

## In-situ X-ray Absorption Spectroscopic Study of Li-Rich $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$ Cathode for Lithium Ion Battery

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Local structural changes in the Li-rich  $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$  cathode are investigated using in-situ X-ray absorption spectroscopy (XAS). The absorption spectra were recorded at the Mn, Ni and Co K-edges of the cathode at various states of charge and/or discharge using a specially designed electrochemical cell (Fig.1). The near-edge region (XANES) of the absorption spectra provided qualitative information about the average valence state of the absorbing atom, its local coordination symmetry and electronic configurations, while the extended region of the absorption spectra (EXAFS) provided quantitative information about the geometrical changes in the vicinity of the absorbing atom.

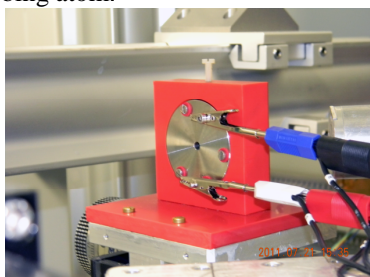


Fig. 1 Electrochemical cell for in-situ XAS

The local structure around the Mn atom (Fig.2) exhibited the features from both the constituting components of the cathode, and hence, could not provide any conclusive information about the solubility between the two components. However, the local structures around the Ni (Fig.3) and Co (Fig.4) atoms are similar to that observed in the  $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$  component, confirming the lack of solubility between the two components of the Li-rich cathode.

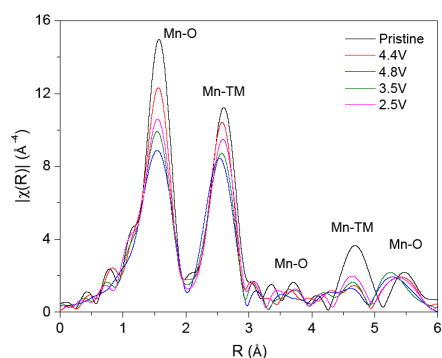


Fig.2 Magnitude of the Fourier transform of EXAFS  $\chi(k)$  signals at the Mn K-edge

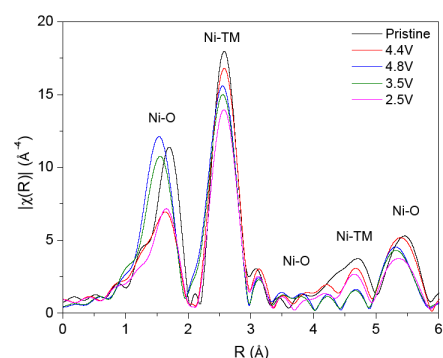


Fig.3 Magnitude of the Fourier transform of EXAFS  $\chi(k)$  signals at the Ni K-edge

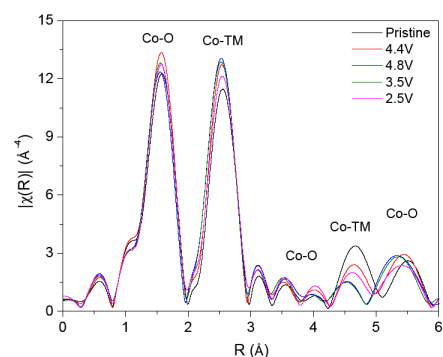


Fig.4 Magnitude of the Fourier transform of EXAFS  $\chi(k)$  signals at the Co K-edge

Both components respond to the electrochemical activation in their own unique ways. Lithium extraction from the  $\text{Li}_2\text{MnO}_3$  component occurs with a simultaneous removal of oxygen which introduces disorder, giving rise to the formation of a layered- $\text{MnO}_2$  (R-3m) type structure.  $\text{Li}^+$  thus extracted is replaced in the structure by  $\text{H}^+$  formed as a result of the electrolyte oxidation. Lithium re-insertion into layered  $\text{MnO}_2$  occurs by exchanging already present  $\text{H}^+$  by  $\text{Li}^+$ , giving rise to formation of a structure which is similar to  $\text{Li}_2\text{MnO}_3$  but lithium and oxygen deficient. The average valence state of Mn in  $\text{Li}_2\text{MnO}_3$  component remains unchanged at 4+. On the contrary, the  $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$  component exhibits conventional redox processes attributed to the transition metal (TM) ions Mn, Ni and Co. Lithium extraction from the  $\text{LiMn}_{0.4}\text{Ni}_{0.4}\text{Co}_{0.2}\text{O}_2$  component converts its original O3 structure (R-3m) to O1-type structure (P-3m1) which is poorly reversible upon lithium re-insertion. A Systematic variation in the TM-O bond length confirmed the charge compensation by TM ions during lithium extraction and re-insertion.