (MIT), Richardson, Kostecki, Doeff, Cabana (LBNL), Gabrisch (UNO), NCEM, ALS, SSRL
• Project lead: John Newman
Objectives

• Investigate phase transition mechanisms and explore kinetic barriers of high-energy cathode materials.

• Establish direct correlations between crystal structure, composition, morphology, performance, and stability.

• Provide guidelines to design and develop electrode materials with improved energy density, rate capability, and safety, especially with regard to thermal stability.

Milestones

• Report thermal stability and performance evaluation of the modified LiMnPO$_4$.

• Report results on the synthesis of layered oxide crystals.
Approach

• Prepare well-formed crystals of cathode materials with various crystal structures, chemical compositions, sizes, and morphologies.

• Characterize physical properties and investigate solid state chemistry of the crystals using chemical and electroanalytical methods, synchrotron based spectroscopies and spectromicroscopies, x-ray and neutron diffractions, vibrational spectroscopies, scanning calorimetry, and electron microscopic techniques.

• Optimize synthesis and processing conditions, improve performance and safety of the cathode materials based on the structural and mechanistic understandings.
Olivines

- LiMnPO$_4$ has high theoretical energy density but low effective energy density. Delithiated LiMnPO$_4$ has poor chemical and thermal stabilities.

- What makes LiMnPO$_4$ kinetically slow and thermally unstable?
- How do chemical composition, crystal size and morphology, and surface treatment affect performance and safety?
- What can be done to make the olivine phosphates (LiMPO$_4$, M=Mn, Co and Ni) practical high-energy cathodes?

- Prepare pristine and substituted LiMnPO$_4$ with controlled morphologies.
- Investigate the effect of size and morphology on the phase transformation process.
- Investigate the effects of substitution and surface treatment on structure, kinetics and stabilities (physical, chemical and thermal).
- Explore other approaches to producing better-performing LiMPO$_4$. 
Crystal Synthesis

- Single crystals of pristine and substituted LiMnPO$_4$ were prepared by the hydrothermal method.
- Particle size and morphology were controlled by synthesis conditions.
**Improved Kinetics**

**Chemical Delithiation (y=0.5)**

\[ \text{LiMg}_x\text{Mn}_{(1-x)}\text{PO}_4 + y(1-x)\text{NO}_2\text{BF}_4 \rightarrow \]
\[ (1-y)\text{LiMg}_x\text{Mn}_{(1-x)}\text{PO}_4 + y\text{Li}_x\text{Mg}_x\text{Mn}_{(1-x)}\text{PO}_4 + y(1-x)\text{LiBF}_4 \]
\[ E_{\text{NO}_2^+/\text{NO}_2} \approx 5.1 \text{ V vs. Li/Li}^+ \]

- Mg substitution improves delithiation efficiency and phase crystallinity.
- Best performance obtained with 20% Mg substitution.
Improved Kinetics
Chemical Delithiation ($y=2$)

• Mg substitution decreases volume mismatch at the phase boundary.

Internal strain limits the growth of the delithiated domain upon further oxidation.
**Improved Kinetics**

**Electrochemical Studies**

- Mg substitution improves electrochemical charge kinetics.

- Mg substitution raises charge and discharge potentials.

![Graph showing improved kinetics](Image)

![Graph showing dQ/dV vs. Cell potential](Image)
Improved Physical Stability

- Internal strain and large volume mismatch at the phase boundary result in crystal decrepitation when Li is removed.
- Morphological instability contributes to poor phase transition kinetics in LiMnPO$_4$.
- Mg substitution dilutes the Jahn-Teller ion (Mn$^{3+}$) in the structure and reduces volume mismatch.
- Crystals retain physical integrity after delithiation.
Improved Thermal Stability

- Unlike FePO$_4$, delithiated LiMnPO$_4$ decomposes and releases O$_2$ around 150 °C.
- The reaction with the electrolyte produces a large amount of heat similar to that of charged LiCoO$_2$. 
Improved Thermal Stability

\[ 2\text{Li}_x\text{Mg}_x\text{Mn}_{1-x}\text{PO}_4 \rightarrow 2x\text{LiMgPO}_4 + (1-x)\text{Mn}_2\text{P}_2\text{O}_7 + 0.5(1-x)\text{O}_2 \]

\[ 3\text{Li}_x\text{Mg}_x\text{Mn}_{1-x}\text{PO}_4 \rightarrow 3x\text{LiMgPO}_4 + (1-x)\text{Mn}_3(\text{PO}_4)_2 + 0.5(1-x)\text{P}_2\text{O}_5 + 0.75(1-x)\text{O}_2 \]

- Unsubstituted phosphate \((x=0)\) decomposes to \(\text{Mn}_2\text{P}_2\text{O}_7\) and releases 0.25 mole \(\text{O}_2\) per mole phosphate.
- Substituted phosphate \((x=0.5)\) decomposes to \(\text{Mn}_3(\text{PO}_4)_2\) and releases 0.125 mole \(\text{O}_2\).
- Both \(\text{Mn}_2\text{P}_2\text{O}_7\) and \(\text{Mn}_3(\text{PO}_4)_2\) were formed in the samples with \(0<x<0.5\).
Improved Thermal Stability

- Released oxygen and generated heat decrease with the decrease of Mn content in the phosphates.
- Total heat evolved: $136 \pm 3$ kJ per mole of Mn in the phosphates.
Layered Oxides, $\text{Li}_{1+x}M_{1-x}\text{O}_2$ (M = Ni, Mn and Co)

- Layered $\text{Li}_{1+x}M_{1-x}\text{O}_2$ (M = Ni, Mn and Co) has over 200 mAh/g capacity. Structure and ordering scheme key to the performance but poorly understood from the studies on aggregated oxide particles.
- At the single crystallite level, how do the local and long-range orders in the oxides correlate to their performance and safety?
- What is the mechanism for oxygen evolution at high voltages? What causes the irreversible capacity loss in the material?
- Is there phase transformation during delithiation and relithiation? What are the mechanisms?
- What is the optimum composition?
- What is the optimum particle morphology?

- Synthesize $\text{Li}_{1+x}M_{1-x}\text{O}_2$ (M = Ni, Mn and Co) single crystals with controlled morphologies.
- Evaluate performance and investigate the effect of Li stoichiometry, transition metal ratios, delithiation and relithiation processes (both chemical and electrochemical) on local and long-range orders.
- Explore synthesis conditions to produce desired structure and ordering scheme for optimum performance and safety.
Crystal Synthesis

- Single crystals were synthesized by the molten salt method.
- Particle size and morphology can be controlled by synthesis conditions.
Crystal Synthesis

- Plate-shaped crystals of “Li-excess” and “Li-stoichiometric” oxides, $\text{Li}_{1+x}(\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33})_{1-x}\text{O}_2$ (NMC333), were prepared.
- $x = 0.14$ and 0 based on ICP analysis.

“Li-excess” NMC333 ($x=0.14$)  “Li-stoichiometric” NMC333 ($x=0$)
Electron Diffraction
“Li-excess” NMC333 Crystals

Simulated pattern from $P3_112$
(001 ZA)
Electron Diffraction

“Li-excess” NMC333 Crystals

• Strong superlattice reflections suggest the presence of superstructures with $\sqrt{3}a_{\text{hex}} \times \sqrt{3}a_{\text{hex}}$ unit cell.

• Diffraction patterns match the patterns simulated from P3$_1$12 cell.
Electron Diffraction
“Li-stoichiometric” NMC333 Crystals

- Lack of superlattice reflections suggests weak or no superstructure.
- Diffraction patterns match the patterns simulated from R-3m cell.
• For $x=0$, no additional peaks in the range $20 \leq 2\theta \leq 28$. The pattern is indexed with R-3m structure.

• For $x=0.14$, the pattern is indexed with P3$_{1}$12 structure to fit the superstructure peaks in the range $20 \leq 2\theta \leq 28$. 
Chemical Delithiation

“Li-excess” NMC333

\[
\text{Li}_{1+x}(\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33})_{1-x}\text{O}_2 + y\text{NO}_2\text{BF}_4 \rightarrow \text{Li}_{1+x-y}(\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33})_{1-x}\text{O}_2 + y\text{NO}_2 + y\text{LiBF}_4
\]

- Intensity of the superlattice peaks gradually decreased upon delithiation. The peaks completely disappeared at \(y=1\).
- Phase transition from O3 (R-3m) to P3 (R3m) occurred when \(y>1\).
• Upon delithiation, the unit cell shrinks and then stabilizes in the $a$ direction. It expands and then shrinks in the $c$ direction.
• The overall cell volume remains nearly constant up to $y=1$.
• Phase crystallinity decreases with chemical delithiation.
Upon delithiation, crystals lose physical integrity even when the volume change is negligible.

Morphological evolution indicates the loss of mass upon delithiation, possibly as Li$_2$O.
Chemical Delithiation

“Li-excess” NMC333

- $\sqrt{3}a_{\text{hex.}} \times \sqrt{3}a_{\text{hex}}$ super cell reflections disappear when Li is removed from the structure.

- The appearance of new superlattice reflections indicate the change of in-plane ordering in the delithiated crystals.
Chemical Relithiation

“Li-excess” NMC333

- Crystals were delithiated with 0.5 mole of NO$_2$BF$_4$ and then relithiated with 2 mole of LiI.
- Original superlattice reflections reappeared on relithiation, indicating the restore of $\sqrt{3}a_{\text{hex}} \times \sqrt{3}a_{\text{hex}}$ super cell structure.
Chemical Delithiation
"Li-stoichiometric" NMC333

- Phase transition from O3 to P3 occurred at oxidation level of $y=0.75$ instead of 1.
- Cell volume decreased 5.4% at $y=1$. 
Chemical Delithiation

Vibrational Spectroscopies

- FTIR and Raman of fresh crystals: significant difference in local structure due to excess Li.

- FTIR of delithiated crystals: larger shift toward higher frequency in x=0 series. Consistent with the larger decrease in unit cell dimension.
Collaborations

• Tom Richardson (LBNL) – Material Synthesis and Characterization
• Clare Grey, Jordi Cabana (Stony Brook) – NMR Spectroscopy
• Heike Gabrisch (U. New Orleans) – TEM study of iron phosphates
• Gerbrand Ceder (MIT) – Theory on hydrothermal synthesized crystals
• Martin Kunz, Nobumichi Tamura (ALS), Sumohan Misra (SSRL) – *in situ* X-ray diffraction and absorption
• Robert Kostechi (LBNL) – Raman and FTIR Spectroscopy
• John Kerr (LBNL) – TGA and DSC
• Vince Battaglia (LBNL) – ICP
• Marca Doeff (LBNL) – Electrode Fabrication
Future Work

• Olivines:
  – Investigate the effect of size, morphology, surface modifications, other
cation and anion substituents on rate capability and stability of
LiMnPO₄.
  – Investigate phase transformation mechanism and phase stability of
  mixed transition metal olivine crystals (LiMPO₄, M=Fe, Mn, Co and Ni).

• Li₁⁺ₓM₁⁻ₓO₂:
  – Further analyze the chemical delithiated series – Li and O contents,
  metal ratio distribution on the crystals, the change of ordering, and the
  possibility of proton insertion in the structure.
  – Compare the structural change during electrochemical charge and
discharge. Investigate O₂ evolution mechanism.
  – Prepare well-formed oxide crystals with other Li content and metal
  ratios. Investigate the structure and evaluate the performance.
  – Investigate the effect of size and morphology on performance.
Summary

• Delithiated LiMnPO₄ has low thermal stability comparable to the charged LiCoO₂.

• Mg substitution in LiMnPO₄ improves kinetics, physical and thermal stabilities of the phosphate.

• The effect of excess Li on structure and performance of LiNi₀.₃₃Mn₀.₃₃Co₀.₃₃O₂ (NMC333) crystals has been investigated.

• Structure of “Li-excess” NMC333 is well ordered with \( \sqrt{3}a_{\text{hex}} \times \sqrt{3}a_{\text{hex}} \) super cells. In-plane ordering scheme changes upon chemical delithiation and restores upon relithiation. Delithiation causes the crystals to disintegrate even with negligible volume change.

• “Li-stoichiometric” NMC333 lacks the same \( \sqrt{3}a_{\text{hex}} \times \sqrt{3}a_{\text{hex}} \) ordering in the structure. There is a larger decrease in unit cell volume upon delithiation.

• O3 structure transforms to P3 in both samples, but occurs at a much higher oxidation state in the “Li-excess” sample.