Bulk and Surface Structural Changes of Layered $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ Material with Cycles

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Introduction

The layered Li_2MnO_3-$LiMO_2$ (M = transition metal) materials are one of the promising positive electrode materials of lithium secondary battery because of their large capacity when operated above 4.6 V [1]. Especially, it has been reported that $Li[Mn_{0.56}Ni_{0.17}Li_{0.2}Co_{0.07}]O_2$ displayed a initial discharge capacity of c.a. 280 mAh/g in the voltage range of 2.5 to 4.8 V and maintained a reversible capacity of c.a. 250 mAh/g after 50 cycles [2]. Detailed information on the crystal and electronic structures above 4.6 V is very important to improve the calendar life and thermal stability of these positive electrode materials. Several papers have reported the mechanism why these materials show large reversible capacity, but the initial charge and discharge processes were still ambiguous. Then, we started the investigation on the structural change with Li de-intercalation from $Li[Mn_{0.56}Ni_{0.17}Li_{0.2}Co_{0.07}]O_2$ and reported the possibility of removing oxygen from the lattice during 1st charge process using synchrotron radiation technique. However the structural change with cycles has not become clear yet. Thus, the structural changes of $Li_{1.20}Ni_{0.17}Co_{0.10}Mn_{0.53}O_2$ with cycles were studied in this paper.

Experimental

De-lithiated samples of $Li_{1.20-y}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ were electrochemically prepared using coin-type cells with Li/1M $LiPF_6$ in EC:DMC(1:2)/samples. Crystal and electronic structures were investigated by synchrotron XRD (BL19B2 at SPring-8), XAFS (BL7C at PF, BL4B at UVSOR, and BL27SU at SPring-8), ND (BL20 at J-PARC), ^{7}Li MAS NMR, and XPS measurements. The crystal structure and bondlength were determined using the analysis programs RIETAN-FP [4], Z-Rietveld, and REX2000.

Results and Discussion

Figure 1 displays the SR XRD and ND patterns for the pristine material. Structural analysis using the space group R-3m demonstrated that the lattice parameters of $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ were a = 2.853 Å, c = 14.236 Å and that the chemical composition could be expressed as $[Li_{0.99}Ni_{0.01}]_{3a}[Mn_{0.55}Li_{0.21}Ni_{0.15}Co_{0.09}]_{3b}O_2$.

Figure 2 displays the cycle performance of the Li/$Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ cell. This cell showed the good reversible capacity of c.a. 230 mAh/g after 14 cycles.

Figure 3 shows the XPS spectra for $Li_{1.20-y}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ before and after cycles. These spectra indicated that Li_2CO_3 or LiCOOR on the surface of $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ increased in charge process and decreased in discharge process.

Detailed bulk and surface changes with cycles will be discussed.

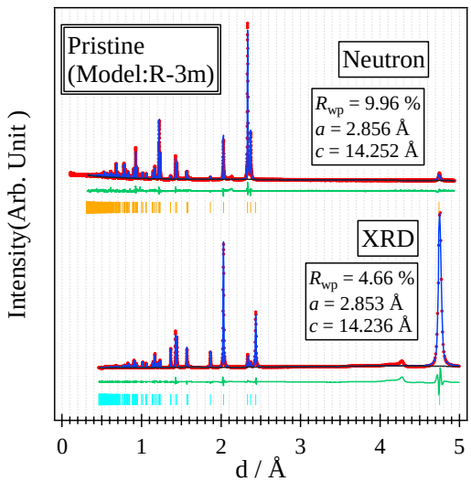

Fig.1 SR XRD and ND Rietveld analysis results for the Li/$Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ cell.

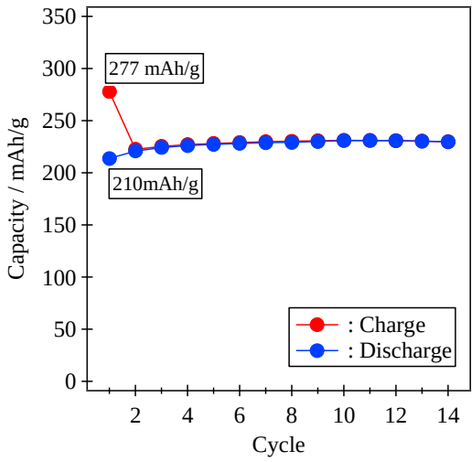

Fig.2 Capacity dependence of cycles of the Li/$Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ cell.

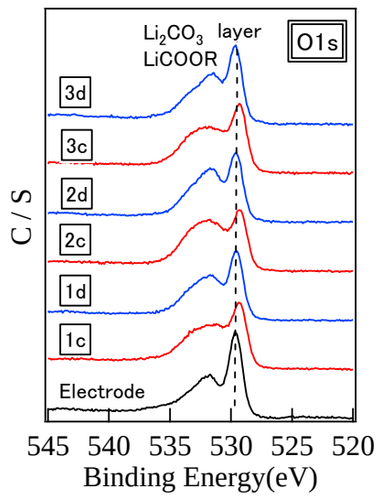

Fig.3 XPS spectra for $Li_{1.20-y}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ before and after cycles. Each 1c and 1d means the 1st charge and discharge test, respectively.

References

[1] A. Ito *et al*, *J. Power Sources*, 183 (2008) 344.
[2] A. Ito *et al*, *J. Power Sources*, 195 (2010) 567.
[3] H. Kobayashi *et al*, *Solid State Ionics*, 225 (2012) 580.
[4] F. Izumi *et al*, *Solid State Phenom.*, 130 (2007) 15.