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The Effects of Al_2O_3 Coating on the Performance of Layered $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ Materials for Lithium-Ion Rechargeable Battery

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1 Introduction

The layered Li_2MnO_3-LiMO_2 (M = transition metal) materials is one of the promising positive electrode materials for lithium secondary battery [1]. Especially, it has been reported that $Li[Mn_{0.56}Ni_{0.17}Co_{0.07}Li_{0.2}]O_2$ 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]. On the other hand, the decomposition of the electrolyte proceeded on the positive electrode material above 4.5 V is a problem to be solved for realizing long cycle life. Recently several efforts have been made to improve the cycle performance through surface modification of positive electrode materials. In addition, limited efforts have been made to improve the cycle performance through surface modification of Li-excess Mn-based layered materials. In this paper, the effect of Al_2O_3-coating on electrochemical properties was studied in $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.08}O_2$.

2 Experiment

Surface modificated-$Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.08}O_2$ was prepared by mechanochemical reaction with nano-Al_2O_3 using NOB-MINI (Hosokawa Micron Co.). The particle morphology was measured by SEM. Crystal and electronic structures were investigated by synchrotron XRD (BL19B2 at SPring-8) and XAFS (BL7C at PF, BL4B at UVSOR) measurements. The crystal structure and bondlength were determined using the programs RIETAN-FP and REX2000. Electrochemical property was measured using coin-type cells with Li/1M $LiPF_6$ in EC:DMC(1:2)/samples.

3 Results and Discussion

Al_2O_3-coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ was prepared using mechanochemical reaction. Rotation speed was 2000 and 4000 rpm and reaction time was 3, 5, 10, and 20 min. The optimal preparation condition of Al_2O_3-coating to $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ was investigated by SEM, XRD, and XANES measurements. Fig. 1 shows the Ni K-edge XANES spectra for $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ before and after the mechanochemical reaction. The Ni K-edge XANES spectrum essentially showed no deviation from the valence state of $Ni^{(2-\alpha)+}$ after mechanochemical reaction. Both XANES using hard X-ray and XRD results indicated that the mechanochemical reaction gave no damage to the bulk structure in all the condition. On the other hands, SEM and XANES using soft X-ray results indicated that the mechanochemical reaction of the rotation speed of 4000 rpm or long time reaction were not suitable to the preparation condition. Therefore, the preparation condition was determined to be the rotation speed of 2000 rpm and the reaction time of 5 min and pristine particles were rather uniformly covered with Al_2O_3 particles. In electrochemical cycle tests at 323 K, the Li/Al_2O_3-coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ cell showed the good capacity retention, compared with that of the Li/pristine $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ cell after 30 cycles.

These results demonstrate that the mechanochemical Al_2O_3-coating process is effective way of improving the cycle performance at high temperature. Further research is needed to improve the cycle performance of the Li/Al_2O_3-coated sample cell using mechanochemical reaction.

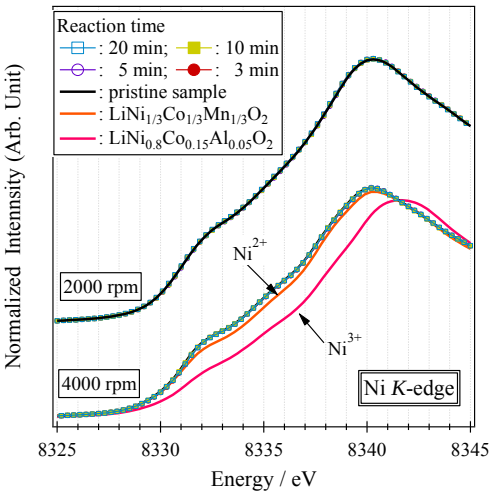

Fig. 1 Ni K-edge XANES spectra for $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ before and after the mechanochemical reaction, together with those of the reference materials $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ and $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$.

References

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