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Won-Sub Yoon, Chemistry Department
Brookhaven National Laboratory
wonsuby@bnl.gov

Investigation of the Charge Compensation Mechanism on the Electrochemically Li-ion deintercalated $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ Electrode System by Combination of Soft and Hard X-ray Absorption Spectroscopy

W.-S. Yoon¹, M. Balasubramanian², K. Yoon Chung¹, X.-Q. Yang¹, J. McBreen¹, C.P. Grey³, and D.A. Fischer⁴

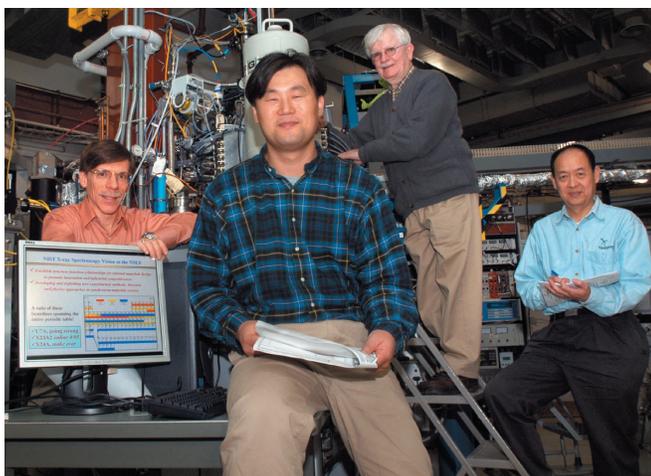
¹Chemistry Department, Brookhaven National Laboratory; ²Advanced Photon Source, Argonne National Laboratory; ³Department of Chemistry, Stony Brook University; ⁴National Institute of Standards and Technology

During the charging and discharging of lithium-ion batteries, lithium ions move back and forth between the cathode (positive) and anode (negative) electrodes. The cathode is a layered transition metal oxide such as LiCoO_2 . The anode is a layered graphitized carbon. During the charge process, lithium is extracted from the cathode and is inserted in the anode. During discharge, lithium is extracted from the anode and is inserted between the oxide layers of the cathode. To accommodate lithium insertion and extraction in the cathode, valence changes occur on the transition metal. X-ray absorption spectroscopy (XAS) was used to follow these valence changes in a new promising cathode material, $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$.

The emergence of portable telecommunications devices, computer equipment, and ultimately hybrid electric vehicles has created a substantial interest in manufacturing Li rechargeable batteries with lower cost, less toxicity, longer life, smaller size, and lighter weight. Although studies on the charge compensation mechanism for the cathode materials of lithium batteries have been reported in literature, the techniques used in most of those studies are limited to hard XAS only. The lack of systematic studies of the charge compensation mechanism for the cathode materials of lithium batteries during Li^+ intercalation/deintercalation has left many important questions unanswered, such as what is the role of oxygen and what are the correlations between transition metal ions and the surrounding oxygen ions. These are the issues we are trying to address in this paper.

We have used a combination of hard and soft XAS techniques, together with simultaneous data collection using both the partial electron yield (PEY) and fluorescence yield (FY) modes in soft XAS. In this study, we studied the electronic structure and local environment of transition metals and oxygen in the electrochemically Li-ion deintercalated $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode material, which is one of

the most promising cathode materials for Li rechargeable batteries. The major charge compensation mechanisms in the $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode system on Li-ion deintercalation are established. This combination of hard and soft XAS analysis gives us a better understanding of the charge compensation mechanism of lithium transition metal oxides during Li intercalation/deintercalation.



Authors (from left) Daniel A. Fischer, Won-Sub Yoon, James McBreen, and Xiao-Qing Yang

Figure 1 shows normalized Mn, Ni, and Co K-edge x-ray absorption near-edge structure (XANES) spectra of the $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode during charge. As the Li ions are deintercalated, the Mn and Co K-edge XANES spectrum exhibits some changes in the shape of the edge due to changes in the local environment, but does not show a rigid shift to higher energy values. This indicates that most of the Mn and Co ions in pristine

$\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ are in the Mn^{4+} and Co^{3+} oxidation state and are not oxidized as a result of the Li de-intercalation. Unlike the Mn and Co K-edge XANES spectra, the Ni K-edge XANES spectra shift to higher energy regions during charge. The entire edge shift to the higher energies indicates that the average oxidation state of the nickel ions increases during charge. The shaded area in **Figure 2** is the integrated pre-edge intensity assigned to the oxygen p character hybridized with the transition metal 3d band. **Figure 3** shows variations

in the pre-edge peak intensity for the O K-edge XAS spectra in FY mode for the $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode during charge. The spectral weight increases by $\sim 37\%$, from $x = 0$ to $x = 0.7$, in $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ compared to that of pristine $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, indicating that a large portion of the holes that compensate the lithium ion deintercalation are located in O 2p states. In contrast, our previous O K-edge results of the $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ system showed relatively little change ($\sim 10\%$ for $x = 0$ to 0.8) in the pre-edge intensity

during charge. Since the Ni content is higher in $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ than in $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, Ni-O covalency would have held more weight in the pre-edge peak in the former if it was the major contributor. Based on the fact that the larger weight of the pre-edge peak was observed in $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, it is reasonable to believe that a large portion of the charge compensation during Li-ion deintercalation appears to be achieved on oxygen sites that are associated with Co.

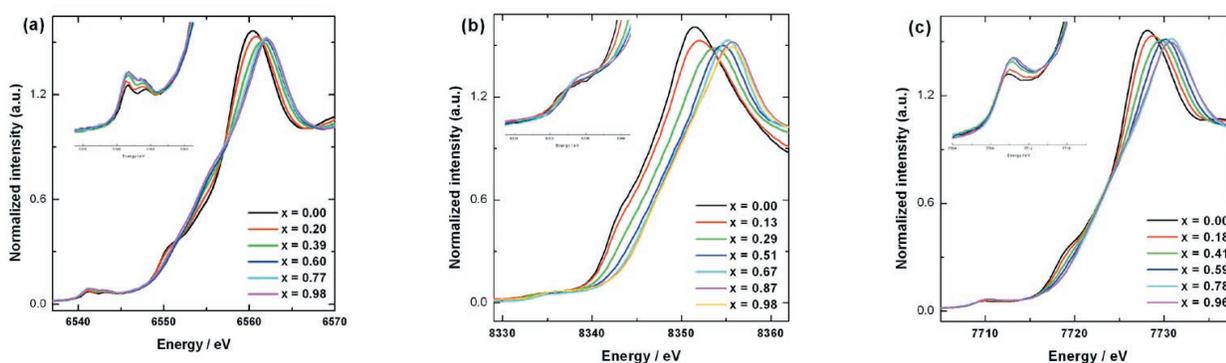


Figure 1. Normalized (a) Mn, (b) Ni, and (c) Co K-edge XANES spectra of $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode during charge.

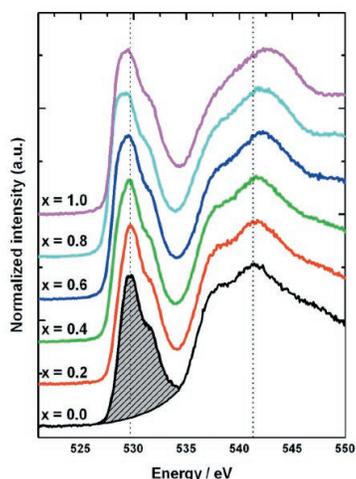


Figure 2. The O K-edge XAS spectra in FY mode for electrochemically Li-ion deintercalated $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode during charge.

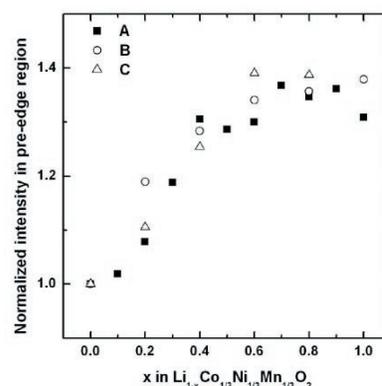


Figure 3. Variations of pre-edge peak intensity for the O K-edge XAS spectra in FY mode for $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode during charge. **A** (filled square) is from Figure 2 and **B** and **C** (open circle and triangle) are from two other sets of XAS experiments performed on the same materials, but at a different time.