Cyclic Properties of Li[Co$_{0.17}$Li$_{0.28}$Mn$_{0.55}$]O$_2$ Cathode Material

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Received May 20, 2003

A Li[Co$_{0.17}$Li$_{0.28}$Mn$_{0.55}$]O$_2$ cathode compound was prepared by a simple combustion method. The X-ray diffraction pattern showed that this compound could be classified as α-NaFeO$_2$ structure type with the lattice constants of $a = 2.8405(9)$ Å and $c = 14.228(4)$ Å. According to XANES analysis, the oxidation state of Mn and Co ions in the compound were +4 and +3, respectively. During the first charge process, the irreversible voltage plateau at around 4.65 V was observed. The similar voltage-plateau was observed in the initial charge profile of other solid solution series between Li$_3$MnO$_3$ and LiMnO$_2$ (M=Ni, Cr…). The first discharge capacity was 187 mAh/g and the second discharge capacity increased to 204 mAh/g. As the increase of cycling number, one smooth discharge profile was converted to two distinct sub-plateaus and the discharge capacity was slowly decreased. From the Co and Mn K-edge XANES spectra measured at different cyclic process, it can be concluded that irreversible transformation of phase is occurred during continuous cycling process.

Key Words : Cathode, Layered structure, Lithium battery, XANES, Cyclic properties

Introduction

Lithium cobalt oxide (LiCoO$_2$) is an useful cathode material with good electrochemical performances for lithium secondary battery. However, the relatively high cost of the cobalt and the lure of larger specific capacity have led to the study of other possible cathode materials. Recently, some groups investigated solid solution series between Li$_2$MnO$_3$ and LiMO$_2$ (M=Cr, Ni) as an alternative cathode material for LiCoO$_2$. The Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$ is well-known to an electrochemically inactive material because the Mn$^{4+}$ in Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$ normally cannot be oxidized beyond the +4 oxidation state in order to extract Li from its lattice. However, it is interesting that the solid solution series between Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$ and LiMO$_2$ (M=Cr, Ni, Co) showed very high discharge capacity over 200 mAh/g when they cycled with an upper cut-off voltage of about 4.8 V.

Paulsen et al. reported that Li[Li$_{1/2}$Co$_{1/2}$]MnO$_2$ can be regarded as a solid solution between Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$ and LiCrO$_2$. Lu et al. also investigated solid solution series between Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$ and LiMO$_2$ (M=Cr, Ni). Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$ and Li[Cr$_{1/3}$Li$_{2/3}$]Mn$_{2/3}$O$_2$, derived from Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$ by substitution of Li$^+$ and Mn$^{4+}$ by Ni$^{2+}$ or Cr$^{3+}$, respectively. When the cells containing such oxides charged to about 4.8 V, it exhibited an irreversible capacity at around 4.5-4.7 V. After the first charge process, the cells were reversibly cycled with a high capacity of over 200 mAh/g in the voltage range of 2.0 and 4.8 V.

In the previous report, we investigated the electrochemical properties of Li[Ni$_{1/3}$Li$_{2/3}$]Mn$_{2/3}$O$_2$ compounds prepared by the simple combustion method. Compared to mixed hydroxide or sol-gel methods adopted by other researcher, the simple combustion method is very simple and it will cut down the manufacturing cost of cathode powders. Among the various compositions in the previous work, the Li[Ni$_{1/3}$Li$_{2/3}$]Mn$_{2/3}$O$_2$ compound (x=0.17 in Li[Ni$_{1/3}$Li$_{2/3}$]Mn$_{2/3}$) showed the largest specific capacity and the most stable cycle performance.

In this study, Li[Co$_{0.17}$Li$_{0.28}$Mn$_{0.55}$]O$_2$ cathode material, which composition is x=0.17 in Li[Co$_{0.17}$Li$_{0.28}$Mn$_{0.55}$]O$_2$, was prepared by the simple combustion method. The stoichiometry of Li[Co$_{0.17}$Li$_{0.28}$Mn$_{0.55}$]O$_2$ is determined from the assumptions that transition metal Co and Mn are in the oxidation states of +3 and +4, respectively. This compound can be derived from Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$ by substitution of Li$^+$ and Mn$^{4+}$ by Co$^{3+}$ and also classified solid solution series between LiCoO$_2$ (17%) and Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$ (83%). The structure and electrochemical properties of the powder were investigated using XRD and charge/discharge method. Specially, phase transformation during the cycling was observed by XANES analysis.

Experimental Section

Li[Co$_{0.17}$Li$_{0.28}$Mn$_{0.55}$]O$_2$ was prepared by the simple combustion method from manganese acetate tetrahydrate [Mn(CH$_3$COO)$_2$·4H$_2$O], cobalt(III) nitrate hexahydrate [Co(NO$_3$)$_2$·6H$_2$O], lithium acetate dihydrate [CH$_3$CO$_2$Li·2H$_2$O] and lithium nitrate [LiNO$_3$]. At first, a stoichiometric amount of source materials of Co, Ni and Li were mixed with distilled water and continuously stirred at 100 °C on a hot plate. After evaporation of excess water, a viscous gel with green color was obtained. When the resulting gel was fired around 400 °C, a vigorous decomposition process of organic material occurred accompanying ash like powders.
The decomposed powder was ground and heated at 500 °C for 3 hours. The heat-treated powder was re-ground and re-heated at 1000 °C in air for 6 hours. Then, it was cooled down to room temperature within a few minutes.

X-ray diffraction (XRD) data were collected using Philips X-ray diffractometer in the 2θ range from 15 to 70° with Cu-Kα radiation (λ = 1.5406 Å). The electrochemical cell was assembled in a dry room using the Li[Co0.17Li0.28Mn0.55]O2 powder, lithium, porous polyethylene film and 1 M LiPF6 solution in 1 : 1 volume ratio of ethylene carbonate/dimethyl carbonate. For the preparation of positive electrode, 0.4 g of polyvinyl difluoride (Aldrich) was dissolved in about 25 g N-methyl-2-pyrrolidone for one hour and then 4 g of Li[Co0.17Li0.28Mn0.55]O2 powder and 0.6 g of Super P black (MMM Carbon Co.) were added. After a day of ball mill process, viscous slurry was coated on an aluminum foil using a doctor blade and obtained a film with uniform thickness. After then, it was dried at 90 °C in an oven. The obtained cathode film was hot pressed at 135 °C to increase tap density. The thickness of the cathode film was about 30 µm. Cyclic voltammograms were measured from the test cells by a Biologic Mac Pile II potentiostat. Sweep range and scan rate were 2.0-5.0 V and 0.05 mVS⁻¹, respectively. The galvanostatic charge-discharge test was carried out using Toyo charge-discharge system. The test cells were charged up to 4.8 or 4.6 V versus Li/Li⁺ with a specific current of 20 mA/g, and then discharged to 2.0 V with the same specific current.

The XANES (X-ray absorption near-edge structure) measurement was carried out during initial charge-discharge process. In detail, cathodes separated from the cell were washed with dimethyl carbonate (DMC) solution and dried in a vacuum oven. These cathodes were put into Mylar film bag and sealed in a glove box to prevent contamination. The Co and Mn K-edge X-ray absorption spectra recorded on the BL7C1(EC) beam line of Pohang Light Source (PLS) with the ring current of 140-170 mA at 2.5 GeV. Si(311) double crystal monochromator has been used with detuning to 75% in intensity to eliminate high-order harmonics. The data have been collected in transmission mode with the nitrogen gas-filled ionization chambers as detectors. In order to remove an energy shift problem, X-ray absorption spectra for the metal foils has been measured simultaneously in every measurement as the metal foil was positioned in front of the window of the third ion chamber.

Results and Discussion

Figure 1 shows the X-ray diffraction patterns of Li[Co0.17Li0.28Mn0.55]O2 compound and references. Small XRD peaks between 20 and 25° are attributed to the superlattice ordering of Li and Mn in the transition-metal containing layers. Except for the superlattice peaks, all peaks of the XRD patterns can be indexed to α-NaFeO₂ structure (space group: R3m) with lattice constant of a = 2.8405(9) Å and c = 14.228(4) Å. A c/a ratio is 5.009, indicating a layer structure. In the previous reports, a similar compound was prepared by a calcination of the source-mixture with constituent elements. However, this method did not successfully form a single phase without excess Li₂O. By contrast, the simple combustion method used in this work makes possible to form a single phase without excess Li₂O.

To examine a oxidation state of Mn and Co, the K-edge XANES spectra for fresh Li[Co0.17Li0.28Mn0.55]O₂ compound were measured. The K-edge XANES spectra of Li₂MnO₃, LiCoO₂ were used as references because Mn oxidation state in Li₂MnO₃ and Co oxidation state in LiCoO₂ are already known to 4+ and 3+, respectively. Figure 2a shows the Mn K-edge XANES spectra for Li[Co0.17Li0.28Mn0.55]O₂ and Li₂MnO₃. The edge positions and spectrum-shape of Li[Co0.17Li0.28Mn0.55]O₂ compound are the same as those of Li₂MnO₃, which indicates that Mn oxidation state in Li[Co0.17Li0.28Mn0.55]O₂ compound is 4+. The very similar edge positions of Co K-edge XANES spectra between Li[Co0.17Li0.28Mn0.55]O₂ and LiCoO₂ are displayed in Figure 2b. This shows Co oxidation state in Li[Co0.17Li0.28Mn0.55]O₂ compound is same as that in LiCoO₂ (Co³⁺). But, a slight difference of spectra-shape implies that there may be a little difference of Co-Co long-range patterns between two compounds. According to the XRD and XANES analyses, it is clear that the Li[Co0.17Li0.28Mn0.55]O₂ compound prepared in this work shows a single phase compound with Mn⁴⁺ and Co³⁺ oxidation states.

The electrochemical property of the compound is investigated from a test cell. Figure 3 shows the cyclic voltammogram for the compound at a sweep range of 2.0-5.0 V with
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Two peaks at around 4.15 and 4.65 V appear in the initial oxidation step. Specially, a large peak at 4.65 V means that there is a long voltage plateau at around this range during first charge process. By contrast, only one peak at around 3.15 V is observed in the subsequent reduction and oxidation curves. This suggests that the irreversible phase transition is occurred during the initial charge process.

Similar irreversible phase transformation has been investigated in the solid-solution series between Li[Li_{1/3}Mn_{2/3}]O$_2$ and LiMO$_2$ (M=Cr, Ni, Co).\textsuperscript{1-6} Lu et al. suggested that the irreversible plateau occurred due to the simultaneous extraction of both Li and O from the material.\textsuperscript{1-5} They assumed that the portion of the first charge to 4.45 V correspond to deintercalation of lithium and oxidation of metal ion (Cr, Ni) and the plateau at about 4.5-4.7 V correspond to the removal of the remaining lithium from the lithium layer, along with the simultaneous ejection of oxygen. On the contrary, Robertson and Bruce have presented that the exchange of Li$^+$ by H$^+$ in non-aqueous media results in the long irreversible plateau.\textsuperscript{12,13} The origin of the plateau and phase transformation during first charge process is still remained unsolved.

Figure 4 shows the discharge capacity vs. the cycle number of a test cell using the Li[Co$_{0.17}$Li$_{0.28}$Mn$_{0.55}$]O$_2$ compound. The specific current and voltage range were 20 mA/g and 4.8-2.0 V, respectively. The compound delivers the 1$^{\text{st}}$ discharge capacity of 187 mAh/g. The 2$^{\text{nd}}$ discharge capacity increased to 204 mAh/g, however, after the 2$^{\text{nd}}$ cycle, the capacity slowly decreased as the increase of cycle number. The 1$^{\text{st}}$, 5$^{\text{th}}$, 10$^{\text{th}}$ and 20$^{\text{th}}$ charge-discharge curves in the voltage range of 2.0-4.8 V are shown in Figure 5a. After the 1$^{\text{st}}$ charge curve with long voltage plateau, the 1$^{\text{st}}$ discharge curve shows smooth profile. This smooth charge-discharge curve after initial charge process corresponds to other solid-solution series between Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$ and LiMO$_2$ (M=Cr, Ni).\textsuperscript{1-6} However, as the increase of cycle number, smooth profile is slowly converted to two sub-plateaus, which indicates that the structure of Li[Co$_{0.17}$Li$_{0.28}$Mn$_{0.55}$]O$_2$ compound is transformed to a spinel phase. This finding is unexpected result since other solid solution series between Li[Li$_{1/3}$Mn$_{2/3}$]O$_2$ and LiMO$_2$ (M=Cr, Ni) are stable after initial charge process. To investigate the effect of voltage range, the cut-off voltage during the charge process is lowered from 4.8 to 4.6 V. Figure 5b shows the change of voltage profile measured in the voltage range of 2.0-4.6 V. The sub-plateau in the discharge profile measured at 20$^{\text{th}}$ cycle becomes a
slight faint, but phase transformation is still observed.

X-ray absorption near-edge structure (XANES) analysis is performed to get more information about change of electronic structure during cycling process. Figure 6 shows the Co K-edge XANES spectra for the compound measured at different cyclic process. For the fresh compound, a weak absorption peak A at 7709.6 eV represents the transition of 1s electron to an unoccupied 3d-e orbital of Co$^{3+}$ ion with low spin (t_{2g}^6) electronic configuration. Although the 1s $\rightarrow$ 3d transition is electric dipole-forbidden transition in an ideal octahedral symmetry, the appearance of weak absorption peak is due to pure electric quadrupole coupling and noncentrosymmetric environment of slightly distorted CoO_{6} octahedral site. Both peaks B and C appear from the electric dipole-allowed transition of a 1s core electron to an unoccupied 4p bound state with T_{1u} symmetry. The peaks B and C correspond to two final states of a 1s$^{1}$3d$^{7}$\textit{L} state with shake down process by ligand to metal charge transfer (LMCT) and a 1s$^{1}$3d$^{6}$4p$^{1}$ without shake down process, respectively, where \textit{c} and \textit{L} indicate a 1s core hole and a ligand hole. The shoulder peak B occurs on the lower energy region of about 10 eV with respect to main absorption C peak at 7729 eV since the 1s core electron of 3d$^{7}$\textit{L} state is less bounded on the more screened nucleus with respect to that of 3d$^{6}$ state.

When the Li[Co_{0.17}Li_{0.28}Mn_{0.55}]O_{2} compound charged to 4.8 V, the edge position of the Co K-edge XANES spectrum shifts to higher energy value. This positive shift shows the increase of average oxidation state of Co ion from 3+ to about 4+. The significant decrease of peak B at the charging to 4.8 V means that the delithiation gives rise to transition of hole state (\textit{L}) from oxygen to Co atom. On the delithiation, the 3d$^{7}$\textit{L} state of LMCT process is replaced by the 3d$^{5}$ state of Co$^{4+}$ ion as another hole state, which means that the hole state is relatively localized at Co atomic site under the local structural distorted environment. The abrupt disappearance of peak B can be also another hint about the local structural distortion by the formation of Co$^{4+}$ ion, in addition to the increase of intensity of peak A.

The spectra marked 'after 1st cycle' and 'after 20th cycle' are measured from a sample discharged to 2.0 V after charging to 4.8 V. After 1st cycle, the edge position back to lower energy value, indicating the reduction of Co ion to lower oxidation state. However, the shape of Co K-edge spectra slightly changed from the pristine state, which corresponds to the irreversible phase transformation during the first cycle. After 20th cycle, more peak-shape change is observed in the Co K-edge spectrum for the compound. Specially, a weak shoulder peak is newly appeared at around ~7725 eV. This change may be attributed to the structural transformation during cycling.

The Mn K-edge XANES spectra for the compound measured at different cyclic process are shown in Figure 7. According to Figure 2, Mn oxidation state in fresh compound is 4+. In the pre-edge region A, spectra display a weak double-peak structure. It is assigned to 1s $\rightarrow$ 3d transition, which is observed with weak intensity for octahedral coordination and strong intensity for tetrahedral coordination ones. The experimental spectra are consistent with octahedral or near-octahedral coordination of manganese. The intermediate bump at 6550 eV is very prominent for pristine sample. Its magnitude is related to the connectivity between MnO_{6} octahedra in the structure. After the sample was charged to 4.8 V, the shape of the near-edge spectrum in the region B
and C was significantly changed. This result does not present increase of Mn oxidation state because Mn$^{3+}$ normally cannot be oxidized beyond 4+ in an octahedral oxygen environment. This change can be explained by possible rearrangement of the Mn local structure. The intermediate bump at 6550 eV also disappears because of the increase of local distortion around Mn site and the following decrease of overlap integral between Mn-O bondings.

The spectra marked after the 1st cycle and after the 20th cycle were measured from the discharged samples cycled between 2.0-4.8 V. The spectrum measured after the 1st cycle showed a slight negative shift compared with that of pristine state. It suggests that the Mn oxidation state is slightly decreased to less than 4+ although the local structure around Mn site is reversible with reappearance of the intermediate bump. But, the pre-edge peak intensity (peak A2) in the higher energy region for 1st cycle is larger than that of LiMn$_2$O$_4$. Since the peak A1 and A2 correspond to electronic transition to unoccupied t$_2g$ and e$_g$ energy levels, respectively, the fact means the Mn$^{3+}$ is relatively rich in the 1st cycle.

More shift of the edge position to negative direction was occurred after the 20th cycle. This Mn K-edge XANES spectrum is almost very similar with that of LiMn$_2$O$_4$ with coexistence of Mn$^{3+}$ and Mn$^{4+}$ ions. Therefore, it suggests that the Mn oxidation state in the compound decreased to about 3.5+ after the 20th cycle. This result can be explained by the phase conversion from layered to spinel-like structure. According to the Shiraiishi et al., the region B and C can be ascribed mainly to the Mn$^{3+}$ and Mn$^{4+}$ in LiMn$_2$O$_4$ compound, respectively. The intermediate bump is almost disappeared after 20 cycles, which suggests that the connectivity between MnO$_6$ octahedra in the structure is destroyed during cycling.

As mentioned earlier, this phase transformation during cycling is unexpected. Similar solid solutions of Li[Ni$_{1/3}$-Li$_{1/3}$-2x/3,Mn$_{2/3}$-x/3]O$_2$ is not detected decrease of Mn oxidation state after 20th cycle. However, Robertson et al. reported that Li$_3$MnO$_4$ converted to spinel-like phase on cycling. They suggested proton exchange between Li$^+$ in the oxide and H$^+$ in the electrolyte is a main reason of electrochemical activity of Li$_3$MnO$_4$. This reaction is partially reversible, so the compound converts spinel-like phase during cycling.

In the case of Li[Co$_{0.17}$Li$_{0.28}$Mn$_{0.55}$]O$_2$ compound, which is a solid solution between Li$_2$MnO$_3$ and LiCoO$_2$, shows similar phase transition with Li$_2$MnO$_3$. The phase transformation can give negative effect to cycle performance of the compound. However, Armstrong et al. reported that the spinel-like material formed during intercalation processes from layered structure have better reversibility compared with the spinel phase prepared at high temperature. Considering high discharge capacity and simple processing method, this material can be adopted as a possible cathode material if cycle life can be improved.

Conclusions

Li[Co$_{0.17}$Li$_{0.28}$Mn$_{0.55}$]O$_2$ compound was prepared by a simple combustion method. This method makes possible form a single phase without excess Li$_2$O. Except for the superlattice peaks, all peaks of the XRD patterns can be indexed to a-NaFeO$_2$ structure (space group: R3m) with the lattice constant of $a = 2.8405(9)$ Å and $c = 14.228(4)$ Å. From the comparison of XANES spectra with those of Li$_2$MnO$_3$ and LiCoO$_2$, the oxidation states of Mn and Co ion in the fresh compound were confirmed to 4+ and 3+, respectively. The irreversible voltage-plateau at 4.65 V is general result for solid-state series between Li$_2$MnO$_3$ and LiMO$_2$ (M=Ni, Co, Cr). The compound delivers a first discharge capacity of 187 mAh/g. Although the second discharge capacity increased to 204 mAh/g, due to the irreversible phase transformation, the capacity slowly decreased as the increase of cycle number.

Acknowledgement. This work was supported by the Korea Ministry of Information and Communication (MIC) (No. 2003-S-003).

References