

Composition Dependence of Local, Average and Electronic Structures and Thermodynamic Stability for $x\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2-(1-x)\text{Li}(\text{Mn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3})\text{O}_2$

Yasushi Idemoto^{1,2}, Masahiro Inoue¹,
Naoto Kitamura^{1,2}

¹ Department of Pure and Applied Chemistry
Faculty of Science & Technology,
Tokyo University of Science,

² Division of Ecosystem Research,
Research Institute for Science and Technology,
Tokyo University of Science,
2641 Yamazaki, Noda, Chiba 278-8510, Japan

INTRODUCTION

In recent years, a demand for the lithium-ion battery with high energy density has been increased considerably, and thus it is required to develop a cathode active material with high discharge capacity. As the candidate, we have focused on the Li_2MnO_3 - $\text{Li}(\text{Mn,Ni,Co})\text{O}_2$ system. It has been reported that the Li_2MnO_3 - $\text{Li}(\text{Mn,Ni,Co})\text{O}_2$ exhibited high capacity by charging above 4.5 V (vs. Li/Li^+), but loss of oxygen occurred in the higher voltage region, which caused irreversible capacity and degradation of cycle performance¹. We have previously reported on the crystal and electronic structures of $0.5\text{Li}_2\text{MnO}_3 - 0.5\text{LiMn}_x\text{Ni}_x\text{Co}_{1-2x}\text{O}_2$ ($x=1/3, 5/12$) samples heat-treated under vacuum reducing conditions². In this work, we focused on the composition dependence of local, average and electronic structures using neutron and synchrotron X-ray sources, the thermodynamic stability and cathode performance of $x\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2-(1-x)\text{Li}(\text{Mn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3})\text{O}_2$ ($0 \leq x \leq 1$).

EXPERIMENTAL

We prepared $x\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2-(1-x)\text{Li}(\text{Mn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3})\text{O}_2$ ($x=0\sim 1$) by a co-precipitation method. The obtained samples were identified by power XRD and the metal composition was determined by the ICP/AES. Their cathode properties were investigated by charge-discharge cycle tests. In order to evaluate thermodynamic stability, the heat of dissolution was measured by a twin-type multi-calorimeter. From the heat of dissolution, the enthalpy change per mole of atoms for the formation reaction, ΔH_R , was calculated by applying Hess's law². In order to clarify the average structure, we measured neutron diffraction (iMATERIA, J-PARC) and synchrotron X-ray diffraction (BL19B2, SPring-8), and then performed the Rietveld (Z-code, RIETAN-FP) and MEM (maximum entropy method) analyses. As for the local-structure investigation, the PDF (pair distribution function) method using PDFgetN was applied to the neutron scattering patterns (NPDF, LANSCE). In addition, X-ray absorption fine structure spectra measurements at BL14B2(SPring-8) was analyzed using REX2000 and FEFF.

RESULTS AND DISCUSSION

XRD measurements confirmed that $x\text{Li}(\text{Li}_{1/3}\text{Mn}_{2/3})\text{O}_2-(1-x)\text{Li}(\text{Mn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3})\text{O}_2$ ($0 \leq x \leq 1$) could be indexed on the basis of the layered structure (S.G.; $R-3m$ and $C2/m$). The metal composition of the samples determined by ICP-AES was almost the same as the normal composition. A significant difference in cathode performance could be confirmed between $x=0.2$ and $x=0.3$. From thermodynamic stability data, it was found that the thermodynamically unstable with

increasing x . In addition, it was suggested that the transition metal ordering was changed by the composition x from the change of ΔH_R .

In order to discuss the average structure, the Rietveld analysis was carried out by neutron diffraction (Fig.1). As a result, Li existed both 2b site and 4g site at $x = 0.2$. On the other hand, Li localized in 2b site and Mn localized in 4g site in the case of $x \geq 0.3$. From a result of electron density, we could be confirm that the change in binding of the Li layer is large and the change in the bonding strength in the transition metal layer was significant between $x = 0.2$ and $x \geq 0.3$. In order to examine the local crystal structure, we carried out PDF and extended X-ray absorption fine structure (XAFS) analysis. The significant difference was seen in the peak of the short distance that derived from transition metal layer among $x = 0.2$ and $x = 0.4$, $x = 0.6$ from PDF analysis. It could be confirmed that there were significant changes in the local structure around the Mn between $x = 0.2$ and $x \geq 0.3$ from EXAFS (Fig.2). Such a difference in this peak may be due to the influence of the ordering of LiMn_6 and LiMn_5Ni . From these results, it was suggested that this ordering affected cathode performance.

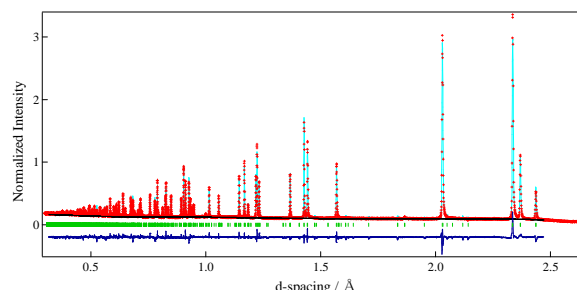


Fig. 1 Rietveld refinement patterns of $x = 0$ in space group $C2/m$. Plus marks show observed neutron diffraction intensities and a solid line represents calculated intensities. The vertical marks indicate positions of allowed Bragg reflections. The curve at the bottom is a difference between the observed and calculated intensities in the same scale.

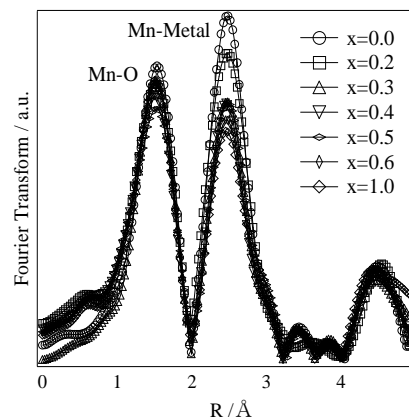


Fig. 2 Fourier transform EXAFS observed at Mn K-edge for $x = 0.0, x = 0.2, x = 0.3, x = 0.4, x = 0.5, x = 0.6, x = 1.0$.

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