

In Situ X-ray Absorption Studies of Cathode Materials for Rechargeable Lithium-Ion Batteries

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Lithium-ion batteries with high energy and power density are needed for a variety of new existing technologies. The materials that are used in the cathode and anodes of these batteries have crystal structures that can accommodate and release lithium over a fairly large composition range. Over 95% of the present day commercial lithium-ion batteries use LiCoO_2 cathode. Due to the high cost of cobalt, there is considerable interest in developing cheaper alternatives. Knowledge of the redox chemistry and changes in the structure during electrochemical cycling is of paramount importance in designing new cathode materials with superior properties. We have explored the changes in the atomic and electronic structure of cathode materials using X-ray Absorption Spectroscopy (XAS) under *in situ* conditions. The element specific nature of the XAS technique and its sensitivity to the local chemical environment make it an ideal tool to study this class of materials. In this presentation our results on nickel and manganese-based cathode materials will be discussed in some detail.

We have investigated the evolution of the local electronic and atomic structure of $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ and $\text{Li}_{1-x}\text{Ni}_{0.908}\text{Co}_{0.085}\text{Ga}_{0.003}\text{O}_2$ cathode material during electrochemical delithiation. The x-ray absorption near edge spectra (XANES) shows that delithiation of $\text{Li}_{1-x}\text{Ni}_{0.85}\text{Co}_{0.15}\text{O}_2$ leads to the oxidation of Ni^{3+} to Ni^{4+} . Ni atoms oxidize during the initial stages of charge and attain a maximum oxidation state of Ni^{4+} well before the end of charge ($x \approx 0.85$). On the other hand, Co atoms do not oxidize during the initial stages of charge but oxidize close to the end of charge. Analysis of the extended x-ray absorption fine structure (EXAFS) shows that the oxidation of Ni^{3+} to Ni^{4+} leads to the expected reduction in the Jahn Teller effect. Also, to within the accuracy of the EXAFS technique, Co absorbers occupy Ni-type sites in the NiO_2 slabs. Furthermore, Co doping has a strong effect on the overall structural evolution and leads to a slight expansion of the a and b axes close to the end of charge¹. The XAS of dilute Ga absorbers in $\text{Li}_{1-x}\text{Ni}_{0.908}\text{Co}_{0.085}\text{Ga}_{0.003}\text{O}_2$ shows that in the fresh electrode Ga^{3+} ions occupy Ni-type sites in the host lattice, as expected. On delithiation, Ga migrates from octahedral Ni-type sites to interstitial tetrahedral sites. The high site preference of Ga^{3+} ions for tetrahedral sites leads to the stabilization of the Ga ions in these sites. We speculate that this migration of the Ga^{3+} ions suppress the transfer of Ni to Li-type sites and also helps to maintain a single hexagonal phase by acting as pillaring ions during high states of charge. We suggest that the high stability of Ga in tetrahedral sites is at the origin of the significant improvement of the cycling and structural properties of Ga-doped cathode materials reported earlier by others².

We have also investigated the electronic and atomic structure of a new layered oxide material $\text{Li}[\text{Li}_{0.2}\text{Cr}_{0.4}\text{Mn}_{0.4}]\text{O}_2$ developed by Dr. Davidson's group at the National Research Council, Ottawa³. Our results indicate that charge compensation in the cathode material is achieved by the oxidation/reduction of octahedral Cr^{3+} ions to tetrahedral Cr^{6+} ions during delithiation/lithiation. Manganese ions are present predominantly in the Mn^{4+}

oxidation state and do not appear to actively participate in the charge compensation process. To accommodate the large changes in coordination symmetry of the Cr^{3+} and Cr^{6+} ions, the chromium ions have to move between the regular octahedral sites in the $\text{R}\bar{3}\text{m}$ -like lattice to interstitial tetrahedral sites during the charge/discharge process. The highly reversible (at least after the first charge) three-electron oxidation/reductions, and the easy mobility of the chromium between octahedral and tetrahedral sites are very unusual and interesting. Equally interesting is the fact that chromium is the active metal undergoing oxidation/reduction rather than manganese. Our results also suggest that in the local scale manganese and chromium ions are not evenly distributed in the as prepared material, but are present in separate domains of Mn and Cr-rich regions.

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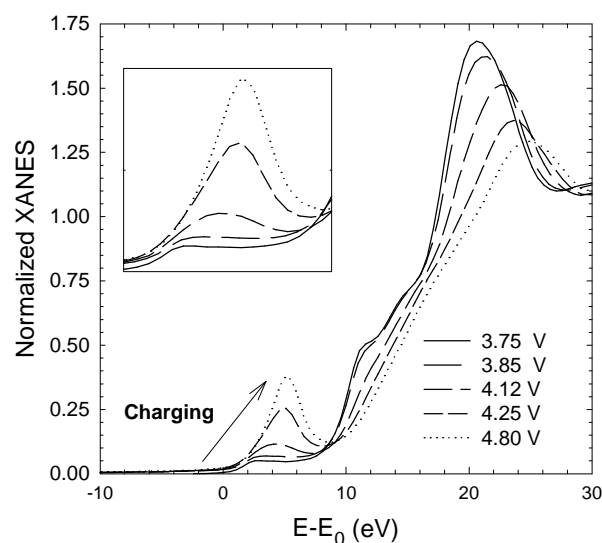


Figure 1: The *in situ* XANES of Cr absorbers in a Cr-Mn based cathode material during electrochemical delithiation. The increase in the intensity of the pre-edge peak (enlarged in the inset) shows the conversion of Cr^{3+} to Cr^{6+} on charging.