Li de-intercalate mechanism of the layered LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$

Hironori KOBAYASHI*[1], Yoshinori ARACHI[2], Shuichi EMURA[3], Hiroyuki KAGEYAMA[1]

[1]AIST, Ikeda, Osaka, 563-8577 Japan

[2]Kansai University, Suita, Osaka, 564-8680 Japan

[3]Osaka University, Ibaraki, Osaka, 567-0047 Japan

Introduction

Layered LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ is one of the promising cathode materials of lithium secondary battery. LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ adopts a hexagonal unit cell like LiCoO$_2$ and LiNiO$_2$ and displays a reversible capacity of 170 mAh/g in the voltage range 2.5 to 4.5 V [1]. In addition, this material shows the superior characteristics of a larger capacity than LiMn$_2$O$_4$ and better thermal stability than LiNiO$_2$. Furthermore, it is expected to be stable at elevated temperatures. On the other hand, the structure and physical properties of the solid solution Li$_{1-y}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ are still ambiguous. Detailed information on the structure and the valence state of the cations in Li$_{1-y}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ is very important in order to improve the electrochemical properties of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ and, therefore, the relationships between the chemical composition, the structure, and electrochemical properties were studied in this study.

Experimental

LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ was synthesized in air at 1273 K for 24 h using appropriate molar ratios of LiOH·H$_2$O, Mn(CH$_3$COO)$_2$·6H$_2$O, Ni(CH$_3$COO)$_2$·6H$_2$O, and Co(CH$_3$COO)$_2$·6H$_2$O and de-lithiated samples were electrochemically prepared using coin-type cells with Li/1M LiPF$_6$ in EC:DEC(1:1)/samples. The Ni/Mn/Co valence states of samples were determined by the Ni/Mn/Co K-edge XANES spectra. Structural changes were investigated by neutron diffraction and Ni/Mn/Co K-edge EXAFS measurements.

Results and discussion

LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ was single-phase and adopted the α-NaFeO$_2$ structure. The Ni, Mn and Co K-edge XANES spectra show that LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ can be represented as Li(Ni$^{2+}_{1/3}$Mn$^{4+}_{1/3}$Co$^{3+}_{1/3}$)O$_2$. The lattice parameters a and c and the fraction of Ni on the $3a$ site decreased compared with LiNi$_{0.5}$Mn$_{0.5}$O$_2$ [2-4]. Structural analysis using neutron diffraction data demonstrated that the lattice parameters of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ are a = 2.860 Å and c = 14.22 Å and that the chemical composition can be expressed referring to the Wyckoff positions $3a$ and $3b$ with space group $R3m$ as [Li$_{0.97}$Ni$_{0.03}$]$_{3a}$[Li$_{0.03}$Mn$_{0.33}$Ni$_{0.30}$Co$_{0.33}$]$_{3b}$O$_2$. All the de-lithiated samples were the single-phasic property and Li$_{1-y}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (y = 0.7) corresponded to the composition for showing charge capacity of 194 mAh/g. Figure 1 shows the Ni K-edge XANES spectra. The Ni K-edge XANES results showed that divalent nickel metal is oxidized to tetravalent through trivalent after charging.

Figure 2 shows the composition dependence of M-O (M=Ni,Mn,Co) bondlength. The Ni and Co K-edge XAFS results showed that the first neighbor M-O bondlength decreased as a result of reduction in the ionic radius of nickel with decreasing in Li content. On the other hand, the Mn-O bondlength almost showed constant values. These results indicated that Li de-intercalation proceeded by the valence state change form Ni^{2+} to Ni$^{3.5+}$ and Co^{3+} to Co$^{3.5+}$.
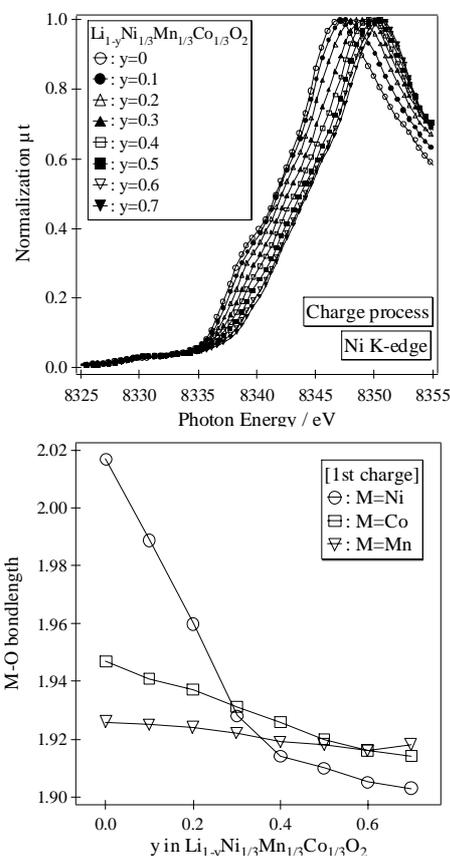

Fig. 1 Ni K-edge XANES spectra for Li$_{1-y}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$.

Fig. 2 Composition dependence of M-O bondlength obtained from XAFS analysis for Li$_{1-y}$Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$.

References

[1] N. Yabuuchi et al., J. Power Sources, 119-121, 171 (2003).

[2] H. Kobayashi et al., J. Mater. Chem., 13, 590 (2003).

[3] Y. Arachi et al, Chemistry Letters 32, 60 (2003).

[4] H. Kobayashi et al., J. Mater. Chem., 14, 40 (2004).

* hironori-kobayashi@aist.go.jp