

X-ray Absorption Spectroscopy Characterization of Mixed-metal Layered Oxide Cathodes for Lithium-ion Batteries

C. S. Johnson, J.-S. Kim, M. M. Thackeray, A. J. Kropf
Chemical Technology Division, Argonne National Laboratory, Argonne, IL, U.S.A.

Introduction

Layered transition metal oxides (LiMO_2 ; M = transition metal ion), such as lithium cobalt oxide (LiCoO_2), lithium nickel oxide (LiNiO_2), or lithium nickel-cobalt oxides ($\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$), are commonly used as cathodes in commercial Li-ion batteries. These materials have an ordered hexagonal structure with a space group R-3m. During battery cycling, the charge is stored and released via redox changes at the metal center. In most cases, the metal undergoes a reversible one-electron process shuttling back and forth from trivalent (M^{3+}) to tetravalent (M^{4+}) [1].

Recent synthetic developments have shown that it is possible to replace some M with Mn to give $\text{LiNi}_{1-y}\text{Mn}_y\text{O}_2$ solid solutions [2]. When half of the nickel is substituted with manganese, the composition is $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, where M nominally has an average oxidation state of three. The objective of this study was to evaluate this material by using x-ray absorption spectroscopy (XAS) in order to ascertain what metal oxidation states were present in this unique composition and to determine what the charge compensation mechanisms were under battery cycling conditions.

Methods and Materials

A pouch-type cell similar to that used in a previous $\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode study [1] was used for the *in situ* XAS experiments. Data were collected in transmission mode.

The XAS measurements, which include both x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectroscopy techniques, were performed on the insertion device beamline of the Materials Research Collaborative Access Team (MR-CAT). The details of the equipment and setup are reported in on in Ref. 1. In this report, we discuss only the *in situ* data of overdischarged $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ electrodes discharged between 3.3 and 1.0 V and qualitatively compare the XANES spectra with standard materials. Note in this XAS analysis and subsequent discussion, a 5% Li_2TiO_3 electrochemically inactive rock-salt component has been omitted for simplicity. The standards for the Mn K edge were as follows: Li_2MnO_3 (Mn^{4+} , Strem Chemical, 99%); Mn_2O_3 (Mn^{3+} , Aldrich, 99%); and $\text{Mn}(\text{acetate})_2$ (Mn^{2+} , Aldrich, 99%). The standards for the Ni K edge were as follows: LiNiO_2 (Ni^{3+} , synthesized in-house, verified by XRD) and NiO (Ni^{2+} , dark green, Alfa-Aesar, 99%). The high-voltage

(2.5–4.8 V) electrochemical behavior and quantitative analytical XANES and XAFS data of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrodes will be reported in a full-length paper in the future [3]. Nickel and manganese metal foils were used to calibrate the energy at each edge.

Results and Discussion

For this experiment, the electrode was initially charged and discharged eight times, off line, between 4.6 and 2.5 V to ensure that the electrode and the pouch cell were functioning properly. After the eighth discharge, the cell was placed on open-circuit (OCV = 3.3 V), the x-ray beam was turned on, and the cell was discharged from 3.3 to 1.0 V at a 1.5-h rate (0.92 mA/cm^2) and at 50°C to improve the electrode kinetics at low voltages. The electrode delivered a total capacity of 166 mAh/g, of which 58 mAh/g was obtained at 1.8 V, 70 mAh/g at 1.3 V, and 38 mAh/g between 1.3 and 1.0 V. This cell was subsequently cycled off line (50°C) between 1.0 and 4.6 V at a slower 26-h rate (0.05 mA/cm^2). The electrode provided 367 mAh/g on charge and 353 mAh/g on discharge and was consistent with the cell behavior with the beam on. The voltage profile of the pouch cell is shown in Fig. 1.

Mn K-edge spectra were recorded throughout the experiment, whereas the Ni K edge was monitored only periodically. The Mn K-edge spectra for the $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ electrode at two representative voltages of 1.4 and 1.0 V are shown in Fig. 2. The Mn K-edge position from 2.5 to about 1.4 V matches the Li_2MnO_3

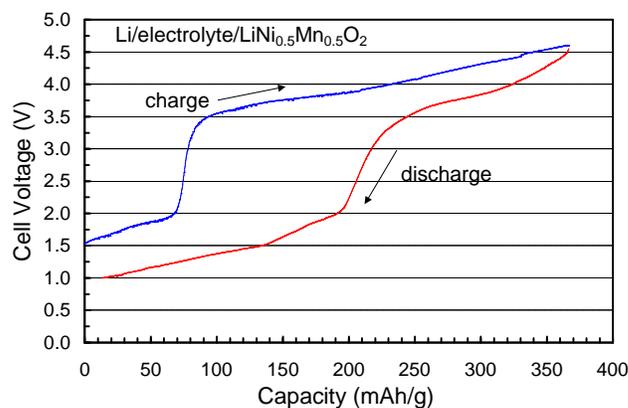


FIG. 1. Voltage profile of *in situ* XAS pouch cell with the configuration $\text{Li}/\text{electrolyte}/\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$.

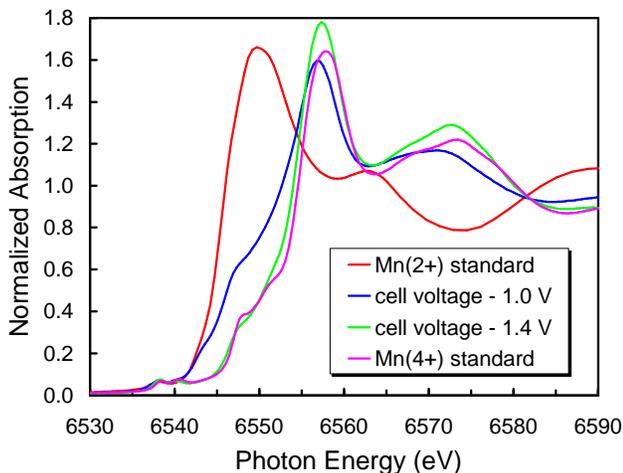
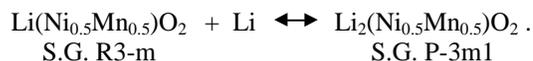


FIG. 2. Calibrated and normalized XANES data (Mn K edge). Reproducibility of the calibration is ± 0.1 eV.

standard closely, indicating that the electrode maintains predominantly tetravalent manganese. The Ni K-edge data (not shown in this short report) indicate that the average oxidation state of the nickel at 2.5 V is about 2.3. From a qualitative assessment of the XANES data, we conclude that the initial discharge capacity below 2.5 V to 1.4 V is associated with the reduction of residual Ni^{3+} in the electrode, after eight cycles at higher voltage, to Ni^{2+} , while the manganese remains tetravalent. At approximately 1.43 V, the Mn K edge begins to change, and a profile associated with Mn^{2+} appears, indicating a reduction of the Mn^{4+} metal center. At the end of discharge at 1.0 V, fitting the XANES data indicates the formation of $23 \pm 4\%$ Mn^{2+} (Fig. 2). By contrast, the analysis of the Ni K edge at 1.0 V showed only a slight change in the structure of the Ni center, suggesting that the predominant oxidation state at this voltage is Ni^{2+} . Furthermore, the XANES results do not reveal that any metallic Ni or Mn is formed at 1.0 V. These XANES results, together with previous reports of the high-voltage behavior of $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrodes [4], suggest that

these types of electrodes operate predominantly off two-electron redox couples, $\text{Ni}^{4+}/\text{Ni}^{2+}$ and $\text{Mn}^{4+}/\text{Mn}^{2+}$, between 4.5 and 2.0 V and between 2.0 and 1.0 V, respectively. The apparent absence of any significant amount of the Jahn-Teller ions, Ni^{3+} and Mn^{3+} , in the low-voltage region may be a factor that contributes to the excellent structural and electrochemical stability of these electrodes.

The identification of Mn^{2+} and Ni^{2+} in the discharged $\text{Li}(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ electrode may suggest that a dilithium compound, $\text{Li}_2(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$, is formed electrochemically at low voltages in the cell. The reaction is depicted in the following equation:



The formation of $\text{Li}_2(\text{Ni}_{0.5}\text{Mn}_{0.5})\text{O}_2$ necessitates a coordination change of lithium from octahedral to tetrahedral in the layers and a shearing of the oxygen atoms from ccp to hcp stacking. This structural change and its reversibility are subjects of interest in this work in the future.

Acknowledgments

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