Effect of Separator and Anode on Electrochemical Characteristics and Crystal Structure of Lithium-ion Battery Cathode Material 0.4Li$_2$MnO$_3$-0.6LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$

Noriko KASAI,a,b,* Ryota FUJISHIMA,a Naoya ISHIDA,a Naoto KITAMURA,a and Yasushi IDEMOTOa,*

a Faculty of Science & Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510, Japan
b Mitsubishi Paper Mills Limited, 46 Wadai, Tsukuba, Ibaraki 300-4247, Japan
* Corresponding authors: 7218701@ed.tus.ac.jp, idemoto@rs.tus.ac.jp

ABSTRACT

We studied the average crystal structural change during charging and discharging of a 0.4Li$_2$MnO$_3$-0.6LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ battery cathode in combination with a Li-metal anode, graphite anodes, and three types of separators. Prelithiation of the graphite anode enabled stable charge and discharge of the cathode. The average structure of the cathode after the 5th discharge did not change significantly in combination with a Li-metal anode, graphite anodes, and three types of separators. Prelithiation of the graphite anode enabled stable charge and discharge of the cathode. The average structure of the cathode after the 5th discharge did not change significantly due to the difference in the anodes and separators. However, after the 55th discharge, the difference in the electron density distribution and the distortion of the M-O$_6$ octahedra for the different separators increased. The findings suggest that the changes in the crystal structure of a cathode over a long-term cycle should be studied with the anodes and separators used in actual batteries rather than Li-metal anodes and conventional separators.

Keywords: Lithium Ion Battery, Prelithiation, Separator, Crystal Structure

1. Introduction

In recent years, lithium-ion secondary batteries (LiBs) have been widely used for mobile devices as well as in-vehicle and power storage applications. Further miniaturization, higher capacity, and higher energy density are currently being investigated. For these purposes, lithium-rich rock-salt-structured oxides $x$Li$_2$MnO$_3$-(1−$x$)LiMO$_2$ (M = Mn, Ni, Co), which exhibit high discharge capacity when charged 4.5 V or above, are attracting attention.1-7 These materials exhibit a very high capacity of over 200 mAh/g when charged at high voltage. Previous works have shown that the Li$_2$MnO$_3$ component of these solid solution materials has relatively good characteristics at $x = 0.4$ and 0.5.8-11 Therefore, we have previously investigated the average and local structural changes associated with charging and discharging for various conditions, such as charge/discharge depth, charge discharge rate, and operating temperature, in this composition.9-11 However, these earlier studies used Li-metal anodes and polypropylene (PP) microporous film separators. Cathode materials are often studied in this combination, but they are different from the anodes and separators used in commercially available LiBs. Carbon-based materials such as graphite or hard carbon are often used for the anode.12 Some lithium-ion batteries use lithium titanate to improve the cycle characteristics and safety,13,14 or use a mix of Si-based or Sn-based materials to increase capacity. Li-metal anodes have problems with lifecycle and safety, and are not common in LiBs on the market.15 Although PP film separators are widely used, polyethylene (PE) film and PP-PE laminated type separators are also available. The structure of the film separator differs greatly depending on whether it is a dry film or wet film and single layer type or laminated type.16,17 Furthermore, some LiBs use nonwoven-based separators, which are very different in structure and properties from film-based separators.16-19 In recent years, many separators have been coated with ceramic to improve safety.18,19 As described above, there are various types of anodes and separators. However, there have been few studies on the influence of anodes or separators on structural changes in electrode materials.

In this work, we investigated how different anodes and separators affect the structure of the solid solution cathode material 0.4Li$_2$MnO$_3$-0.6LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$. We used Li-metal and graphite as anode materials, and PP films and nonwoven-based separators as separators. Charging and discharging were performed over 5 cycles to compare steady states and 55 cycles to compare cycle characteristics. The average crystal structure and electronic structure were analyzed using neutron diffraction and synchrotron X-ray diffraction measurements using the cathode after charging and discharging, and the valence and local structure of each element were investigated by X-ray absorption fine-structure (XAFS) measurements.
2. Experimental

2.1 Cathode material synthesis\textsuperscript{8-11}

0.4Li\textsubscript{2}MnO\textsubscript{3}-0.6LiMn\textsubscript{1/3}Ni\textsubscript{1/3}Co\textsubscript{1/3}O\textsubscript{2} (Li\textsubscript{1.167}Mn\textsubscript{0.5}Ni\textsubscript{1.67}Co\textsubscript{1.67}O\textsubscript{2}) was synthesized by coprecipitation. Manganese nitrate hexahydrate (98\% Wako Pure Chemical Industries, Ltd.), nickel nitrate hexahydrate (98\% Wako Pure Chemical Industries, Ltd.), and cobalt nitrate hexahydrate (98\% Wako Pure Chemical Industries, Ltd.) in specific ratios were measured and dissolved in twice-distilled water. This mixture was then dripped into sufficient quantities of an aqueous solution of lithium hydroxide monohydrate (98–102\% Wako Pure Chemical Industries, Ltd.) to form a precursor. This was suction filtered and dried in air for 24 h at 100°C. From the results of inductively coupled plasma atomic emission spectroscopy (ICP-AES), the degree of lithium deficiency with regard to the target composition was determined. To compensate for this deficiency, an appropriate quantity of lithium hydroxide monohydrate was added. Lithium hydroxide monohydrate was then added to the dried precursor and blended. This mixture was subjected to preliminary sintering at 600°C for 15 h in air, ground into powder, blended, and finally subjected to primary sintering at 950°C for 15 h in air to yield the target samples.

2.2 Characterization of the cathode material

The phase of the synthesized cathode material was identified by powder X-ray diffraction measurements (Panalytical, Empyrean, CuKα radiation, 45 kV, 40 mA). The lattice constants were estimated using a least squares technique based on the diffraction data. The composition of the metallic components in the material was determined by inductively coupled plasma–atomic emission spectroscopy (ICP-AES, Shimadzu Corporation, ICPE-9000). For the pristine material, the sum of the composition ratio of the metal components was normalized to be 2. For the electrode samples, the sum of the metal components does not equal 2 due to Li loss. Therefore, the Li composition was calculated so that the sum of the compositions of Mn, Ni, and Co was equal to that of the pristine.

2.3 Electrochemical measurements

For the cathode, 0.4Li\textsubscript{2}MnO\textsubscript{3}-0.6LiMn\textsubscript{1/3}Ni\textsubscript{1/3}Co\textsubscript{1/3}O\textsubscript{2}, Super C65 (TIMCAL Ltd.) was used as a conductive agent, and KF polymer #1100 (KUREHA Corp.) as PVDF binder in a weight ratio of 80:10:10 and formed into a sheet. The sheet was pressure bonded at roughly 40 MPa and vacuum deaerated at 110°C for 12 hours. For electrochemical measurements, a two-electrode cell (Toyo System Co., Ltd.) was used. Lithium metal (thickness: 0.2 mm, purity: 99.0\% or higher, Honjo Metal Co., Ltd.) or graphite was used for the anodes. The graphite anode was prepared by mixing artificial graphite (MCMB, D50 = 11.7µm, BTR New Energy Materials Co., Ltd.), DENKA Black Li-400 (Denka Co., Ltd.) as a conductive agent, and KF polymer #1100 (KUREHA Corp.) as PVDF binder in a weight ratio of 95.5:0.5:4, and applying it to Cu foil. In the case of the graphite anode, coating weight of cathode was adjusted so that negative to positive electrode capacity ratio (N/P ratio) was 1.05–1.60. 1-mol/L LiPF\textsubscript{6}-EC:DMC solution (volume ratio 1:2, Kishida Chemical Co., Ltd.) was used as the electrolyte. Table 1 shows the three types of separators used in this study. In addition to the conventional PP film separator, two types of nonwoven-based separators, which have completely different structures from the PP film, were used. CCNW (Mitsubishi paper Mills Ltd.) is a ceramic-coated polyethylene terephthalate (PET) nonwoven separator, and NW (Mitsubishi paper Mills Ltd.) is a nonwoven separator consisting of cellulose and PET fibers. The nonwoven separators have submicron-scale pores, while the PP film has tens of nm-scale pores. The SEM images of CCNW and NW are shown in Fig. S1. Electrolyte uptake, ionic conductivity and wettability of the separators are shown in Table S1 and Fig. S2. The cells were assembled in an argon environment inside a purge-type glove box (dew point < -80°C, Miwa Manufacturing Co., Ltd.).

Charging/discharging experiments were conducted in a constant temperature bath at 25°C using charge/discharge measurement instruments (Aska Electronic Co., Ltd.). The first 5 cycles of charge and discharge had a constant current of 20 mA/g (0.1 C), and the final charge and discharge voltage was 4.8 V, 2.5 V vs. Li/Li\textsuperscript{+} for the Li-metal anode, and 4.7 V, 2.0 V for the graphite anode. There was an open circuit time of 5 min between each charge and discharge. For the cycle test, 50 cycles of charge and discharge with a constant current of 200 mA/g (1 C) were performed after the 5th cycle.

The graphite anode was preprocessed by the following method using Li-metal as a counter electrode (prelimitation).\textsuperscript{20,21} After charging and discharging for one cycle at a constant current of 0.1 C with a charge termination voltage of 5 mV and a discharge end voltage of 1.5 V, it was recharged at 0.1 C for 1 hour and used as a state of charge (SOC) of 10\%.

2.4 Crystal and electronic structure analysis

Neutron diffraction measurements were conducted at BL20 at J-PARC, Japan. The average crystal structure was analyzed by the Rietveld method (Z-Rietveld ver. 1.1.0).\textsuperscript{22} Synchrotron X-ray diffraction measurements were performed at BL19B2 at SPring-8, Japan. The average crystal structure was analyzed by the Rietveld method (RIETAN-FP ver. 2.83)\textsuperscript{23} and the electron density distribution for the samples was investigated based on the maximum entropy method (MEM) using the Dysnomia (ver. 1.0) program.\textsuperscript{24} XAFS measurements were performed at the BL14B2 beamline of SPring-8; electronic structure and local structure analyses were carried out using Athena (ver. 0.9.26).\textsuperscript{25}
3. Results and Discussion

3.1 Characterization of cathode material and electrochemical performance

Figure 1 shows a powder X-ray diffraction pattern for the synthesized cathode material. The main peak can be assigned to the Li$_2$MnO$_3$ type structure (space group $C2/m$), and was confirmed as being single phase without impurities. The lattice constants calculated by the least squares method are $a = 0.494(1)$ nm, $b = 0.852(2)$ nm, $c = 0.503(1)$ nm, $\beta = 109.3(2)$ degrees. In the composition analysis of the synthesized cathode material by ICP-AES, the metal composition of the synthesized material was almost similar to the nominal ratio of the material hexahydrates. (Li : Mn : Ni : Co = 1.144(4) : 0.516(1) : 0.1687(5) : 0.1705(5)).

Figure 2 shows 5 cycles charge and discharge curves and dQ/dV plots of 0.4Li$_2$MnO$_3$-0.6LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ with (a) Li-metal anode, (b) graphite anode without prelithiation, and (c) prelithiated graphite anode. For the Li-metal anode and prelithiated graphite anode, a stable capacity of about 200 mAh/g was obtained, whereas for the graphite anode without prelithiation, the cycle capacity was significantly reduced. The results of the three-electrode cell using the cathode, graphite anode without prelithiation, and the reference electrode Li-metal, showed that the graphite anode potential did not decrease and the cathode potential became too high. It might be the cause of cycle capacity deterioration in Fig. 2(b). When using prelithiated graphite anode, the anode potential was normal. In this work, the graphite anodes were recharged to SOC 10% as prelithiation. The effect of prelithiation could not be obtained with SOC 0%, and if the SOC was too high, the anode capacity was insufficient for the cathode capacity. Therefore, about 10–20% SOC was appropriate for recharging. Preliminary study indicated that the effect of prelithiation could be obtained even with a LiMn$_{1/3}$Ni$_{1/3}$-Co$_{1/3}$O$_2$ cathode instead of Li-metal (Fig. S3). Prelithiation might enable stable charging and discharging by forming SEI on the surface of the graphite anode, inserting Li into the graphite anode, or lowering the electrode potential.

Figure 3 shows the charge and discharge curves for 5 cycles at 0.1 C and 50 cycles at 1 C, for a total of 55 cycles, and dQ/dV plots of 0.4Li$_2$MnO$_3$-0.6LiMn$_{1/3}$Ni$_{1/3}$Co$_{1/3}$O$_2$ with a prelithiated graphite anode and three types of separators. The shape of the charge and discharge curve and the peak position of the dQ/dV plot did not change due to the difference in the separator. Figure 4 shows (a) discharge capacity, (b) discharge capacity retention rate, and (c) coulomb efficiency during the 55 cycles. While the capacity of the
PP film gradually decreased during the 1-C cycles, the nonwoven separators maintained a stable capacity. Since the nonwoven separators have a higher electrolyte retention property and larger pore size than the film separator, the electrolyte solution is less likely to dry up and the separator is less likely to be clogged. These factors may improve the cycle characteristics of the nonwoven separators. The coulombic efficiency was high in all separators except for the 1st cycle and the 6th cycle in which the rate was switched, but CCNW maintained a higher coulombic efficiency than the others during both the 0.1-C and 1-C cycles.

3.2 Variations in local structure and electronic structure determined by XAFS measurements

XAFS measurements were performed on the cathode after charging and discharging for 5 cycles using the prelithiated graphite anode and the three types of separators. Figure 5 shows (a) Mn $K$-edge X-ray absorption near edge structure (XANES) spectra, (b) Ni $K$-edge XANES spectra, and (c) Co $K$-edge XANES spectra. The high energy shows high valence, indicating that the elements are oxidized. In general, the curve shifts to the high energy side by Li deinsertion during charging and to the low energy side by Li insertion during discharging. Compared with the pristine material, the cathodes after charging and discharging tended to shift to the low energy side. From a comparison with standards, the valence of Mn was close to 4+, that of Ni was 2+ or 3+, and Co was nearly 3+ in the cathodes after 5th discharge. This is similar to the previous data for the Li-metal anode. There was no difference in redox valence when the separator was changed. Figure 5 shows the Fourier transform spectrum of the Extended X-ray absorption fine structure (EXAFS) of the (d) Mn $K$-edge, (e) Ni $K$-edge, and (f) Co $K$-edge. The Fourier transform spectrum of EXAFS represents the radial distribution function and shows the number and position of atoms surrounding the target atom. The value on the vertical axis depends on the distortion of the bond, with a larger value indicating less distortion. The peak on the left side of the graph is due to the first neighbor (M-O), and the peak on the right side is due to the second neighbor (M-M). Compared with the pristine material, the peak intensities of the Mn-O bond and Co-O bond decreased after the 5th discharge, with the decrease being particularly large for the Mn-O bond. This indicates a large influence of Mn on the local structure after the 5th discharge.

3.3 Analysis of average crystal structure by neutron and synchrotron X-ray diffraction, and determination of electronic structure

Synchrotron X-ray diffraction measurements and neutron diffraction measurements were performed using the pristine material and the cathodes after the 5th and 55th discharge. Figure 6 shows the fitting pattern of the pristine material and Table 2 shows the corresponding crystal structure parameters. The complementary use of neutrons and synchrotron radiation X-rays improved the fitting. Table 3 shows the site occupancies of the pristine material and the cathodes after the 5th and 55th discharge.
Figure 4. Cyclic characteristics of 5 cycles at 0.1 C and 50 cycles at 1 C; (a) discharge capacity, (b) discharge capacity retention rate and (c) coulombic efficiency.

Figure 5. XANES spectra at (a) Mn K-edge, (b) Ni K-edge and (c) Co K-edge, and Fourier-transforms of EXAFS spectra of (d) Mn K-edge, (e) Ni K-edge and (f) Co K-edge.
Figure 6. Rietveld refinement patterns of pristine in space group $C2/m$ by (a) neutron diffraction and (b) synchrotron X-ray diffraction.

Table 2. Final results of Rietveld refinement for $0.4Li_2MnO_3-0.6LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$. R-factor: $R_{wp} = 10.70\%$, $R_p = 7.35\%$, $R_e = 3.43\%$, Space group: $C2/m$, $a = 0.49338(1)$ nm, $b = 0.85418(1)$ nm, $c = 0.50193(1)$ nm, $\beta = 109.229(1)$ deg.

| Atom | Site | $x$   | $y$   | $z$   | 100 x $B$ (nm$^2$) | Site Occupancy |
|------|------|-------|-------|-------|--------------------|----------------|
| Li1  | 4g   | 0.107(2) | 0.0826 | 0.0833 | 0.0585             | 0.107(2)       |
| Ni1  | 4g   | 0.158(1) | 0.067(6) | 0.098(8) | 0.076(8) | 0.093(5) | 0.078(6) | 0.074(4) | 0.131(9) | 0.012(2) |
| Mn1  | 4g   | 0.560(3) | 0.562(9) | 0.585(21) | 0.568(12) | 0.616(20) | 0.573(10) | 0.572(18) | 0.502(11) | 0.012(1) |
| Co1  | 4g   | 0.203(2) | 0.2017 | 0.172 | 0.124(33) | 0.128(38) | 0.133(39) | 0.214(60) | 0.199(8) |
| Li2  | 2h   | 0.270(2) | 0.2193(4) | 0.2017 | 0.172 | 0.124(33) | 0.128(38) | 0.133(39) | 0.214(60) | 0.199(8) |
| Ni2  | 2h   | 0.205(1) | 0.238(7) | 0.2419 | 0.241(8) | 0.242 | 0.249(8) | 0.25 | 0.199(8) |
| Mn2  | 2h   | 0.324(5) | 0.348(18) | 0.2982 | 0.334(23) | 0.257(40) | 0.317(20) | 0.319(36) | 0.442(23) |
| Co2  | 2h   | 0.202(2) | 0.155(28) | 0.1989 | 0.163(35) | 0.217(60) | 0.164(31) | 0.161(54) | 0.166(34) |
| Li3  | 2c   | 0.2254(9) | 0.2257(12) | 0.17 | 1 |
| Ni3  | 2c   | 0.2254(9) | 0.2257(12) | 0.17 | 1 |
| Li4  | 4h   | 0.2518(7) | 0.3222(4) | 0.2253(6) | 0.30 | 1 |
| Ni4  | 4h   | 0.2518(7) | 0.3222(4) | 0.2253(6) | 0.30 | 1 |

Table 3. Site occupancies of $0.4Li_2MnO_3-0.6LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ materials.

| Atoms | Site | Pristine | PP film | CCNW | NW | PP film-Li | PP film | CCNW | NW |
|-------|------|----------|---------|------|----|------------|---------|------|----|
| Li1   | 4g   | 0.107(2) | 0.0826  | 0.0833 | 0.0585  | 0.0674  | 0.05 | 0.059 | 0.059 |
| Ni1   | 4g   | 0.158(1) | 0.067(6) | 0.098(8) | 0.076(8) | 0.093(5) | 0.078(6) | 0.074(4) | 0.131(9) | 0.012(2) |
| Mn1   | 4g   | 0.560(3) | 0.562(9) | 0.585(21) | 0.568(12) | 0.616(20) | 0.573(10) | 0.572(18) | 0.502(11) | 0.012(1) |
| Co1   | 4g   | 0.203(2) | 0.2017 | 0.172 | 0.124(33) | 0.128(38) | 0.133(39) | 0.214(60) | 0.199(8) |
| Li2   | 2h   | 0.270(2) | 0.191(34) | 0.2017 | 0.172 | 0.124(33) | 0.128(38) | 0.133(39) | 0.214(60) | 0.199(8) |
| Ni2   | 2h   | 0.205(1) | 0.238(7) | 0.2419 | 0.241(8) | 0.242 | 0.249(8) | 0.25 | 0.199(8) |
| Mn2   | 2h   | 0.324(5) | 0.348(18) | 0.2982 | 0.334(23) | 0.257(40) | 0.317(20) | 0.319(36) | 0.442(23) |
| Co2   | 2h   | 0.202(2) | 0.155(28) | 0.1989 | 0.163(35) | 0.217(60) | 0.164(31) | 0.161(54) | 0.166(34) |
| Li3   | 2c   | 0.988(2) | 0.593 | 0.581 | 0.589 | 0.52 | 0.508 | 0.5263 | 0.51 |
| Ni3   | 2c   | 0.988(2) | 0.593 | 0.581 | 0.589 | 0.52 | 0.508 | 0.5263 | 0.51 |
| Li4   | 4h   | 0.988(1) | 0.563(17) | 0.567 | 0.565 | 0.513 | 0.511(19) | 0.506(20) | 0.507(30) |
| Ni4   | 4h   | 0.988(1) | 0.563(17) | 0.567 | 0.565 | 0.513 | 0.511(19) | 0.506(20) | 0.507(30) |
| O1    | 4i   | 0.987(62) | 0.959(53) | 0.976(70) | 0.971 | 0.993 | 0.994 | 0.977 |
| O2    | 8j   | 0.980(39) | 0.988(46) | 0.986(47) | 0.982 | 0.943(44) | 0.946(40) | 0.980(47) |
cathode samples. The occupancies and positions of each site are not significantly different from the samples of the same composition previously reported. In the cathode samples after discharging, the Ni occupancy of the 4g site decreased and that of the 2c and 4h sites tended to increase compared with the pristine material. This may be due to lithium/nickel mixing between the transition metal layer 4g and Li layers 2c and 4h. The same tendency was observed for different anodes and separators. Table 4 shows the bond length between each metal site and oxygen site for the pristine material and cathode samples. Table 5 shows the distortion calculated from the bond length (d), the distortion calculated from the bond angle (2) of the M-O6 octahedra consisting of each metal site and oxygen, and the bond valence sum (BVS) of each site. After charging and discharging, the distortion of the TM layer 4g site was larger, while that of the 2b site was smaller than for the pristine material. After the 5th discharge, there was no significant difference in the distortion between the separators. However, after the 55th discharge with CCNW, the distortion of the transition metal layer 2b was smaller than the other separators, and that of the Li layer 2c was larger. The low distortion of the transition metal layer may affect the cycle characteristics of CCNW.

3.4 Electron density distribution by maximum entropy method

MEM analysis was performed based on Rietveld analysis using synchrotron radiation X-ray diffraction data, and the electron density distribution was studied. Figure 7 shows the electron density distribution between transition metal (TM) layer site or Li layer site and O layer site; (a) the TM layer 4g site and O layer 2i site, (b) 4g site and O layer 2j site, (c) the TM layer 2b site and 4i site, and (d) 2b site and 8j site, (e) the Li layer 4h site and 4i site, and (f) 4h site and 8j site. Comparing the bond length shown in Table 4 with the electron density in Fig. 7, as the bond length becomes shorter, the electron density increases and the covalent bond becomes stronger. When the bond length becomes longer, the electron density decreases and the covalent bond becomes weaker. Therefore, it was found that the bond length is dominated by the strength of the covalent bond. The electron density of 4h-O is lower than that of 4g-O or 2b-O, which indicates that Li-ions can easily diffuse. After the 55th discharge with CCNW, the electron density for 4g–4i and 4h–4i was higher than for the other separators, while the electron density for 4g–8j and 4h–8j was lower. After the 55th discharge with NW, the electron density for 2b–O was higher than the other separators. Regarding CCNW and NW after 55 cycles, the electron density of the transition metal layers 4g and 2b was high or the distortion was small (Table 5, CCNW, 2b). This would stabilized the

Table 4. Bond lengths between metal and oxygen of pristine, 5th, and 55th discharge electrodes.

| Site | Pristine | PP film | CCNW | NW | PP film | CCNW | NW |
|------|----------|---------|------|----|---------|------|----|
|      | 5th      | 5th     | 5th  |    | 5th     | 5th  | 5th |
| d (nm) | d (nm) | d (nm) | d (nm) | d (nm) | d (nm) | d (nm) | d (nm) |
| 4g–4i | 0.1936(3) | 0.1983(6) | 0.1958(7) | 0.1970(6) | 0.1964(7) | 0.1915(9) | 0.1936(12) | 0.1917(8) |
| 2b–4i | 0.2032(6) | 0.1841(11) | 0.1864(13) | 0.1841(11) | 0.1868(13) | 0.1892(18) | 0.1870(3) | 0.1813(16) |
| 4g–8j | 0.1906(3) | 0.1900(6) | 0.1896(7) | 0.1899(5) | 0.1925(6) | 0.1903(8) | 0.2012(12) | 0.1912(10) |
| 4g–8/2 | 0.1923(4) | 0.1989(8) | 0.2001(8) | 0.1983(7) | 0.1976(8) | 0.1996(13) | 0.1947(19) | 0.2006(9) |
| 2b–8j | 0.2050(3) | 0.2028(7) | 0.2044(6) | 0.2027(5) | 0.2016(6) | 0.2010(8) | 0.1939(13) | 0.2001(10) |
| 2c–4i | 0.2035(7) | 0.2235(11) | 0.2215(12) | 0.2234(10) | 0.2017(13) | 0.2193(16) | 0.2200(3) | 0.2269(15) |
| 4h–4i | 0.2216(4) | 0.2030(6) | 0.2140(6) | 0.2043(6) | 0.2145(7) | 0.2268(8) | 0.2036(12) | 0.2213(8) |
| 4h–8j | 0.1931(3) | 0.2137(7) | 0.2028(6) | 0.2136(5) | 0.2054(6) | 0.1982(8) | 0.2248(12) | 0.2058(10) |
| 4h–8/2 | 0.2139(4) | 0.2098(8) | 0.2077(8) | 0.2099(7) | 0.2108(8) | 0.2080(12) | 0.2128(18) | 0.2060(8) |

Table 5. Distortion parameters, , and of M-O6 octahedra, and BVS in the transition metal layer and Li layer obtained by Rietveld analysis of pristine, 5th, and 55th discharge electrodes.

| Sample | Site |  | BVS |
|--------|------|------------------|-----|
|        | 4g   | 1.003 | 11.91 | 3.27 |
|        | 2b   | 1.009 | 29.24 | 2.05 |
|        | 2c   | 1.010 | 29.77 | 1.08 |
|        | 4h   | 1.013 | 36.91 | 1.17 |
|        | 4g   | 1.007 | 19.09 | 3.04 |
|        | 2b   | 1.008 | 19.61 | 2.70 |
|        | 2c   | 1.003 | 13.75 | 0.91 |
|        | 4h   | 1.016 | 58.67 | 1.21 |
|        | 4g   | 1.006 | 18.89 | 3.09 |
|        | 2b   | 1.010 | 19.74 | 2.74 |
|        | 2c   | 1.005 | 14.29 | 0.91 |
|        | 4h   | 1.017 | 62.20 | 1.18 |
|        | 4g   | 1.006 | 18.10 | 3.11 |
|        | 2b   | 1.008 | 17.10 | 2.69 |
|        | 2c   | 1.006 | 19.55 | 0.93 |
|        | 4h   | 1.012 | 44.38 | 1.14 |
|        | 4g   | 1.007 | 21.18 | 3.27 |
|        | 2b   | 1.009 | 25.22 | 2.70 |
|        | 2c   | 1.007 | 24.56 | 0.95 |
|        | 4h   | 1.018 | 56.94 | 1.17 |
|        | 4g   | 1.007 | 23.32 | 3.02 |
|        | 2b   | 1.005 | 15.26 | 3.08 |
|        | 2c   | 1.013 | 41.99 | 1.12 |
|        | 4h   | 1.016 | 53.32 | 1.06 |
|        | 4g   | 1.010 | 31.65 | 3.13 |
|        | 2b   | 1.011 | 21.79 | 2.90 |
|        | 2c   | 1.008 | 24.22 | 0.92 |
|        | 4h   | 1.017 | 58.11 | 1.103 |
crystal structure of the cathode and reduce the cycle deterioration. Regarding the electron density distribution for 4\(h\)-8\(j\), the results after the 5th discharge showed that the electron density when using the graphite anode was higher than when using the Li metal anode. From the ICP data, the cathode after the 5th discharge with the graphite anode had more Li than with the Li-metal anode (graphite anode: 0.692(2), Li metal anode: 0.601(1)), indicating that the cathode using the graphite anode was closer to the discharged state than using the Li-metal anode. From the previous data, the electron density distribution for 4\(h\)-8\(j\) increased in the discharge state. Therefore, the difference in the electron density between Li-metal anode and graphite anode may be due to the difference in the charge state of the cathode.

4. Conclusion

Prelithiation of the graphite anode led to stable charging and discharging of the solid solution material 0.4Li\(_2\)MnO\(_3\)-0.6LiMn\(_{1/3}\)Ni\(_{1/3}\)Co\(_{1/3}\)O\(_2\) cathode. After the 5th discharge, there was no significant difference in the average structure of the cathodes, regardless of the separator. When the anode was changed, there was a difference in the electron density between the sites, but there was no difference in the valence change of the transition metal and the tendency of Ni mixing. These results indicate that the previous data with the Li-metal anode and PP film separator can be applied to the graphite anode and the nonwoven separators. After the 55th discharge, the differences in the electron density distribution and distortion of the M-O\(_6\) octahedra between the separators were greater. The nonwoven separators have large pore size, are easily wetted with an electrolyte solution, and have high ionic conductivity, so that Li-ions can easily spread in the cathode. Li deinserted from the transition metal layer during charge stably returns to its original position during discharge, which might suppress distortion of the transition metal layer and strengthen covalent bond. These differences may affect the structural stability of the cathode, resulting in different cycle characteristics. To investigate the crystal structure change of the cathode over a long cycle, the anodes and separators used in actual batteries should be applied.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-00126.
Acknowledgments

We are very grateful for the cooperation of Dr. Keiichi Osaka for the synchrotron XRD measurements (BL19B2, SPring-8; 2018B1777, 2019A1760, 2019B1882, 2020A1728) and Dr. Tetsuo Honma and Dr. Hironori Ofuchi for the XAFS measurements (BL14B2, SPring-8; 2018B1596, 2019A1626, 2019B1714). We are also very appreciative of the cooperation of Prof. Toru Ishigaki and Assoc. Prof. Akinori Hoshikawa for the neutron diffraction measurements (iMATERIA, J-PARC; 2018PM0006, 2019A0048, 2019PM2003).

References

1. C. S. Johnson, J. S. Kim, C. Leftief, N. Li, J. T. Vaughey, and M. M. Thackeray, Electrochem. Commun., 6, 1085 (2004).
2. Y. J. Park, Y.-S. Hong, X. Wu, M. G. Kim, K. S. Ryu, and S. H. Chang, J. Electrochem. Soc., 151, A720 (2004).
3. M. M. Thackeray, C. S. Johnson, J. T. Vaughey, N. Li, and S. A. Hackney, J. Mater. Chem., 15, 2257 (2005).
4. N. Kumagai, J.-M. Kim, S. Tsuruta, Y. Kadoma, and K. Ui, Electrochim. Acta, 53, 5287 (2008).
5. N. Tran, L. Croguennec, M. Ménièrret, F. Weill, Ph. Biensan, C. Jordy, and C. Delmas, Chem. Mater., 20, 4815 (2008).
6. T. A. Arunkumar, Y. Wu, and A. Manthiram, Chem. Mater., 19, 3067 (2007).
7. A. Ito, D. Li, Y. Ohsawa, and Y. Sato, J. Power Sources, 183, 344 (2008).
8. Y. Idemoto, R. Yamamoto, N. Ishida, and N. Kitamura, Electrochim. Acta, 153, 399 (2015).
9. Y. Idemoto, Y. Sera, N. Ishida, and N. Kitamura, Electrochemistry, 83, 879 (2015).
10. Y. Idemoto, T. Sekine, N. Ishida, and N. Kitamura, J. Mater. Sci., 52, 8630 (2017).
11. Y. Idemoto, T. Hiramuma, N. Ishida, and N. Kitamura, J. Power Sources, 378, 198 (2018).
12. N. Takami, H. Inagaki, T. Kishi, Y. Harada, Y. Fujita, and K. Hoshina, J. Electrochem. Soc., 156, A128 (2009).
13. N. Takami, H. Inagaki, Y. Tatebayashi, H. Saruwatari, K. Honda, and S. Egusa, J. Power Sources, 244, 469 (2013).
14. Y. Nishi, J. Power Sources, 100, 101 (2001).
15. X.-B. Cheng, R. Zhang, C.-Z. Zhao, and Q. Zhang, Chem. Rev., 117, 10403 (2017).
16. S. S. Zhang, J. Power Sources, 164, 351 (2007).
17. H. Lee, M. Yanilmaz, O. Toprakci, K. Fu, and X. Zhang, Energy Environ. Sci., 7, 3857 (2014).
18. T.-H. Cho, M. Tanaka, H. Ominishi, Y. Kondo, Y. Miyata, T. Nakamura, and T. Sakai, J. Power Sources, 195, 4272 (2010).
19. J. Lee, C.-L. Lee, K. Park, and I.-D. Kim, J. Power Sources, 248, 1211 (2014).
20. E. de la Llave, V. Borgel, K. J. Park, J. Y. Hwang, Y. K. Sun, P. Hartmann, F. F. Chesneau, and D. Aurbach, ACS Appl. Mater. Interfaces, 8, 1867 (2016).
21. P. K. Nayak, T. R. Penki, B. Markovsky, and D. Aurbach, ACS Energy Lett., 2, 544 (2017).
22. R. Oishi, M. Yonemura, Y. Nishimaki, S. Torii, A. Hoshikawa, T. Ishigaki, T. Morishima, K. Mori, and T. Kamiyama, Nucl. Instrum. Methods Phys. Res. Sect. A, 600, 94 (2009).
23. F. Iizumi and K. Momma, Solid State Phenom., 130, 15 (2007).
24. K. Momma, T. Ikeda, A. A. Belik, and F. Iizumi, Powder Diff., 28, 184 (2013).
25. B. Ravel and M. Newville, J. Synchrotron Radiat., 12, 537 (2005).
26. K. Robinson, G. V. Gibbs, and P. H. Ribbe, Science, 172, 567 (1971).
27. J. D. Brown and D. Altermatt, Acta Crystallogr., Sect. B, 41, 244 (1985).
28. Y. Kozitabashi, N. Ishida, N. Kitamura, and Y. Idemoto, The 60th Battery Symposium in Japan, abstract, 2A06 (2019).