Investigation on Electrochemical Property of AB/Al_2O_3-coated Li-excess Mn-based Layered Oxides

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Abstract. The AB and/or Al_2O_3-coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ were prepared by the mechanochemical reaction. The optimal condition for sample preparation was selected to be the rotation speed of 2000 rpm and the reaction time of 5 minutes by SEM and XANES measurements. Surface analysis using SEM and XANES data demonstrated that all the samples were rather uniformly covered with AB and/or nano-Al_2O_3 particles. The Al_2O_3-coated samples showed less discharge capacity and C-rate performance compared with the pristine sample, while the AB/Al_2O_3-coated sample showed almost the same discharge capacity and C-rate performance and had better cycle performance at 318 K compared with the pristine sample. These results demonstrate that the mechanochemical AB/Al_2O_3-coating process is an effective way of improving the cycle performance at high temperature without degrading the discharge capacity and C-rate performance.

1. Introduction

The layered Li_2MnO_3-LiMO_2 (M = transition metal) materials are 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 an 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 big 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. We investigated the structural change with Li de-intercalation from $Li[Mn_{0.56}Ni_{0.17}Co_{0.07}Li_{0.2}]O_2$ and reported the possibility of removing oxygen from the lattice during the 1st charge process using synchrotron radiation technique [3]. In addition, limited efforts have been made to improve the cycle performance through surface modification of Li-excess Mn-based layered materials. Recently, we reported that the mechanochemical Al_2O_3-coating process is an effective way of improving the cycle performance of $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ at high temperature [4]. In this paper, the effect of acetylene black(AB)/Al_2O_3-coating on electrochemical properties was studied in the same chemical composition of $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$.

2. Experimental

We used the $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ powder (Toda Industrial Corp), the AB powder (Denki Kagaku Kogyo Kabushiki Kaisha), and the nano-Al_2O_3 powder with the order of 10-20 nm (TECNAN) in this study. The coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ were prepared by mechanochemical reaction with the nano-powder (AB and Al_2O_3) using NOB-MINI (Hosokawa Micron Co.) [4]. The particle morphology was measured by SEM (JSM-6700FV, JEOL). Crystal and electronic structures were investigated by synchrotron XRD (BL19B2 at SPring-8 / Proposal No. 2012B1574) and XAFS (BL9C at PF / Proposal No. 2010G599 and BL4B at UVSOR / Proposal No. 25-521) measurements. The crystal and electronic structures were determined using the analysis programs RIETAN-FP [5] and REX2000. Electrochemical property was measured using coin-type cells with Li/1M $LiPF_6$ in EC:DMC(1:2)/samples. The stepwise pre-cycling treatment was carried out by increasing the upper voltage limit by 0.1 V every two cycles from 4.5 V to 4.8 V [3].

3. Results and Discussion

The mechanochemical reaction was used to prepare the 5 wt% AB-coated, 5 wt% Al_2O_3-coated, and 5 wt% AB and 5 wt% Al_2O_3-coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ and the 2000 rpm of the rotation speed and 5 minutes of the reaction time were selected as the optimal preparation condition. Figure 1 shows the SEM images of the AB and/or Al_2O_3-coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ together with the pristine sample. The SEM images of all the coated samples showed that these particles of AB and Al_2O_3 were uniformly distributed over the surface of $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ particles. The XRD patterns of the pristine and coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ showed that the coated samples were well defined layered phases without additional impurity peak. The crystal structure was refined using the synchrotron XRD data, the initial model being that of $LiNi_{1/2}Mn_{1/2}O_2$ [6], and lattice parameters for all the samples were almost the same values of $a = 2.855$ Å and $c = 14.245$ Å. In order to obtain information on the bulk structure of the coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$, we collected the Ni, Co, and Mn *K*-edge XAFS data. The Ni, Co, and Mn *K*-edge XANES spectrum essentially showed no deviation from the valence state of $Ni^{(2-\alpha)+}$, $Co^{(3+\beta)+}$, and Mn^{4+}, respectively, after mechanochemical reaction. These XRD and XANES

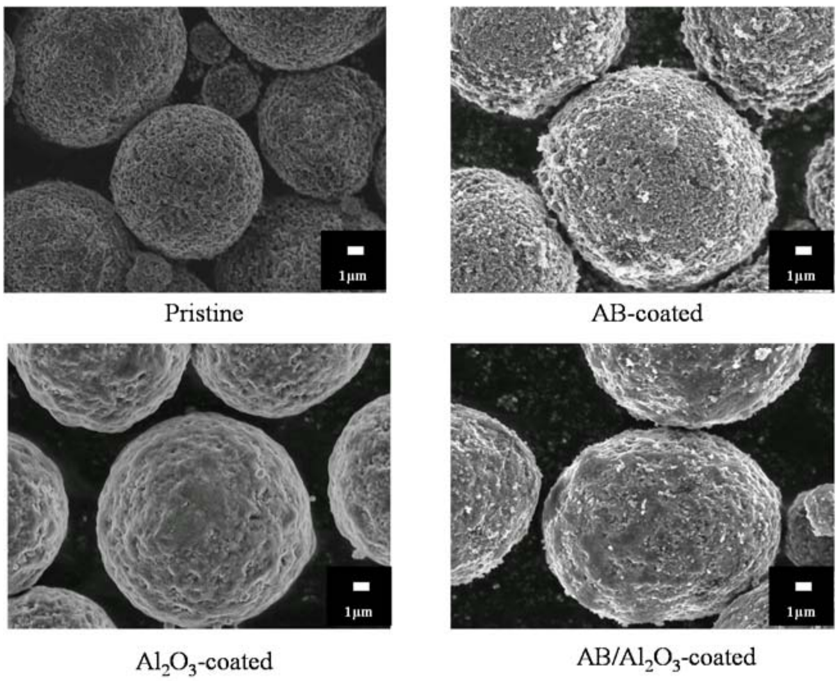

Figure 1. SEM images of the AB and/or Al_2O_3-coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ together with the pristine sample

results clarified that the bulk structure and the valance state of AB and/or Al_2O_3-coated samples were essentially same as those of the pristine sample.

In order to obtain information on the surface of the coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$, we collected the O *K*-edge and Mn *L*-edge XANES spectra in TEY mode. Figure 2 shows the O *K*-edge and Mn *L*-edge XANES spectra for the pristine and coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$. The O *K*-edge spectra contained two pre-edge peaks of A and B originating from the layered structures [3,4] and the Mn L_{III}-edge spectra contained two peaks of C and D originating from the layered structured [3,4]. For the O *K*-edge XANES spectra, the intensity of peaks A and B clearly decreased for Al_2O_3 and AB/Al_2O_3-coated samples, as shown in Fig. 2(a). On the other hands, the new peaks originated from AB were observed for AB-coated sample. For the Mn *L*-edge XANES spectra, the intensity of peaks C and D clearly decreased for Al_2O_3 and AB/Al_2O_3-coated samples, as shown in Fig. 2(b). On the other hands, the intensity of peaks C and D was strongly observed for AB-coated sample because the AB has only six electrons and X-ray penetrates AB easily. These results indicated that the nano-Al_2O_3 particles were rather uniformly distributed over the surface of $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ particles, even if AB particles were mixed with nano-Al_2O_3 particles, because a decrease in the intensity of the peaks A and B in the O *K*-edge spectra and peaks C and D in the Mn *L*-edge spectra corresponding to the layered structure means that the surface of $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ particles was well covered with nano-Al_2O_3 powder.

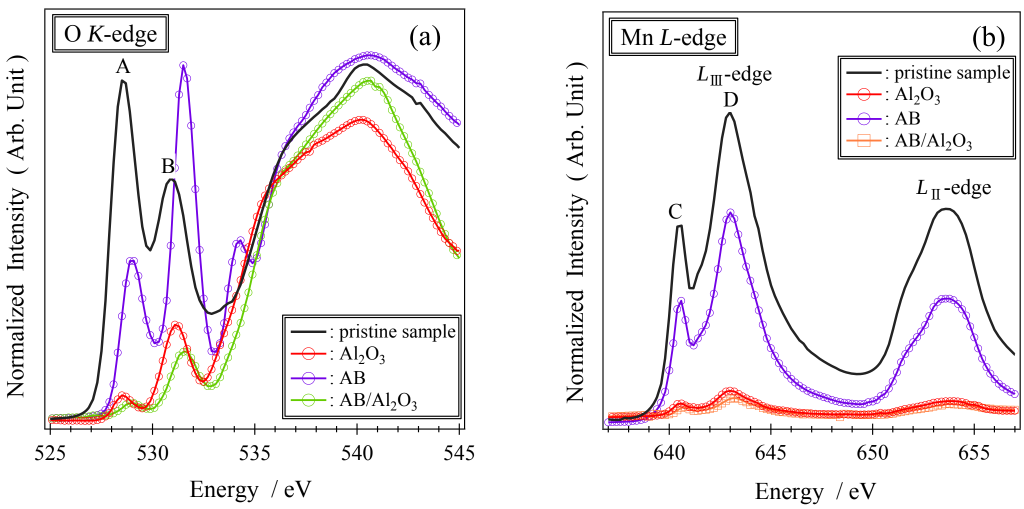

Figure 2. (a) O *K*-edge and (b) Mn *L*-edge XANES spectra for the pristine and coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ (UVSOR/BL4B).

Figure 3(a) shows the C-rate dependence of discharge capacity retention of the Li/pristine and coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ cells after stepwise pre-cycling treatment at 298 K. The Al_2O_3-coated sample showed the smaller discharge capacity retention with C-rate when it was compared with the pristine sample. Al_2O_3 is an insulating material without Li-ion conductivity, therefore, it is thought that the diffusion of Li-ion on the surface of $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ was barred by Al_2O_3 layer. On the other hand, the AB and AB/Al_2O_3-coated samples showed almost the same discharge capacity retention. Figure 3(b) shows the cycle dependence of discharge capacity of the Li/pristine and coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ cells at 318 K. The Al_2O_3-coated sample showed the smaller initial discharge capacity compared with that of the pristine sample. With cycles, the discharge capacity of the Li/pristine and AB-coated samples cells decreased gradually, while the discharge capacity of the Li/Al_2O_3 and AB/Al_2O_3-coated samples cells were almost constant value after 35 cycles. In this case, it is thought that the cycle performance at high temperature was improved since the chemical reaction between $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ and electrolyte was suppressed by the existence of oxide-layer.

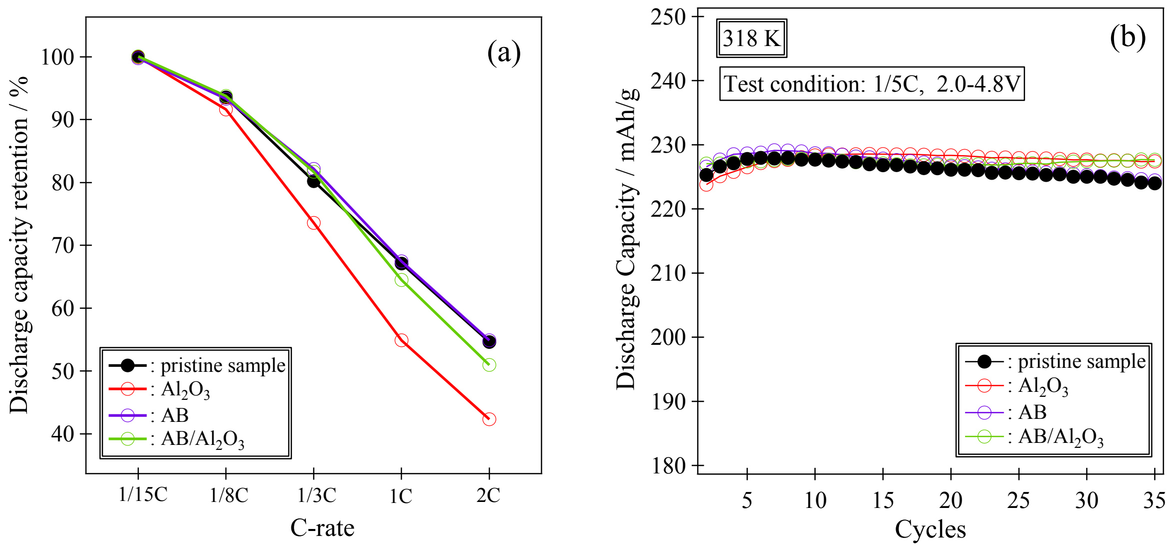

Figure 3. (a) C-rate dependence of discharge capacity retention of the Li/pristine and coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ cell after stepwise pre-cycling treatment at 298 K. (b) Cycle dependence of discharge capacity of the Li/pristine and coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ cells at 318 K with a current density of 1/5C and cut-off voltages of 2.0 and 4.8 V.

4. Summary

In this study, AB and/or Al_2O_3-coated $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ were prepared using mechanochemical reaction. The optimal preparation condition of coating to $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ was investigated by SEM, XRD, and XANES measurements. In electrochemical tests, the AB/Al_2O_3-coated sample showed the better cycle performance at 318 K, compared with that of the Li/pristine $Li_{1.20}Mn_{0.55}Ni_{0.16}Co_{0.09}O_2$ cell, without degrading the discharge capacity and C-rate performance. These results demonstrate that the mechanochemical AB/Al_2O_3-coating process is an effective way of improving the electrochemical performance.

References

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