In Situ Structural Investigations of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ During Cycling by X-ray Absorption Spectroscopy

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The emergence of portable telecommunications, computer equipment and, ultimately, electric and hybrid vehicles has created a growing demand for improvements in energy storage devices that are cost effective, operate for a longer time, and are smaller in size and weight [1]. The commercially employed cathode, $LiCoO_2$ possesses a theoretical capacity of 274 mAh/g. However, the practically attainable capacity is found to be 120-130 mAh/g in the 2.7-4.2 V range. To improve operational capacity there has been different reports on other cathode materials such as $LiNiO_2$, $LiMnO_2$ and its Co doped derivatives $Li(Mn_{1-x}Co_x)O_2$ ($x<0.6$). But their capacity fading and conversion to spinel structure on cycling has been of primary concern.

Recently, $LiNi_xCo_{1-2x}Mn_xO_2$ system has been found to be one of the attractive cathode materials in terms of safety and cost [2], where the valence states of Ni, Co and Mn have been predicted to be Ni^{2+}, Co^{3+} and Mn^{4+} respectively. The present system under investigation is a special case where x=1/3, which exhibits a specific capacity of 160 mAh/g over the 2.6-4.5 V range.

Synchrotron based x-ray absorption spectroscopy is a very useful tool to investigate the structural and electronic properties of this compound. X-ray absorption near edge spectroscopy (XANES) is an element-specific technique sensitive to the local atomic and electronic structure of the element of interest. XANES and extended x-ray absorption fine-structure spectroscopy (EXAFS) studies have revealed details about the local coordination, site symmetry, oxidation state, and bond character in Mn oxides and Mn-containing molecular compounds. But until now, to the best of our knowledge, there have been no in-situ reports in the literature of XANES and EXAFS studies on this promising cathode material. In order to study the atomic and electronic structure of this material and understand the changes occurring upon cycling, we performed in-situ XANES and EXAFS on this material. The in-situ experiments were performed at the DND-CAT beamline at Advanced Photon Source. We have used Mn, Co and Ni K-edge X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) to perform the *in-situ* study on this cathode material, to determine the local atomic and electronic structure and the stability during electrochemical cycling (repeated charging and discharging).

The XANES studies reveal that in $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ system Ni is Ni(II), Co is Co(III) and Mn is Mn(IV). During charging, Ni(II) is oxidized to Ni(IV) [shown in Figure 1], while Co remains at Co(III) and Mn remains at Mn(IV) respectively. The EXAFS analysis during repeated cycling exhibits small volumetric changes.

References
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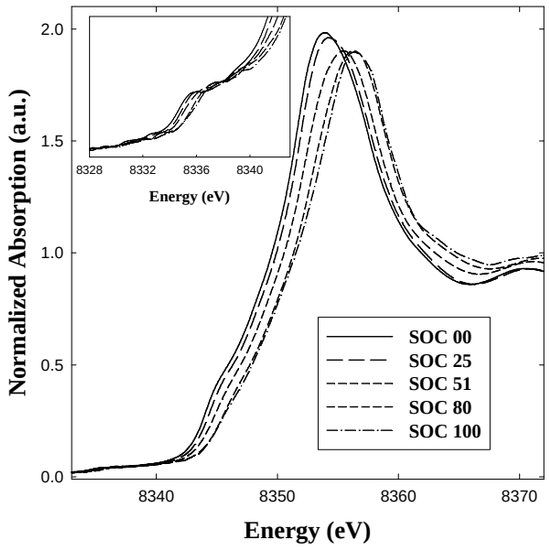

Figure 1. Normalized XANES data at the Ni K edge at different SOC (state of charge). The inset shows the magnified pre-edge of each of the respective spectra.