

## *In Situ* X-ray Absorption Spectroscopic Study on the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ Cathode Material During Electrochemical Cycling

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*Lithium ion batteries consist of a layered-lithium first-row transition metal oxide cathode (positive) and a graphite anode (negative) that can intercalate lithium ions. In the intercalation process,  $\text{Li}^+$  ions migrate into the empty space between the metal oxide or graphite layers. Oppositely, egress of the  $\text{Li}^+$  ions is called deintercalation. During the repeated charging and discharging of the battery, called cycling, the lithium ions shuttle between the anode and cathode, electrons flow in the external circuit, and the metal in the cathode undergoes a redox process. In this process, the metal's oxidation state is changed. In situ x-ray absorption spectroscopy (XAS) was used to study the redox processes in  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ . The results indicate that the redox process occurs on the nickel ions, with the conversion of  $\text{Ni}^{2+}$  to  $\text{Ni}^{3+}$  occurring first and the  $\text{Ni}^{3+}$  to  $\text{Ni}^{4+}$  conversion occurring second. The manganese remains  $\text{Mn}^{4+}$  during normal battery cycling.*



Authors (from left): Xiao-Qing Yang, Won-Sub Yoon, James McBreen, (top) Clare P. Grey, and (bottom) Mahalingam Balasubramanian

Rechargeable lithium ion batteries are a key component in portable electronic equipment, such as laptop computers and cellular phones. These batteries consist of a layered-lithium first-row transition metal oxide cathode (positive) and a graphite anode (negative)

that can intercalate lithium ions. Commercial lithium ion batteries have  $\text{LiCoO}_2$  cathodes. During cycling, the lithium ions shuttle between the anode and cathode through a non-aqueous electrolyte. During charging,  $\text{Li}^+$  ions are removed from the cathode and inserted between the graphite layers in the anode. Concomitant with the removal of the  $\text{Li}^+$ , a  $\text{Co}^{4+}/\text{Co}^{3+}$  charge-compensation process converts  $\text{Co}^{3+}$  to  $\text{Co}^{4+}$ . This is called a redox process, and it causes electrons to flow in the external circuit from the cathode to the anode. Then, during discharging, all the processes are reversed. This type of reaction yields a long cycle life because no new phases crystallize on the electrodes and cause the battery to degrade and ultimately fail. For example, as a Pb-acid ( $\text{PbSO}_4$ ) battery charges, lead metal with a textured consistency, called a lead sponge, forms on the anode and  $\text{PbO}_2$  forms on the cathode. As the battery discharges,  $\text{PbSO}_4$  forms on both electrodes. But in a lithium ion battery, the electrode materials do not undergo major structural changes. Instead, they merely act as intercalation hosts that accommodate the ingress and egress of  $\text{Li}^+$  ions. This yields a long-life battery.

In practice, only 50 percent of the  $\text{Li}^+$  ions are removed from the  $\text{LiCoO}_2$  cathodes during the charging process. Removal of more than this severely limits the battery's cycle life. Fortunately, during charging, the cell voltage has a well-defined positive slope (**Figure 1**), making it possible to remove only 50 percent of the  $\text{Li}^+$  ions by simply terminating the charge at 4.2 V. However, this results in the utilization of only half the theoretical charge capacity that could be obtained by completely removing the  $\text{Li}^+$  ions. Because of the low cathode capacity and the cost of  $\text{LiCoO}_2$ , extensive research is underway to find alterna-

### BEAMLINE X18B

#### Funding

U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Office of Freedom CAR and Vehicle Technologies

#### Publication

W.-S. Yoon, C.P. Grey, M. Balasubramanian, X.-Q. Yang, and J. McBreen, "In Situ X-ray Absorption Spectroscopic Study on the  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  Cathode Material During Electrochemical Cycling," *Chem. Mater.*, 15, 3161 (2003).

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tive cathode materials with larger operating capacities and lower costs.  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  is one of the more promising new materials. It has a lower cost, a higher capacity, and is more resistant to thermal abuse than  $\text{LiCoO}_2$ .

We reported an *in situ* XAS study of  $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$  at the Ni and Mn K-edges, as it was charged and discharged. The XAS study was done in the transmission mode in a two-electrode cell with thin mylar windows. The respective K-edges of Mn and Ni metal are at 6539 eV and 8333 eV. At these energies, the x-ray can eject *1s* core electrons and there is a large increase in the x-ray absorption. As the oxidation state of the metals increases, there are less electrons to screen the nucleus and the edge position shifts to higher energies because it becomes more difficult to eject the *1s* electrons. By monitoring the edge shifts, we can follow the redox processes on both Mn and Ni.

**Figure 1** shows a voltage profile of the cell as it was charged over a 50-hour period to remove all the  $\text{Li}^+$ , while continuously recording XAS spectra. Representative XAS scans are indicated on the plot.

**Figure 2a** shows the Mn K-edge x-ray absorption near-edge structure (XANES) and **Figure 2b** shows the Ni K-edge XANES. Even though there are changes in the Mn XANES during charging, there is no rigid shift of the Mn XANES to higher energies, indicating that the Mn remains  $\text{Mn}^{4+}$  throughout charging. However, the Ni XANES shows a rigid shift, indicating the conversion of the initial  $\text{Ni}^{2+}$  to  $\text{Ni}^{4+}$ . Analysis of the Mn extended x-ray absorption fine structure (EXAFS) shows very few changes in the Mn O first-shell interactions, which supports our conclusion from the XANES analysis that Mn remains  $\text{Mn}^{4+}$ . The Ni EXAFS shows major changes in the Ni O first-shell interactions, which is consistent with the XANES. All of this clearly indicates that charge compensation, during charging, occurs via the oxidation of  $\text{Ni}^{2+}$  to  $\text{Ni}^{4+}$ . Analysis of the EXAFS indicates that this occurs in two steps: first, from  $\text{Ni}^{2+}$  to  $\text{Ni}^{3+}$ , and then from  $\text{Ni}^{3+}$  to  $\text{Ni}^{4+}$ .

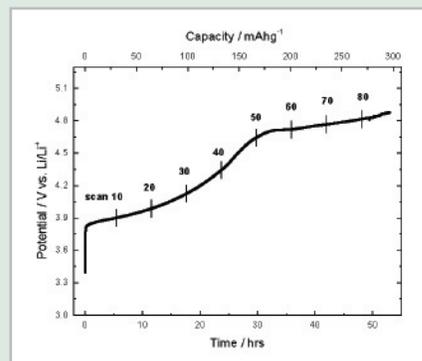


Figure 1. Voltage profile of cell on first charge. Representative XAS scans are indicated.

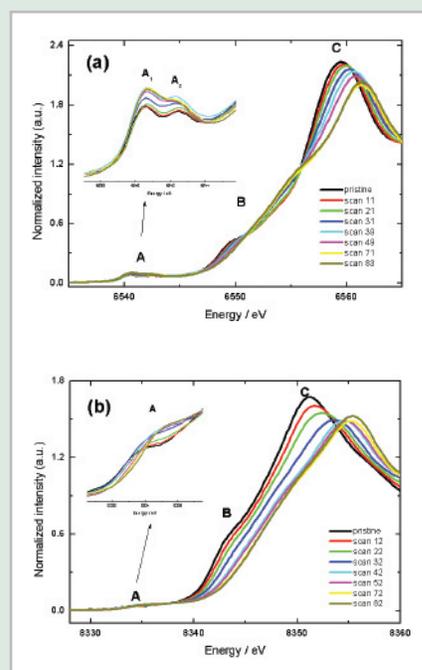


Figure 2. Normalized (a) Mn K-edge and (b) Ni K-edge XANES.