

# Synchrotron x-ray examinations of local structure and redox chemistry in lithium battery cathode materials

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## Introduction

The emergence and use of portable telecommunications and computer equipment has created a substantial need for improvements in energy storage devices, namely more inexpensive batteries that can operate for a longer time, in a smaller size, and with less weight. The Li-ion battery possesses the highest energy density of all rechargeable battery chemistries available on the market today, yet there is still an array of new battery materials that is currently being developed for the Li-ion battery and these compounds require investigation and further physical characterization.

The Li-ion cathode material of choice is the  $\text{Li}_{1-x}\text{CoO}_2$ , a hexagonally (S.G. R-3m) layered oxide material, that makes up a Li-ion cell when it is coupled with a graphite or coke anode ( $\text{Li}_x\text{C}_6$ ) and a 1 M  $\text{LiPF}_6$  electrolyte salt in an organic solvent. This battery operates at 4.0 V, has excellent cyclability and a long life, but consists of expensive raw materials. The  $\text{Li}_{1-x}\text{NiO}_2$  is much less expensive, but suffers from a lower rate capability. The rate problem has been associated with Ni migration into sites within the depleted Li layer for  $x \leq 0.5$  causing a deleterious change in the cathode structure [1]. Cobalt has been substituted into the Ni structure to improve the stability of the cathode. Why electrochemical performance is improved by this substitution is poorly understood from a structural standpoint. The objective of this work was, therefore, to implement x-ray absorption fine structure (XAFS) as a diagnostic tool for studying the structure of the  $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  cathode material *in situ* while the battery is charging and discharging.

## Methods and Materials

An electrochemical cell was designed to use on the beamline at sector 10, the MR-CAT. This ‘pouch’ cell mimics a real coin cell in its battery cycling performance. The pouch cell was discharged and charged while x-ray absorption spectra were collected in transmission mode. The x-ray energy was scanned over the Ni and Co edges, and the XAFS portion of the spectra. As a result, we were able to collect a series of spectra during cell cycling. After the run, the cycling curve was reassembled with the corresponding x-ray absorption spectra in order to distinguish the short-range order effects around the Ni and/or Co octahedra during the cycling, as well as the extent of redox changes that occurred at the redox active metal centers. Analysis was done using the *feff* and *feffit* software [1, 2].

## Results

The cycling of the pouch cell mimicked that of a coin cell. The cathode delivered 195 mAh/g capacity on its first charge step. After the subsequent discharge, the cell underwent x-ray absorption analysis during its next full cycle carried out at a C/5 rate ( $I = 0.875 \text{ mA/cm}^2$ ) between 4.1 and 3.0 V vs. Li. The capacity in the second cycle in C2 and D2 was 134 mAh/g and 120 mAh/g, respectively. This corresponds to the cathode cycling approximately 0.5 Li into and out of its structure. The results of an XAFS analysis on the first shell Co-O and Ni-O bond lengths and the changes they undergo during cell cycling are shown in Figure 1.

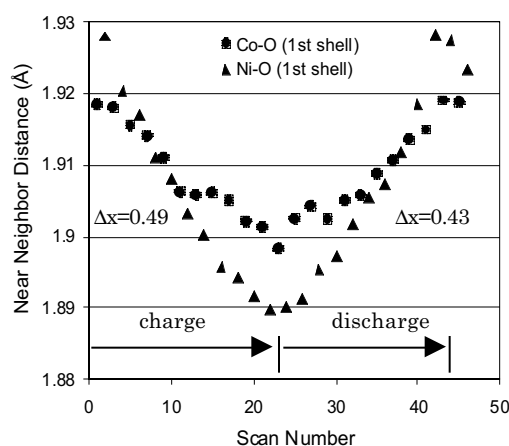


Figure 1: First-shell metal-oxygen bond lengths during  $\text{Li}/\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  pouch cell cycling.

The Ni-O and Co-O bonds both contract as the Li is removed from the structure during the charge (scan numbers 0–22). Both the Co and the Ni become oxidized during this process, going from a nominal oxidation state of  $3^+$  to  $4^+$ . During discharge (scan numbers 23–44), this process is reversed electrochemically; Li is reinserted back into the structure, the  $\text{Ni}^{4+}$  and  $\text{Co}^{4+}$  are reduced down to their trivalent states, and their bonds with oxygen return to their original crystallographic positions.

## Discussion

Unlike pure  $\text{Li}_{1-x}\text{NiO}_2$  or  $\text{Li}_{1-x}\text{CoO}_2$ ,  $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  has a hexagonally layered structure that may not undergo phase changes to inactive secondary monoclinic or hexagonal phases when Li is cycled into and out of its lattice. This effect was shown with previous x-ray diffraction (XRD) data collected from an *in situ* coin cell [3, 4]. In  $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ , it has been postulated that the Ni and Co interlayer slab has a higher degree of covalency;

consequently, the Ni-O and Co-O bond strengths are greater than the undoped parent materials [5].

The XAFS results demonstrate that only small changes are occurring in the layered structure of  $\text{Li}_{0.8-x}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  during Li insertion and removal ( $0 \leq x \leq 0.5$ ) [6]. The bond lengths respond as a result of the change in the metal center's oxidation state. The short-range order in the mixed Ni/Co oxide layered system exhibits good reversibility during the Li insertion/removal processes. The Ni-O bond length changes linearly with the cathode state of charge; the overall change from fully discharged to fully charged is greater than the Co-O bond length changes. The oxygen atom sublattice undergoes only subtle changes during Li cycling. The coordination environment of the Co-O octahedra exhibits small changes in the Co-O distance. However, the Ni-O octahedra undergo a subtle, but significant change. The XAFS Debye-Waller factor decreases dramatically, from  $\sigma^2 = 0.0063(4) \text{ \AA}^2$  at  $x = 0.04$  to  $\sigma^2 = 0.0026(4) \text{ \AA}^2$  at  $x = 0.49$ . This signals that the Ni-O octahedron likely undergoes a Jahn-Teller distortion as the oxidation state of Ni changes from +4 to +3 as has been proposed by other investigators [7, 8]. Finally, from an analysis of the XANES, it was determined that the charge compensation mechanism is different for the cobalt atoms versus the nickel atoms near the top of charge.

XAFS has provided us with an excellent tool for analyzing the changes that occur when Li is cycled into and out of the layered crystal of  $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$  in a Li-ion battery. This material possesses good characteristics for an electrode such as small volumetric changes and retention of its structure making it an excellent choice for high power Li-ion battery applications.

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### References

- [1] S.I. Zabinsky, J.J. Rehr, A. Ankudinov, R.C. Albers, and M.J. Eller, *Phys. Rev. B* **52**, 2995 (1995).
- [2] E.A. Stern, M. Newville, B. Ravel, Y. Yacoby, and D. Haskel, *Physica B* **208-209**, 117 (1995).
- [3] J.N. Riemers and J.R. Dahn, *J. Electrochem. Soc.* **139**, 2091 (1992).
- [4] X. Sun, Q. Yang, J. McBreen, Y. Gao, M.V. Yakovleva, X.K. Xing, and M.L. Daroux, submitted to *1999 Joint International Meeting of the Electrochemical Society and the Electrochemical Society of Japan* (1999).
- [5] Y. Saadoune and C. Delmas, *J. Mater. Chem.* **6**, 193 (1996).
- [6] A.J. Kropf and C.S. Johnson, *Applications of Synchrotron Radiation Techniques to Materials Science V*, Proceedings of the Fall 1999 Meeting of the Materials Research Society, to be published.
- [7] I.J. Pickering, G.N. George, J.T. Lewandowski, and A.J. Jacobson, *J. Am. Chem. Soc.* **115**, 4137-4144 (1993).
- [8] A. Rougier, C. Delmas, and A.V. Chadwick, *Solid State Comm.* **94**(2), 123-127 (1995).