X-ray Absorption Spectroscopy (XAS) Characterization of 5 V Li[Co$_x$Ni$_{0.5-x}$Mn$_{1.5}$]O$_4$ (x=0, 0.1, 0.2, 0.4, and 0.5) Spinel Cathodes for Lithium Batteries

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Introduction

Higher-voltage batteries coupled with multi-electron transfer reactions can yield large amounts of energy storage per mole of battery material, and current research is aimed at exploring the electrochemistry and structures of such electroactive materials.

In the Li[Ni$_{0.5}$Mn$_{1.5}$]O$_4$ spinel electrode, which provides approximately 4.7 V against metallic lithium, the nickel and manganese ions are formally divalent and tetravalent respectively. Analogous to the charge-compensation mechanism in the novel layered Li[Ni$^{II}_{0.5}$Mn$^{IV}_{0.5}$]O$_2$ electrode [1], a Ni(II/IV) two-electron redox couple also occurs on cycling the spinel electrode (between 5.0 and 3.7 V) during which the Mn(IV) remains electrochemically inert.

Results and Discussion

In this work, a series of Co-substituted spinel compounds Li[Co$_x$Ni$_{0.5-x}$Mn$_{1.5}$]O$_4$ (x=0, 0.1, 0.2, 0.4, and 0.5) were synthesized by solution-precipitation methods and characterized. Rietveld profile refinements of powder XRD patterns (laboratory X-ray) for the cubic, cation-ordered spinels (space group P4$_3$32) were used to calculate the lattice parameter, a, and non-lithium (Ni, Co) occupancy of the 8c tetrahedral site. The lattice parameter decreases linearly with the amount of substituted Co in the spinel structure, consistent with solid-solution behavior and the direct substitution of the slightly smaller Co(II) ions for Ni(II) ions. Figure 1 shows the spinel structure and Figure 2 highlights the monotonic decrease in lattice parameter as a function of Co.
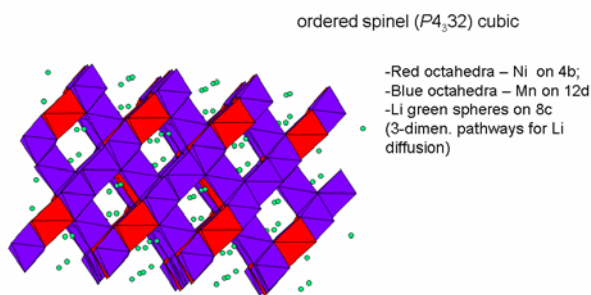

Figure 1. Cubic spinel structure of Li[Co$_x$Ni$_{0.5-x}$Mn$_{1.5}$]O$_4$ (x=0, 0.1, 0.2, 0.4, and 0.5) materials.

A solid-solution series exists between end members Ni and Co in Li[(Ni$_{0.5-x}$Co$_x$)Mn$_{1.5}$]O$_4$ (0≤x≤0.5). This result taken from XRD powder data suggests that the structural mechanism behind the shrinkage with greater Co x substituted amount is because Co^{3+} to Ni^{2+} size difference (Δ 0.285 Å) is greater than Mn^{3+} to Mn^{4+} (Δ 0.115 Å) change. Oxidation states of the various compounds were analyzed by XANES at the APS and the MRCAT (Sector 10).
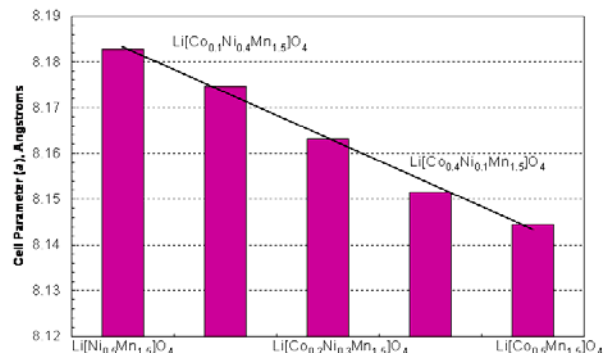

Figure 2. Change in lattice parameter (XRD) from Li[Co$_x$Ni$_{0.5-x}$Mn$_{1.5}$]O$_4$ (x=0, 0.1, 0.2, 0.4, and 0.5) materials.

The Ni, Co and Mn K-edge XANES data were collected on as-prepared powders (ex situ) mounted in holes with boron nitride (BN) as diluent on a multi-sample plate holder. Data collection and experimental details followed previous procedures [1]. The XANES data for the Ni, Mn and Co are shown in Fig. 3, 4 and 5 respectively. For x=0.1, the cobalt ions are divalent, the Mn ions tetravalent, and Ni ions divalent. For higher values of x, charge-transfer to Mn occurs, creating Mn(III) with Co(III), while Ni(II) persists.

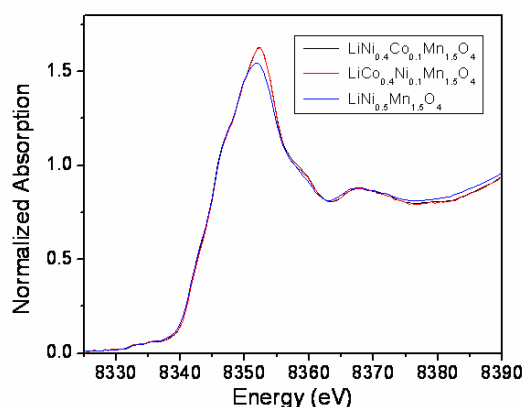The Ni K-edge data in Fig. 3 matches a Ni(II)O standard quite well within the x=0, 0.1 and 0.4 series.

Figure 3. Ni K-edge XANES data.

For the Mn metal center in the material, the Mn^{4+} moves towards Mn^{3+} as x increases (Fig. 4) from x=0 to 0.5. Also a ~0.9 eV shift occurs in the series. This result confirms a charge transfer from the Co center to the Mn center as the content of Co increases.
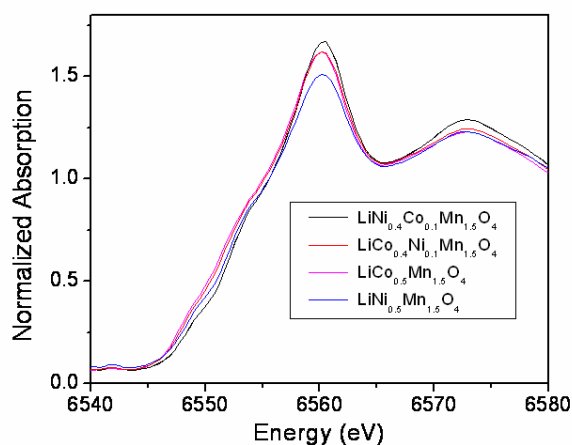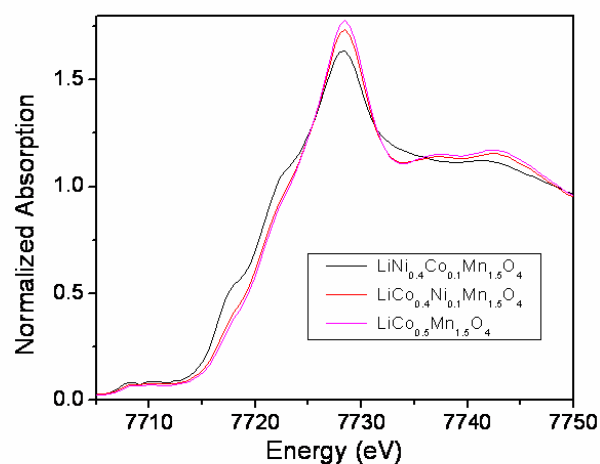
Figure 4. Mn K-edge XANES data.

Figure 5. Co K-edge XANES data.

Predominantly Co^{3+} was found in x=0.5 sample, and moves towards Co^{2+} standard in x=0.1. The edge position for x=0.1 was equivalent to a Co_3O_4 standard where the average oxidation state is 2.67. Further, a unique EXAFS pattern was observed for $Li[(Ni_{0.4}Co_{0.1})Mn_{1.5}]O_4$, which indicated a short-range ordered structure was present for this composition. Interestingly, this composition (x= 0.1) also provides the best electrochemical cycling performance in lithium batteries as shown in Fig. 6, where the capacity and capacity fade are shown as a function of cycle number.
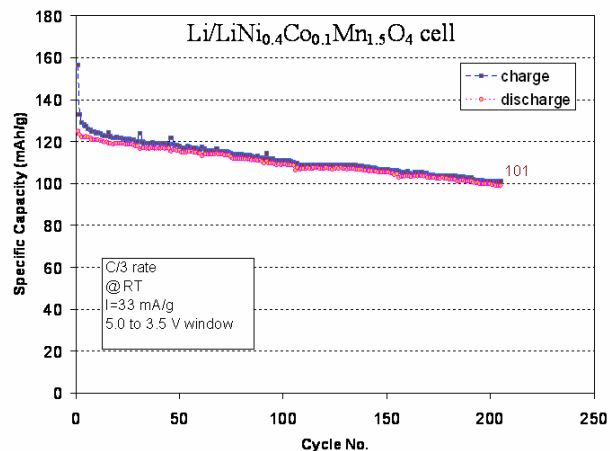

Figure 6. Cycling performance of $Li[(Ni_{0.4}Co_{0.1})Mn_{1.5}]O_4$ in lithium coin cell.

Conclusions

A series of spinels were synthesized with compositions $Li[(Ni_{0.5-x}Co_x)Mn_{1.5}]O_4$ ($0\leq x\leq 0.5$). Superior cycling resulted for the x=0.1 composition. The XANES results shows more Co^{2+}, Mn^{4+} and Ni^{2+} character and greater short-range ordering for x=0.1.

The charge-transfer interaction along the 12d octahedra sites occurs between Mn^{4+} and Co^{2+}, to form Mn^{3+} and Co^{3+} in the cubic $P4_332$ spinel structure, while the Ni^{2+} was unaffected.

References

1. [1] C. S. Johnson, J.-S. Kim, A. J. Kropf, A. J. Kahaian, J. T. Vaughey, L. Fransson, K. Edstrom, and M. M. Thackeray, Chemistry of Materials, **15**, 2313-2322 (2003).