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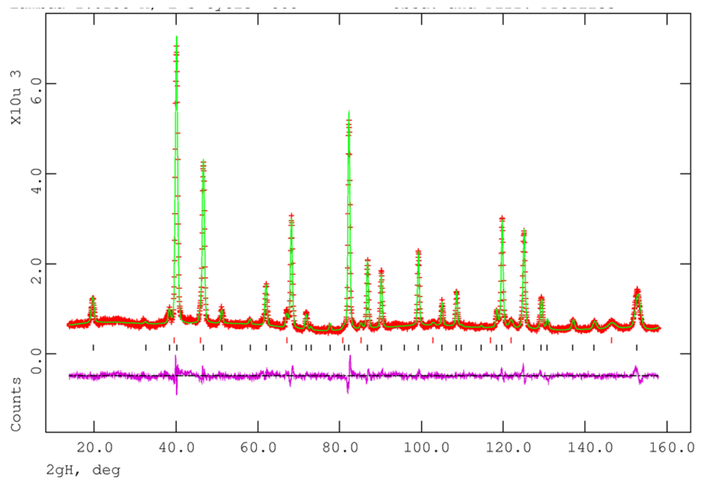
HZB Helmholtz Zentrum Berlin

In-situ X-ray Absorption Spectroscopic Study of $LiMn_{1.5}Ni_{0.4}Fe_{0.1}O_4$ Spinel Cathode for Rechargeable Li-Ion Batteries

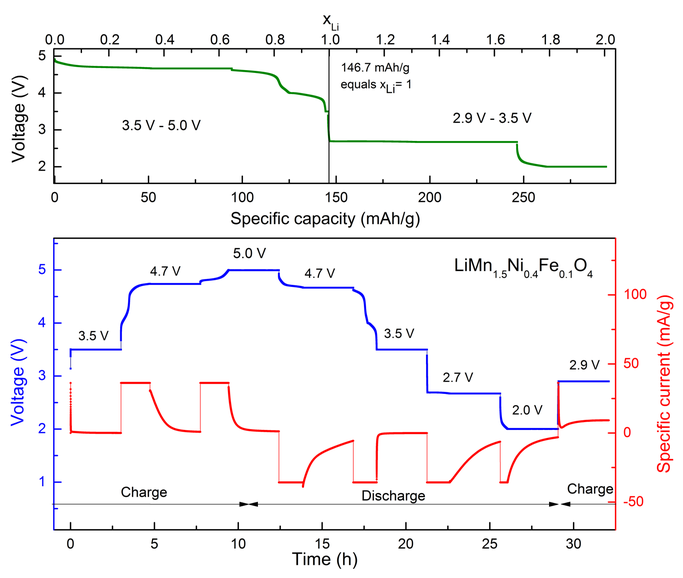


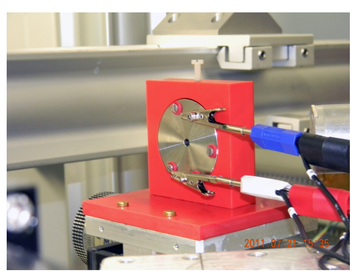
⇒ Space group : Fd-3m

⇒ Mn, Ni and Fe share same crystallographic site

⇒ Small amount of impurity phase $Li_xNi_{1-x}O$ (~1 - 2 %)

Fig.1. Rietveld refinement results of neutron diffraction data of as-synthesized $LiMn_{1.5}Ni_{0.4}Fe_{0.1}O_4$.

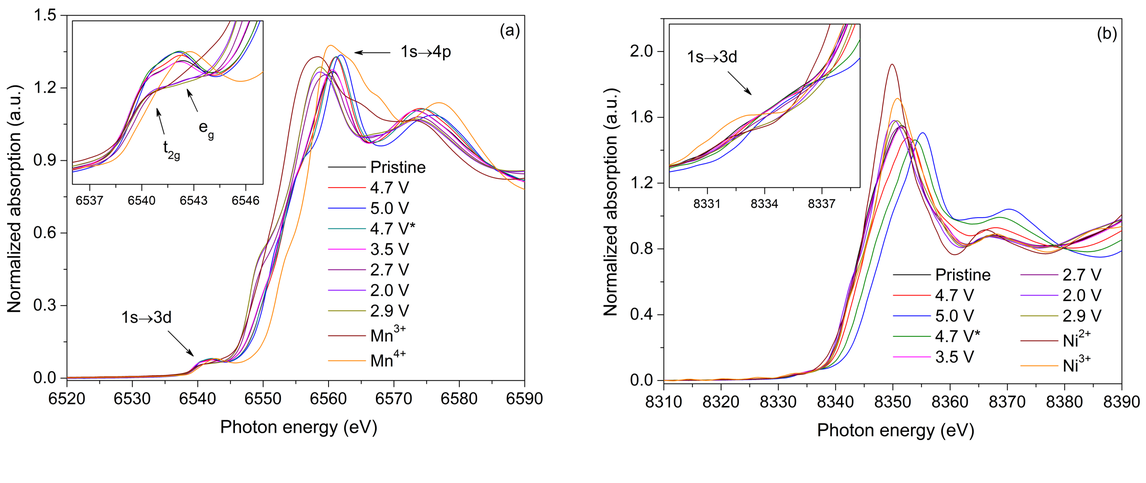


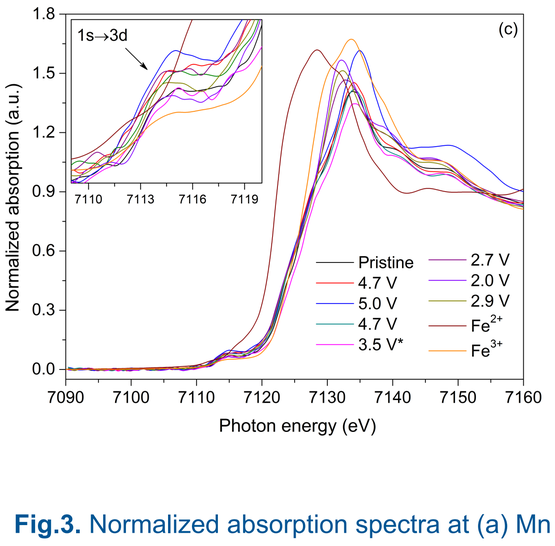


In-situ cell

Fig.2. Electrochemical profile of $LiMn_{1.5}Ni_{0.4}Fe_{0.1}O_4$ during in-situ XAS study.

XANES





⇒Complex chemical shifts at the Mn K-edge

⇒Difficult to judge the valence state of Mn

⇒Splitting of Mn *3d* orbitals due to crystal field of oxygen ligands

⇒Mixture of Ni^{2+} and Ni^{3+} in the pristine state

⇒Oxidation of $Ni^{2+}/Ni^{3+} \rightarrow Ni^{4+}$ during charge

⇒Reduction of $Ni^{4+} \rightarrow Ni^{3+}/Ni^{2+}$ during discharge

⇒Presence of Fe^{3+} in the pristine state

⇒Oxidation of $Fe^{3+} \rightarrow Fe^{4+}$ during charge

⇒Reduction of $Fe^{4+} \rightarrow Fe^{3+}$ during discharge

Fig.3. Normalized absorption spectra at (a) Mn K-edge (b) Ni K-edge and (c) Fe K-edge of $LiMn_{1.5}Ni_{0.4}Fe_{0.1}O_4$ at various states of charge and/or discharge.

EXAFS

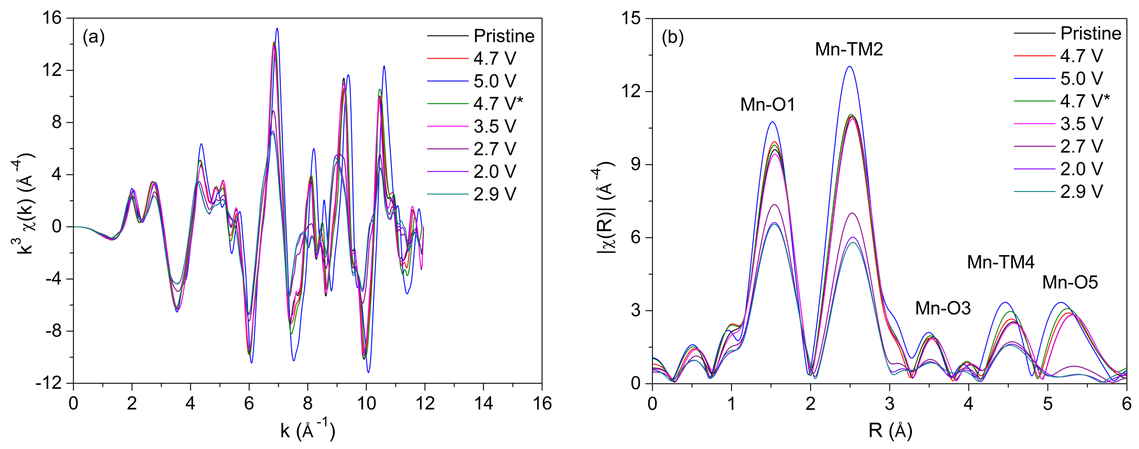


Fig.4. (a) k^3-weighted X(k) signals and (b) their Fourier transforms at the Mn K-edge of $LiMn_{1.5}Ni_{0.4}Fe_{0.1}O_4$ at various states of charge and/or discharge.

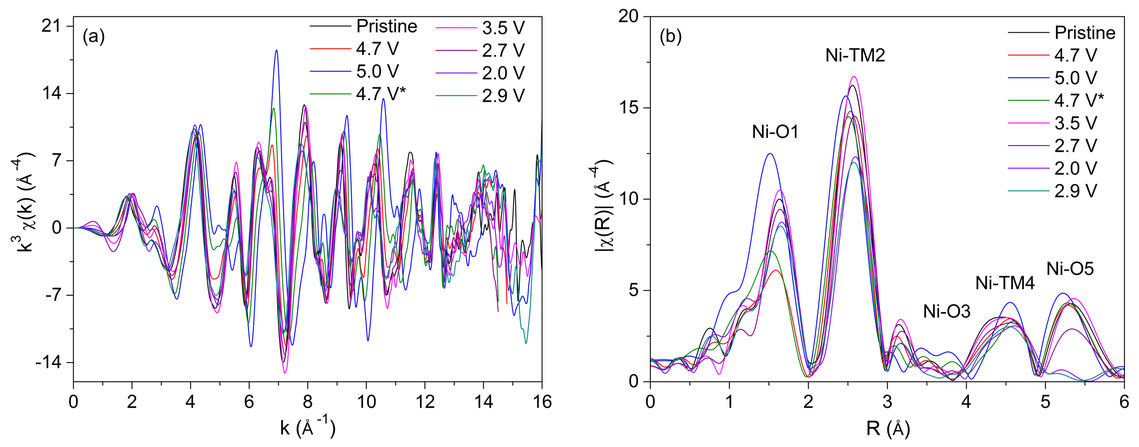


Fig.5. (a) k^3-weighted X(k) signals and (b) their Fourier transforms at the Ni K-edge of $LiMn_{1.5}Ni_{0.4}Fe_{0.1}O_4$ at various states of charge and/or discharge.

⇒Structural changes are reversible between 3.5 V - 5.0 V

⇒Significant changes in the EXAFS signals below 3.5 V : Tetragonal phase $Li_2M_2O_4$[1] (~30 %)

⇒Regions around Mn atoms undergo Spinel→Tetragonal transition earlier than regions around Ni atoms

⇒Spinel→Tetragonal transition irreversible upon subsequent charge to 2.9 V

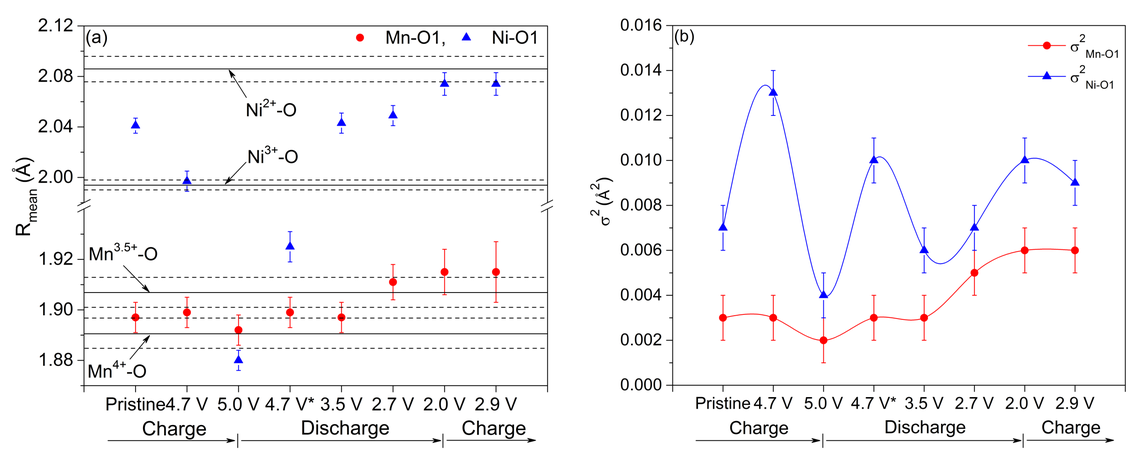


Fig.6. Variation in the (a) metal-ligand bond lengths and (b) their distribution around Mn and Ni atoms at various states of charge and/or discharge of $LiMn_{1.5}Ni_{0.4}Fe_{0.1}O_4$. Solid lines indicate metal-ligand bond lengths obtained by fitting the EXAFS data of various reference compounds and dotted lines indicate uncertainities of the fitted values.

⇒Presence of Ni^{2+}/Ni^{3+} and a small fraction of Mn^{3+} in the pristine state

⇒Two-step Ni^{2+}/Ni^{4+} redox reaction

⇒Small activity from Mn^{3+}/Mn^{4+} redox couple

⇒Deep discharge below 3.5 V involves the reduction of $Mn^{4+} \rightarrow Mn^{3+}$

Reference

1. Thackeray, M. M., David, W. I. F., Bruce, P. G., & Goodenough, J. B. *Mat. Res. Bull.*, **1983**, *18*, 461–472.

Summary

⇒ Between 3.5 V - 5.0 V, electrochemical activity is largely attributed to Ni^{2+}/Ni^{4+} and Fe^{3+}/Fe^{4+} redox couples, besides a small contribution from Mn^{3+}/Mn^{4+} redox reaction.

⇒ Deep discharge below 3.5 V gives rise to Spinel→Tetragonal transition with the concurrent reduction of a fraction of $Mn^{4+} \rightarrow Mn^{3+}$ and that of $Fe^{3+} \rightarrow Fe^{2+}$

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