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Structural Investigations of oxide materials for PHEV applications

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Daniel P. Abraham

M. Balasubramanian, S.-H. Kang, M. Furczon

Argonne National Laboratory

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Vehicle Technologies Program

Overview

Timeline

- Start date: FY09 (new project)
- End date: On-going
- Percent complete:

  - project on-going

Budget

- Total project funding

  - 100% DOE
- FY09: $200K

Barriers

Barriers

- Performance
- Calendar/Cycle Life
- Abuse tolerance

Targets

- Composition/Structure/Performance Correlations

Partners

- University of Illinois at Urbana-Champaign
- University of Puerto-Rico
- Linköping University, Sweden

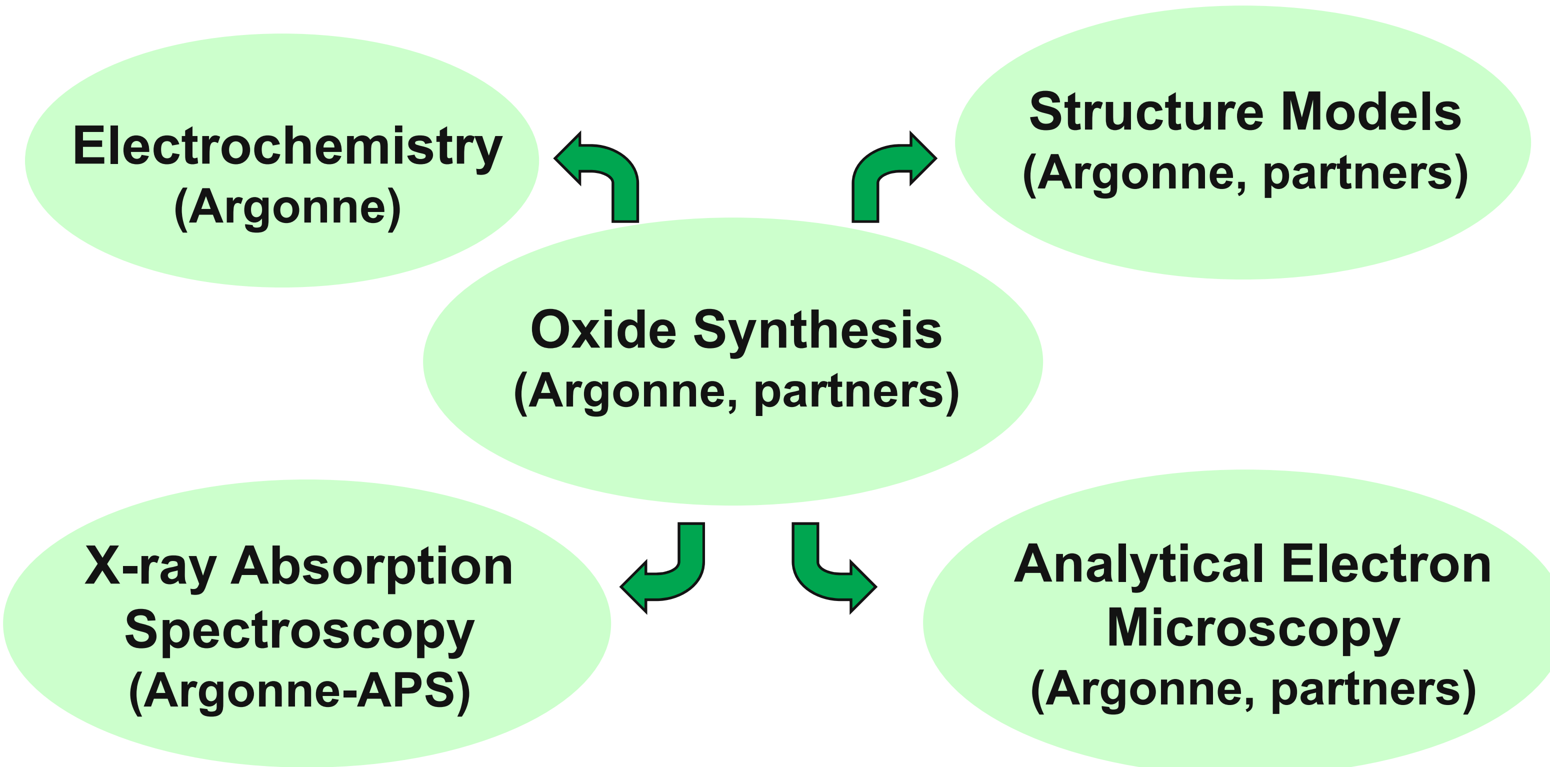
Objectives

The structure and structural rearrangements in Mn-based oxides, which show anomalously high-capacities when cycled at high-voltages, have a significant effect on cell performance, calendar-life, and safety.

- Our goal is to obtain a detailed structural understanding of the $Li_{1+a}(Mn_xNi_yM'_z)O_2$ family of materials. Our experiments are designed to answer some of the following questions:
  - ✓ What are the local atomic arrangements in the as-prepared oxides and how are these arrangements influenced by composition?
  - ✓ What are the charge compensation mechanisms during oxide delithiation & lithiation, i.e., during electrochemical cycling?
  - ✓ What phase transformations result on cycling/aging? How does this affect the oxide's capacity and rate performance?
  - ✓ Do all these oxides lose oxygen during the first high-voltage charge cycle? Is this oxygen loss random?

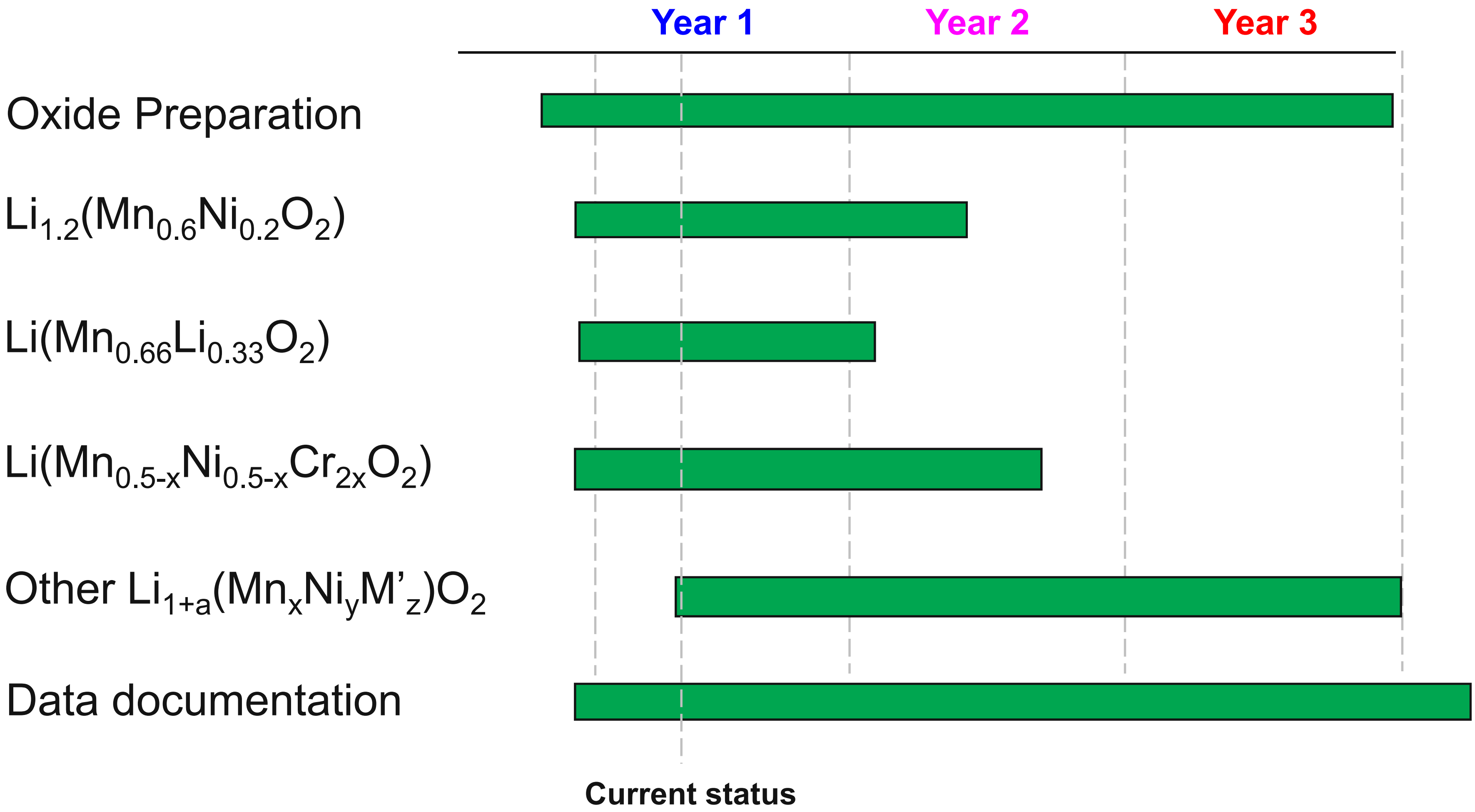
Approach

- **Multi-institution effort to synthesize, characterize, and model oxide structures. These efforts include development of new diagnostic tools and protocols for structure examination.**



- Suggest material compositions to overcome technical barriers

Milestones

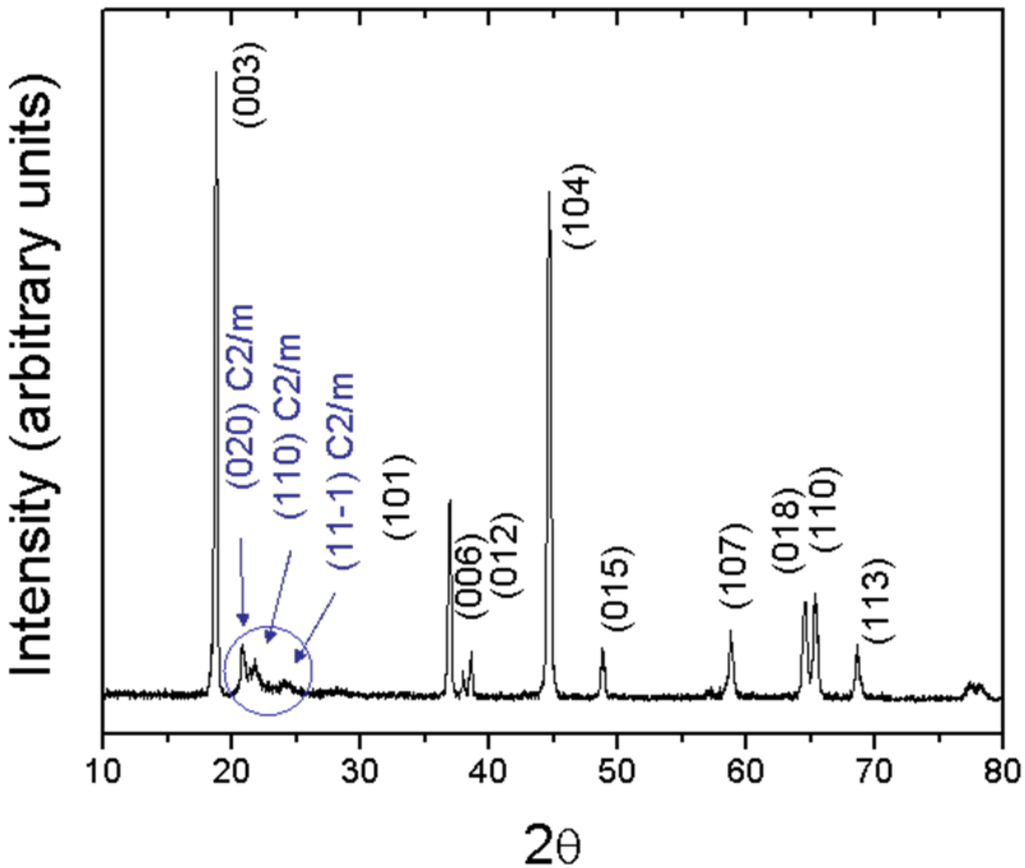


- The “other” compositions are being selected based on their relevance to answering the questions listed earlier

Technical Accomplishments

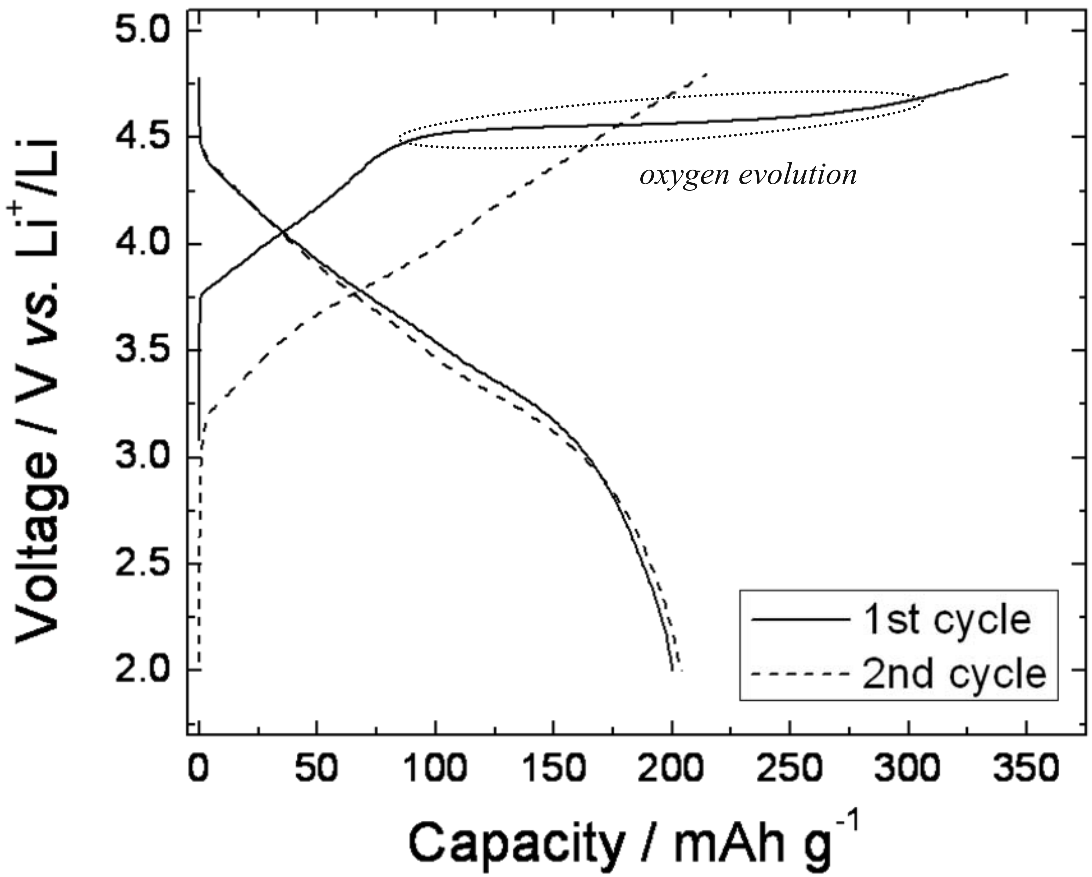
- Conducted experiments on $Li(Li_{0.2}Mn_{0.6}Ni_{0.2})O_2$ samples
  - In addition to occupying the Li-layers, Li atoms occupy the TM-layers in a ordered manner following a Li-TM-TM-Li sequence.
  - A probe of the local Mn-environment indicates a dearth of TM atoms, which suggests that Li atoms preferentially surround (i.e., order around) Mn forming $LiMn_6$-like areas.
  - There is no evidence of long-range ordering or phase segregation
  - Structural changes result from charging above 4.5 V; these changes and their effect on performance are currently being examined.
- Conducted experiments on $Li(Mn_{0.5-x}Ni_{0.5-x}Cr_{2x})O_2$ samples
  - Partial exchange of Li and Ni among the sites (i.e., cation mixing) decreases with increasing Cr content.
  - As-prepared samples contain Ni^{+2}, Cr^{+3}, and Mn^{+4}. Charge compensation on delithiation is accomplished by simultaneous oxidation of Ni^{+2} and Cr^{+3}.
- Initiated experiments on Li_2MnO_3 and $Li_{1.2}Mn_{0.4}Co_{0.4}O_2$ samples
  - Performance measurements and structural characterization in progress

X-ray diffraction data – $Li(Li_{0.2}Mn_{0.6}Ni_{0.2})O_2$



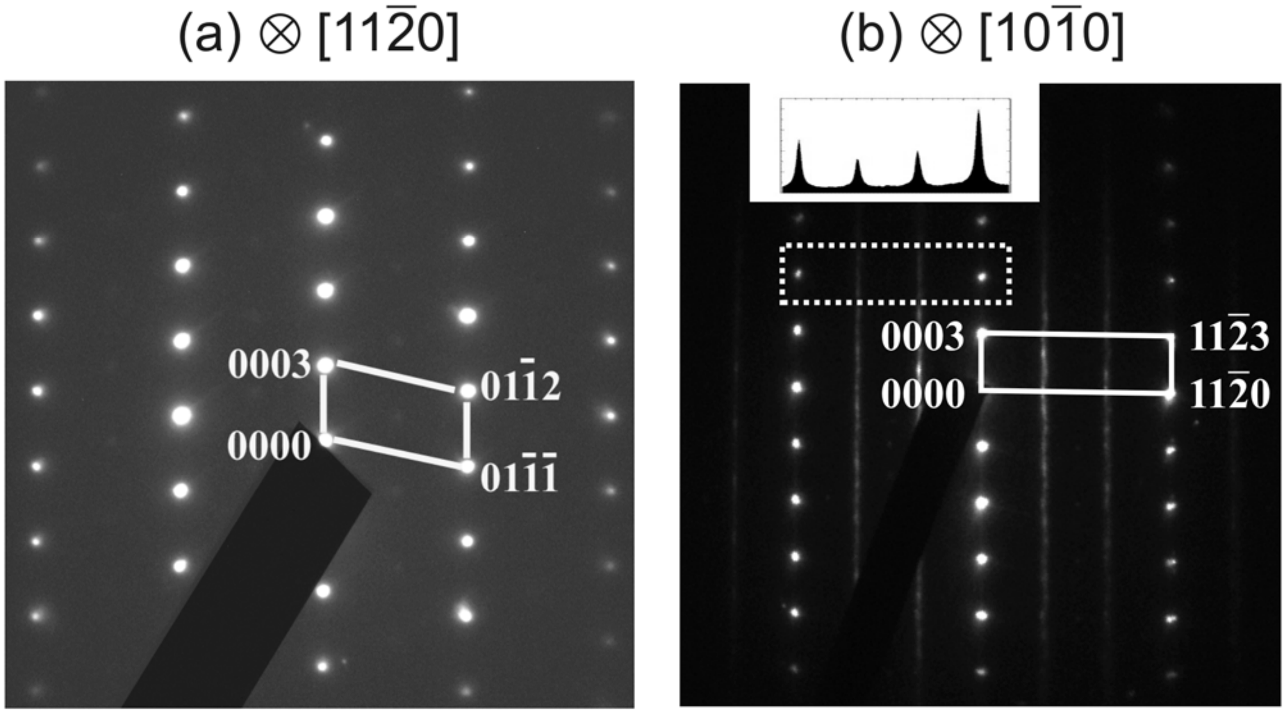
X-ray Diffraction powder pattern of as-synthesized $Li(Li_{0.2}Ni_{0.2}Mn_{0.6})O_2$. The pattern is indexed with respect to the R-3m structure, with lattice constants a = 0.2854 nm and c = 1.4225 nm. Additional weaker peaks in the range 20 ≤ 2θ ≤ 25 suggest Li-ordering in TM-planes.

Electrochemical Cycling – $Li(Li_{0.2}Mn_{0.6}Ni_{0.2})O_2$



Charge-discharge cycling data from a $Li(Li_{0.2}Ni_{0.2}Mn_{0.6})O_2$//Li cell showing a ~4.5V plateau during the first charge. Note that the plateau is not seen during the second charge. The plateau is apparently associated with oxygen evolution from the oxide.

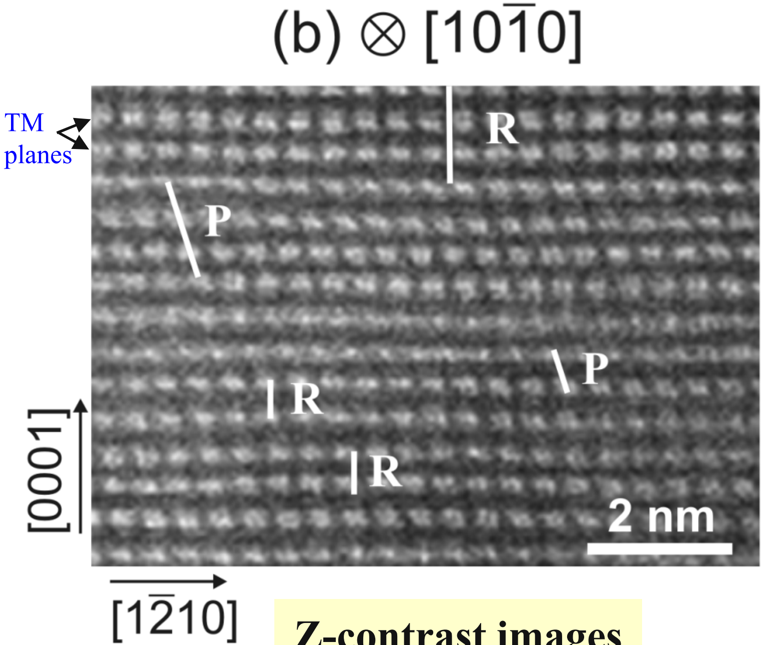
Electron Diffraction – $Li(Li_{0.2}Mn_{0.6}Ni_{0.2})O_2$



The [11-20] zone axis pattern shows only the expected reflections from the R-3m structure, while the [10-10] zone axis pattern shows additional streaks at the n/3 (11-20) positions, which suggests ordering in the TM-planes. The presence of streaks (*not individual spots*) indicates a small ordered-domain size and a lack of domain-periodicity along the c axis (*the direction of the streak*).

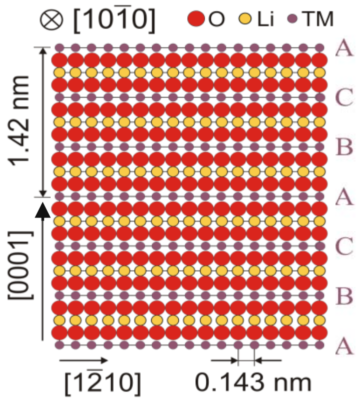
Electron Microscopy - $Li(Li_{0.2}Mn_{0.6}Ni_{0.2})O_2$

Sample volume probed for information on local structure and composition variations

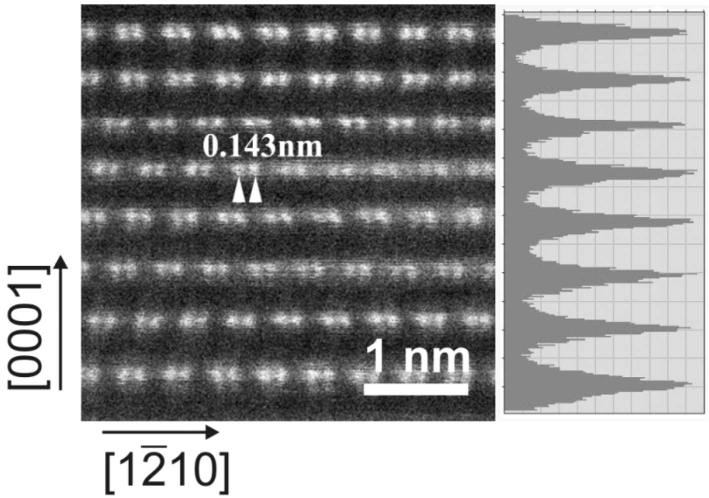


The transition metal planes follow several stacking sequences, bounded by stacking faults along the c-axis. Meshes with rectangular (R) and parallelogram (P) periodicity are observed.

Z-contrast images



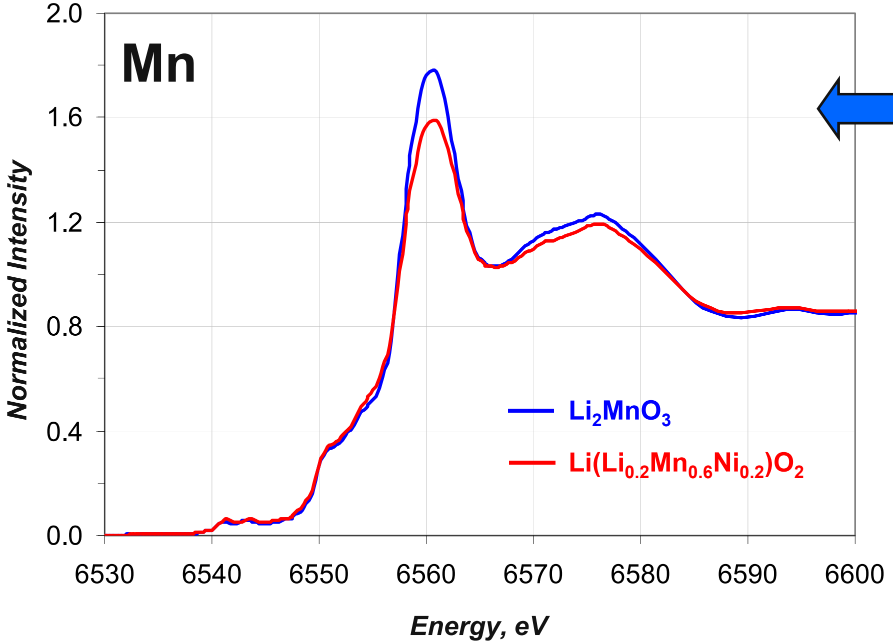
Schematic of ideal layered structure



Higher-magnification image showing Li-ordering in TM-planes. In addition to occupying the Li-layers, the Li atoms occupy the TM-layers following a Li-TM-TM-Li sequence. A plot of the intensity (horizontal axis), integrated along the [1-210] direction, indicates that the average TM-plane composition is similar along the c-axis, i.e., there is no evidence of long-range ordering or phase segregation.

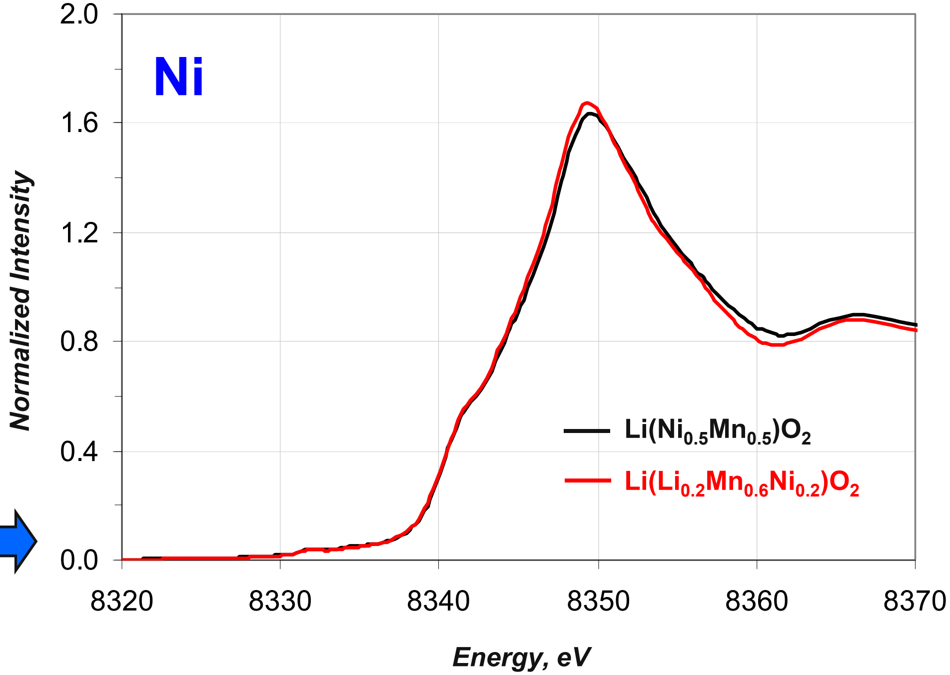
X-ray Absorption Spectroscopy - $Li(Li_{0.2}Mn_{0.6}Ni_{0.2})O_2$

XANES data provides information on transition metal (TM) oxidation states



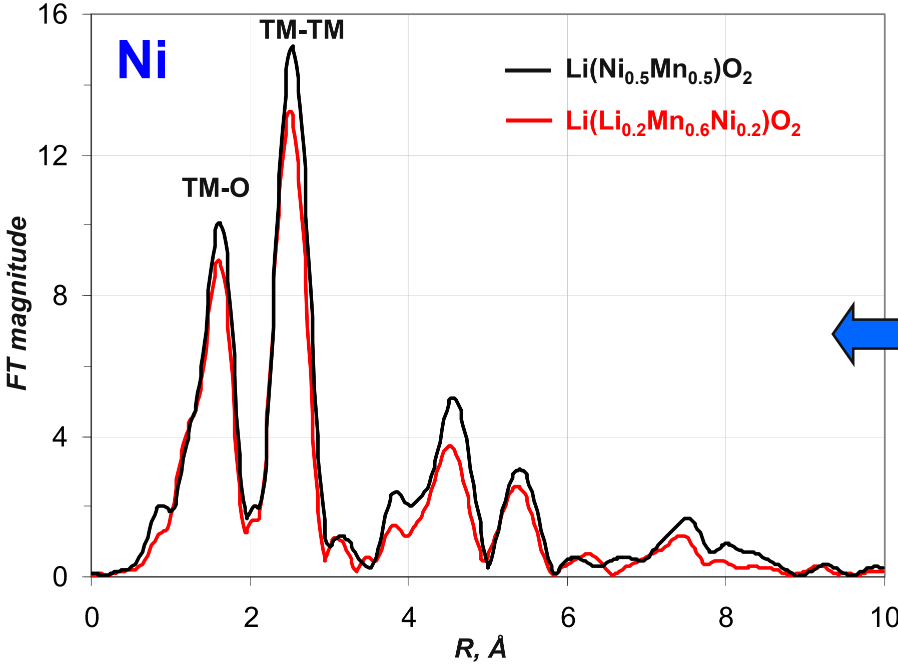
The similarity of the $Li(Li_{0.2}Mn_{0.6}Ni_{0.2})O_2$ XANES spectrum with that of the Li_2MnO_3 spectrum indicates that Mn^{+4} is present in the sample.

The similarity of the $Li(Li_{0.2}Mn_{0.6}Ni_{0.2})O_2$ XANES spectrum with that of the $Li(Ni_{0.5}Mn_{0.5})O_2$ spectrum indicates that Ni^{+2} is present in the sample.



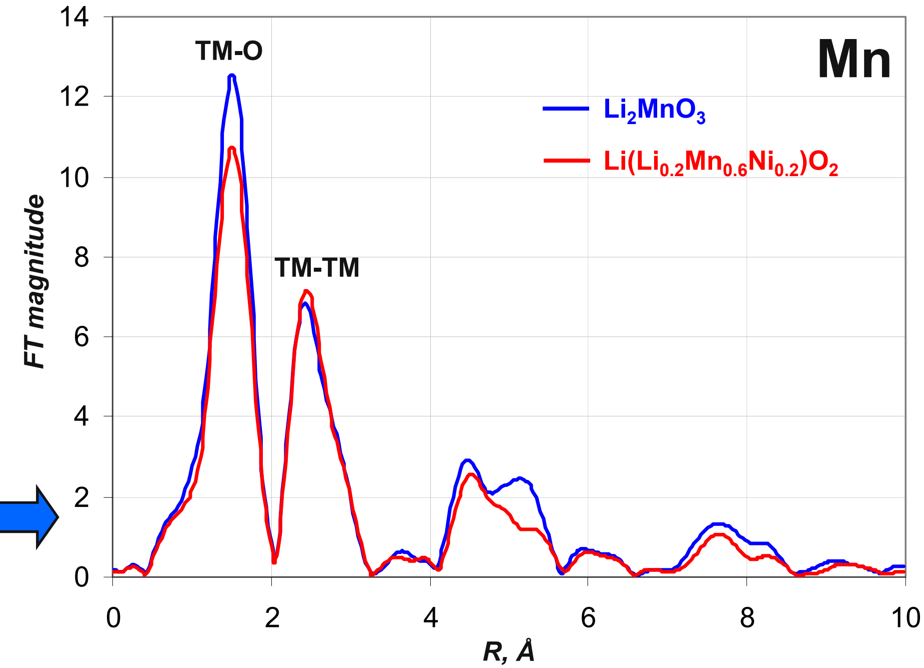
X-ray Absorption Spectroscopy - $Li(Li_{0.2}Mn_{0.6}Ni_{0.2})O_2$

EXAFS data provides information on environment around TM atoms

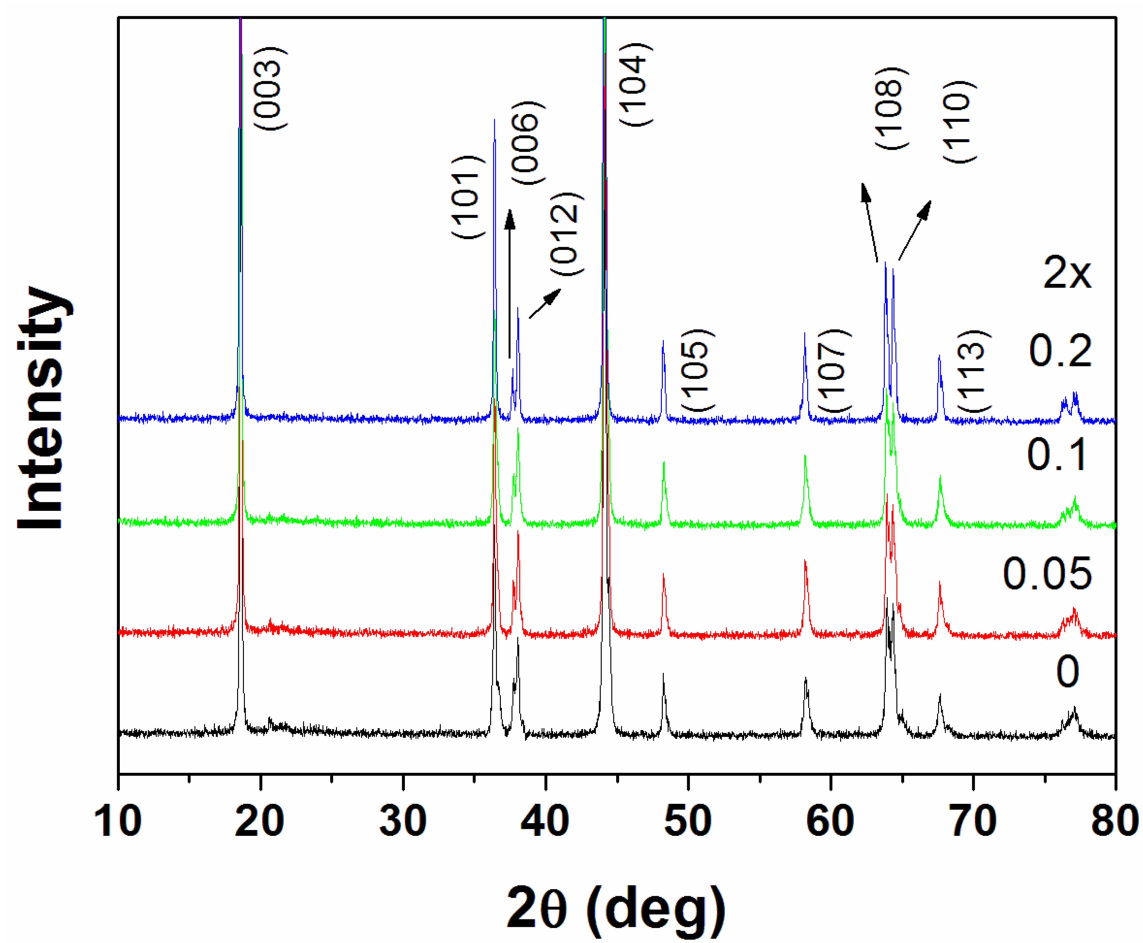


Fourier Transforms of both $Li(Li_{0.2}Mn_{0.6}Ni_{0.2})O_2$ and $Li(Ni_{0.5}Mn_{0.5})O_2$ spectra indicate that the Ni atoms are surrounded by transition metal atoms, i.e., there is no indication of Li-ordering around Ni

Fourier Transform (FT) of $Li(Li_{0.2}Mn_{0.6}Ni_{0.2})O_2$ and Li_2MnO_3 spectra are similar, at least up to ~4 Å. These data suggest very local ordering of Li around Mn, resulting in $LiMn_6$-like areas, in the TM planes

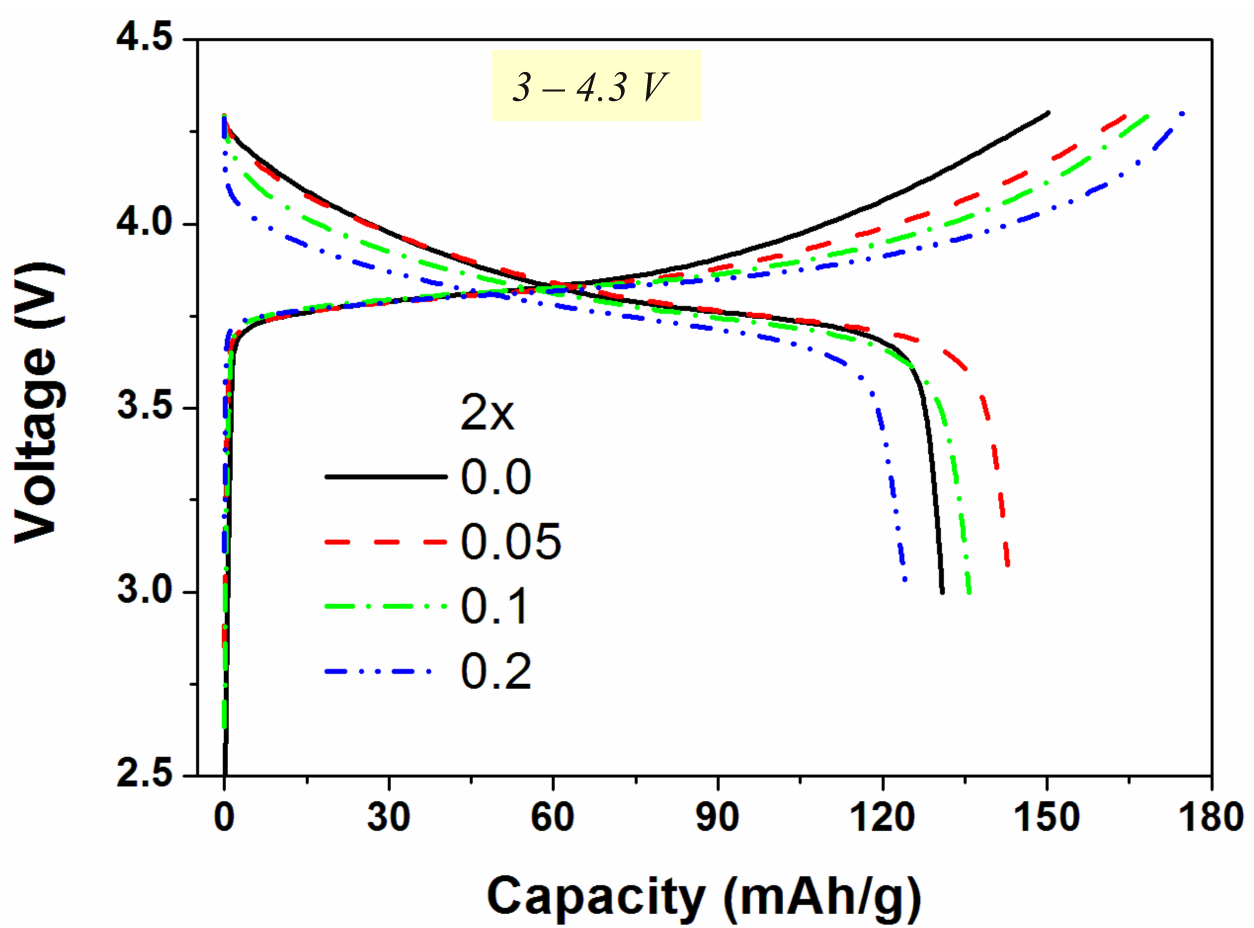


X-ray Diffraction - $Li(Mn_{0.5-x}Ni_{0.5-x}Cr_{2x})O_2$



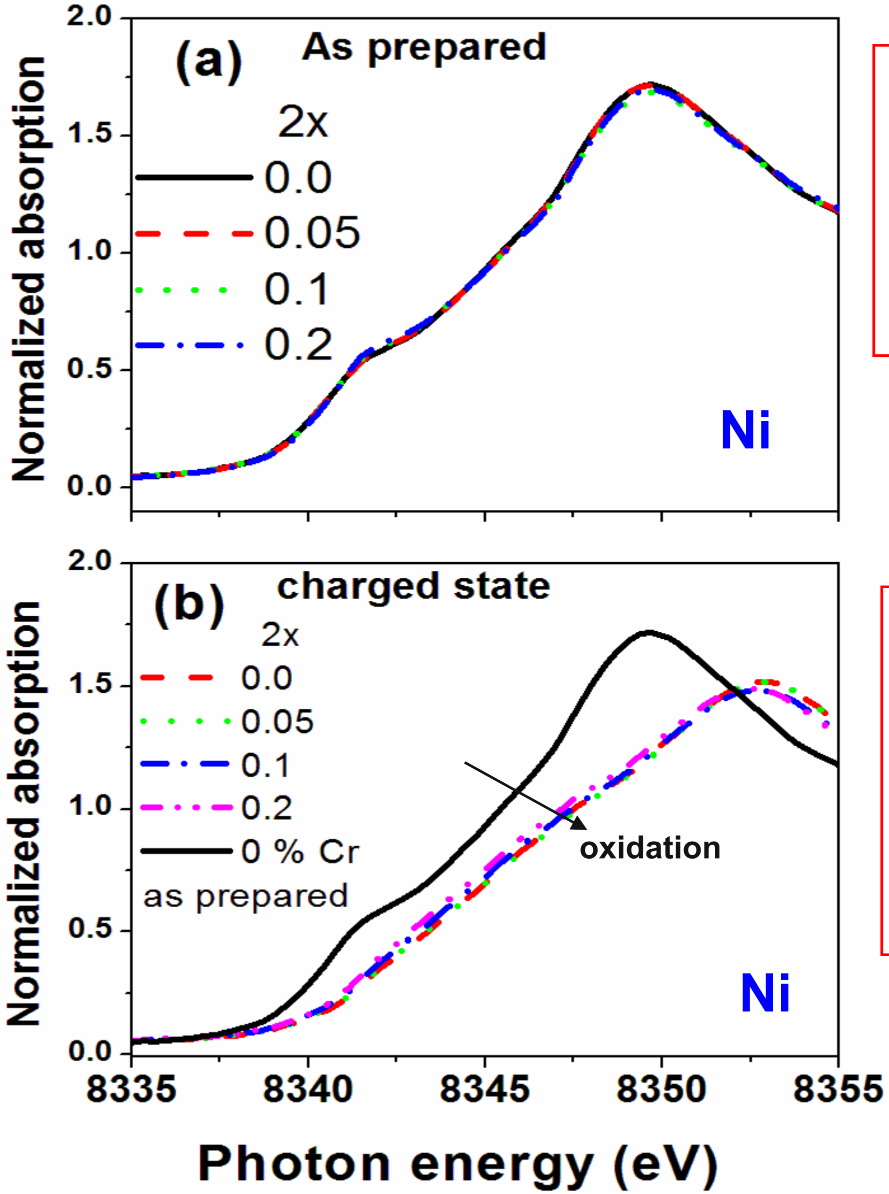
XRD peaks could be indexed based on the R-3m space group (layered oxide). Rietveld refinement of the various patterns indicated that the partial exchange of Li and Ni among the sites (cation mixing) decreases with increasing Cr content.

Electrochemical Cycling - $Li(Mn_{0.5-x}Ni_{0.5-x}Cr_{2x})O_2$



Charge capacity increased with increasing Cr content. However, the discharge capacity is highest for the 2x = 0.05 composition, and decreases at higher Cr contents; the 2x = 0.2 composition shows the lowest discharge capacity.

X-ray absorption spectroscopy - $Li(Mn_{0.5-x}Ni_{0.5-x}Cr_{2x})O_2$



The Ni-XANES data show that Ni^{+2} is present in the as-prepared samples. Cr- and Mn-XANES data (*not shown*) indicate Cr^{+3} and Mn^{+4} in these samples; some Cr^{+6} is also seen in the 2x=0.2 sample.

On electrochemical delithiation *(~145 mAh/g capacity*), charge compensation in the oxide structure is accomplished by the simultaneous oxidation of Ni^{+2} and Cr^{+3} ions, while the oxidation state of the Mn ions remains unchanged.

Future Work/Work in Progress

- Structure investigation of Li_2MnO_3
  - ✓ Analytical electron microscopy experiments in progress
  - ✓ Regions with and without "defects" are being analyzed

- Structural examination of $Li(Mn_{0.5-x}Ni_{0.5-x}Cr_{2x}O_2)$ charged beyond the oxygen evolution regime (>4.5 V)
  - ✓ Electrochemistry and X-ray absorption experiments
  - ✓ Initial data show significant structural rearrangements that affect oxide performance

- Studies on $Li_{1.2}Mn_{0.4}Co_{0.4}O_2$ and $Li_{1.2}Mn_{0.4}Cr_{0.4}O_2$
  - ✓ Initial data show that structure and electrochemical performance of Co- and Cr- bearing oxides are very different from those of Ni-bearing oxides

Summary

- Some of the Mn-based layered oxide materials being developed for PHEV applications show anomalously high capacities when cycled between 2.5 and 5V. However, the structural rearrangement in the oxide during this high voltage cycling has been the subject of much speculation, and needs to be better understood in order to improve oxide performance, calendar life, and safety characteristics.
- Our approach is to synthesize oxides, examine their electrochemical performance, and investigate their structures using X-ray absorption spectroscopy (XAS) and Analytical Electron Microscopy (AEM). The XAS studies provide information on oxidation states of, and coordination around, the transition metal elements. The AEM studies provide information on local (< 2 nm) structure variations and composition variations.
- Our initial studies on $Li(Li_{0.2}Ni_{0.2}Mn_{0.6})O_2$ show that Li atoms are ordered both in, and normal, to the transition metal planes in the as-synthesized material. Studies on cycled electrodes indicate loss of lithium ordering in the TM planes after high-voltage cycling (> 4.5V).
- We are also examining the structures of other oxides including Li_2MnO_3, $Li(Mn_{0.5-x}Ni_{0.5-x}Cr_{2x}O_2)$ ($0 \le x \le 0.2$), $Li_{1.2}Mn_{0.4}Co_{0.4}O_2$ and $Li_{1.2}Mn_{0.4}Cr_{0.4}O_2$ to answer the questions listed in our objectives.