Investigation of critical parameters in Li-ion battery electrodes

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ES70_Cabana

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Overview

Timeline

- PI joined BATT and LBNL in FY09
- Project start Sep ‘09
- Project end Aug ‘11
- 80% complete

Barriers

- Barriers addressed
  - Gravimetric and volumetric Energy Density
  - Cycle life
  - Safety

Budget

- Funding FY09: $420k
- Funding FY10: $440k
- Funding FY11: $630k

Partners

- Persson, Doeff, Richardson, Chen, Kostecki, Battaglia (LBNL), Grey (SUNY-SB), Whittingham (SUNY-B)
- A. Mehta, (SSRL, Stanford), M. Casas-Cabanas (Caen, France), M.R. Palacin (ICMAB, Spain), A. Dong (MF, LBNL), M.A. Marcus (ALS, LBNL)
Relevance - Objectives

• To achieve cycle life and energy density targets using high voltage (>4.5 V) electrode materials.
  – Synthesize materials with controlled crystal-chemistry and microstructure
  – Establish chemistry-structure-properties correlations that aid in the design of better materials.
  – Assess origins of in-cycle and cycling inefficiencies.
  – barriers: energy density, cycle life, safety

• To understand impact of materials and electrode design on performance.
  – Develop methods to couple electrode performance and transformations at multiple length scales.
  – barriers: energy density, cycle life
## Milestones

<table>
<thead>
<tr>
<th>Date</th>
<th>Task Description</th>
<th>Status</th>
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<tbody>
<tr>
<td>Mar. 10</td>
<td>Report the cycling performance of LiNi$<em>{1/2}$Mn$</em>{3/2}$O$_4$ made solvothermally.</td>
<td>Completed</td>
</tr>
<tr>
<td>Jul. 10</td>
<td>Choose promising Cu-M-O (M=transition metal, Al, P, Si) phases and test them.</td>
<td>Completed</td>
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<tr>
<td>Sep. 10</td>
<td>Report the characterization of cycled NiO electrodes by NMR, XAS and TEM.</td>
<td>Completed</td>
</tr>
<tr>
<td>Sep. 10</td>
<td>Synthesize Sn-based nanoalloys with controlled microstructure and report their performance as electrodes.</td>
<td>Postponed to FY11</td>
</tr>
<tr>
<td>Mar. 11</td>
<td>Report the thermal analysis of cycled LiNi$<em>{1/2}$Mn$</em>{3/2}$O$_4$ electrodes and the results of annealing using different treatments.</td>
<td>Ongoing</td>
</tr>
<tr>
<td>Sep. 11</td>
<td>Report the analysis of Sn nanoparticles at different stages of cycling.</td>
<td>On schedule</td>
</tr>
<tr>
<td>Sep. 11</td>
<td>Report the electrochemical response of NiO when cycled at high temperatures.</td>
<td>On schedule</td>
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Approach/Strategy

• Understand the correlation between crystal structure, microstructure, composition and electrochemical performance in LiNi$_{1/2}$Mn$_{3/2}$O$_{4}$.
  – Synthesize samples with controlled microstructure, composition, ordering.
  – Study changes in structural order and composition with synthesis conditions using a variety of characterization techniques.
  – Evaluate performance at moderate and high rates. Ultimate goal: 100% utilization at 2C rate, 85% 1$^{\text{st}}$ cycle efficiency and 99.99% steady-state efficiency at C/2 rate.

• Analyze inefficiencies of high voltage LiNi$_{1/2}$Mn$_{3/2}$O$_{4}$.
  – Study existence of irreversibility in the lithium intercalation reaction in high voltage materials and surface layer formation.
  – Understand the effect of surface modifications.

• Use synchrotron radiation to characterize electrode materials at multiple length scales.
  – Spectroscopy to analyze chemical changes at interfaces, surface and bulk of materials.
  – Combination of spectroscopy and imaging to evaluate inhomogeneities at nano as well as macro scale.
Technical accomplishments:

LiNi$_{1/2}$Mn$_{3/2}$O$_4$, Neutron Diffraction

- Rietveld-refined neutron diffraction data.
- Samples synthesized from hydroxide precursors at $500^\circ C \leq T \leq 1000^\circ C$ for 12 h.
Technical accomplishments:

LiNi$_{1/2}$Mn$_{3/2}$O$_4$, Ni-Mn ordering

- Clear **Ni-Mn ordering transition at 700°C**. Diffuse scattering at 600°C and 800°C denotes partial ordering.
- Patterns at $T \neq 700°C$ were refined with disordered cell (Fd-3m). Pattern at $T=700°C$ was refined with ordered supercell (P4$_3$32): detected partial Ni-Mn exchange.
- Consistent with ordering schemes revealed by $^6$Li MAS NMR.
Technical accomplishments:  
LiNi$_{1/2}$Mn$_{3/2}$O$_4$, Chemical composition

- Increase in Mn/Ni ratio upon heating ⇒ increase in Mn$^{3+}$ + unit cell parameter.
- Increase in Mn$^{3+}$ correlates with electrochemical activity around 4.0 V. Washed out profile for OH500C could be due to defective/poorly crystallized particles.
- No evidence for O vacancies found. Mn enriching is due to segregation of Ni in a rocksalt impurity.
Composition by EDS-TEM analysis from ~30 particles.

Rocksalt-type impurity can segregate to the surface of the particles. It contains Mn (not Li_{1-x}Ni_{x}O), probably in +3 state (deduced from XANES).

The process is exacerbated as the calcination temperature is increased.
Technical accomplishments:
LiNi$_{1/2}$Mn$_{3/2}$O$_4$, Impurity vs. performance

- **Li extraction is not possible from rocksalt impurity** ⇒ cripples performance, especially if it accumulates on the surface of spinel particles.
- **Minimization is desirable.** Important implications when annealing is used to increase particle size, which is needed for better performance.
Technical accomplishments:
LiNi$_{1/2}$Mn$_{3/2}$O$_4$, Effect of annealing

Samples synthesized from hydroxide precursors: heated in air at 900°C, 1 h + 12 h at 500 or 700°C.

- No notable changes in particle size/morphology observed (consistent with absence of major coarsening below 800°C, *vid. J. Cabana – 2010 AMR*.)
- Annealing at 700°C: mechanism of **ordered spinel**. Smaller Mn$^{3+}$ signal.
- Annealing at 500°C: mechanism of **disordered spinel**. Similar Mn$^{3+}$ signal.
- Decouple microstructure from crystal-chemistry: higher capacity/efficiencies at 900°C (under study).
Technical accomplishments:
LiNi$_{1/2}$Mn$_{3/2}$O$_4$, Full Li-ion cells

• **Unacceptable capacity loss** of 75% in Li-ion cell after 100 cycles.
• The low coulombic efficiencies observed (~99.5%) even upon extended cycling likely produce losses in the negative electrode that cripple the lifetime of the battery.
• Coulombic efficiency appears to be a **pressing issue**.
Technical accomplishments:

LiNi$_{1/2}$Mn$_{3/2}$O$_4$, Electrochemical reversibility

- Synchrotron XRD patterns (referenced to Cu Kα) collected during 2 cycles of Li/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ at 900°C.
- Multiple processes are observed during lithium extraction/reinsertion.
Technical accomplishments:
LiNi$_{1/2}$Mn$_{3/2}$O$_4$, Electrochemical reversibility (II)

- Changes in cell parameter (~2% volume change) and phase distribution are largely reversible even after 2 cycles.
Technical accomplishments:
LiNi$_{1/2}$Mn$_{3/2}$O$_4$, Crystal-chemical inefficiency?

**ΔQ$_{irrev}$ is not related** to crystallographic or chemical inefficiencies: structure and Ni$^{2+}$ content recovered after 1 cycle.

- ~130 mAh/g discharge capacity ⇒ ~88% theoretical capacity. Is Li completely removed upon charge?
Technical accomplishments:
\( \mu \text{-XAS} \) as a technique to study electrode inhomogeneities

- Small (down to 1x1 \( \mu \text{m} \)) spot size on the sample allows collection of multiple X-ray absorption spectra with spatial resolution \( \Rightarrow \) good for complex inhomogeneous samples.
- Three detectors available: total electron yield (probes \(~10 \text{ nm}\)), fluorescence yield (<1 \( \mu \text{m} \)), transmission (through sample).
Technical accomplishments:

μ-XAS, NiO as proof of concept

- NiO + 2Li ⇄ Ni + Li$_2$O ⇒ reversible conversion reaction that leads to high storage capacity.
- Ni species involved are easily resolvable ⇒ good model system to test the efficacy of the technique.
Technical accomplishments:
\(\mu\)-XAS, Identification of homogeneities

- Inhomogeneities in the phase transformation identified at mm scale. Aggravated as rate is increased ⇒ risk of capacity losses, overdischarge, localized heat.
- Methodology can be extended to other systems (including those showing amorphous phases) → generate input for electrode design.
Collaboration and Coordination with Other Institutions

• Within BATT:
  – Dr. V. Battaglia (LBNL): testing of spinel electrodes in Li-ion cells.
  – Dr. M. M. Doeff (LBNL): XAS and XRD of electrode materials.
  – Dr. R. Kostecki (LBNL): understanding surface reactivity in cathode materials.
  – Prof. C.P. Grey (SUNY-SB): MAS-NMR of electrode materials.
  – Prof. Whittingham (SUNY-Binghamton): magnetic susceptibility of spinels.

• Outside BATT:
  – Dr. M. Casas-Cabanas (ENSICaen, France): neutron diffraction and electron microscopy of electrode materials.
  – Dr. A. Mehta (SSRL): XAS and XRD of electrode materials.
  – Dr. M.A. Marcus (LBNL): $\mu$-XAS of electrode materials.
  – Dr. A. Dong (LBNL): synthesis of materials with controlled nanostructures.
Future Work

• Continue to understand parameters that control performance of LiNi$_{1/2}$Mn$_{3/2}$O$_4$ (within BATT Focus Group):
  – Continue using NMR (with Grey group) as core technique for analysis of ordering.
  – Collaboration has been established with Whittingham group to analyze Mn$^{3+}$ content using magnetic susceptibility.
  – Establish sensitivity of XANES to small amounts of Mn$^{3+}$.
  – Analyze role of crystal-chemistry on electrode performance in samples where microstructure effects are decoupled.

• Continue to investigate sources of coulombic inefficiency in LiNi$_{1/2}$Mn$_{3/2}$O$_4$ (within BATT Focus Group):
  – Samples at full charge: Is there Li$^+$ left? Is there Ni$^{4+}$? Are holes created into O 2p bands? What is the composition of electrolyte decomposition layers on surface of electrode? Use combination of soft and hard XAS.
  – Analyze the effect of simply adding inorganic additives to electrode on coulombic efficiency. Compare to traditional coatings.

• Extend $\mu$-XAS method to commercially relevant systems (alloys, intercalation).
Summary

- \( \text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4 \) crystallizes in a variety of patterns with different Ni/Mn ordering. Ni/Mn mixing can be found in samples showing unit cell superstructures.
- All samples made in this study show Mn over-stoichiometry, but no evidence of \( \text{O}^{2-} \) vacancies. \( \text{Mn}^{3+} \) is due to a preferential segregation of Ni in a rock salt impurity, which also contains Mn.
- Amounts of impurity and \( \text{Mn}^{3+} \) increase with synthesis temperature. Impurity is detrimental to performance; needs to be minimized during material preparation.
- Annealing of samples prepared at high temperature leads to decoupling of microstructure from ordering/composition.
- Poor performance of \( \text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4 \) in Li-ion cell, most likely due to coulombic inefficiencies. These are not related to crystal-chemical irreversibilities.
- Developed a \( \mu \)-XAS method to evaluate charge distribution with high spatial resolution. Analyzed discharge inefficiency dependence on rate for conversion model system.