Relaxation Analysis of LiNi_{0.5}Mn_{1.5}O_{4} 5 V Cathode Material by Means of the Rietveld Refinement

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ABSTRACT

After electrochemically extracting lithium ions from LiNi_{0.5}Mn_{1.5}O_{4}, we have investigated the structural variation during the relaxation process by means of X-ray diffraction coupled with the Rietveld analysis, assuming Li-rich and Li-lean spinel phases with Fd3m symmetry coexistence. For both $x = 0.1$ and $0.2$ of LiNi_{0.5}Mn_{1.5}O_{4}, mole fraction of Li-lean phase decreases with the relaxation time, although any apparent change in lattice parameter does not occur for both phases. This indicates that Li-lean phase with larger oxygen tetrahedron size, presumably favorable for lithium diffusion, is formed with excess amount during the lithium extraction, and then it transforms into Li-rich and Li-lean phases with smaller lithium concentration during the relaxation process. Slight increase in the size of oxygen tetrahedron and decrease in that of octahedron during relaxation for Li-lean phase of $x = 0.1$ are also consistent with above phase change.

Keywords : Li Ion Battery, Relaxation Analysis, LNMO, 5 V Class Cathode Material

1. Introduction

LiNi_{0.5}Mn_{1.5}O_{4} (LNMO) is a promising cathode material for lithium ion secondary batteries because of its high operating voltage at c.a. 4.7 V vs. Li/Li+, 5D lithium ion diffusion path, high energy density and good cycling performance.1-4 It has been reported that the “nonstoichiometric disordered spinel” with the space group Fd3m exhibits an enhanced rate capability in comparison with the ordered form of P4_32.5,6 When the lithium ion is extracted from the disordered LNMO cathode, solid solution-type reaction at first occurs to form Li$_x$Ni$_{0.5}$Mn$_{1.5}$O$_4$, thereafter delithiation proceeds by two-phase reaction creating Ni$_3$O$_4$.5-8 It has been also reported that, Ni$^{2+}$ ion is oxidized to Ni$^{3+}$ ion through Ni$^{4+}$, while almost all of manganese remains in tetravalent.6,9 In the higher voltage region with small lithium concentration, it is important to investigate the lithium diffusion and phase transformation between the two phases to achieve better cell performance.

In recent years, we have investigated the change in structure of electrode materials after the termination of lithium insertion and/or extraction by using X-ray diffraction accompanied by the Rietveld analysis.10-17 Assuming that the structural variation corresponds to the transient from kinetically favorable state into equilibrium one, we named this method “relaxation analysis” and applied to various electrode materials, such as $γ$-Fe$_2$O$_3$,10,11 LiFePO$_4$,12 LiMn$_2$O$_4$,13 and LiMn$_{0.5}$Fe$_{0.5}$PO$_4$.15,17

In the present study, we have carried out the relaxation analyses on the lithium extracted LiNi$_{0.5}$Mn$_{1.5}$O$_4$ to reveal the charging process and relaxation behavior of the high-voltage cathode material focusing on the molar ratio of coexisting two phases.

2. Experimental

2.1 Sample preparation

Working electrode was prepared by mixing LiNi$_{0.5}$Mn$_{1.5}$O$_4$ powder (TOSHIMA Manufacturing Co. Ltd, particle size of 5-10 μm), acetylene black (AB) as a supplemental conductor and PVdF powder as an adhesive agent with the ratio of 80:10:10 (weight ratio), then spread onto aluminum foil current collector (~16). Typical amount of active material employed is 8–10 mg. After drying the working electrode at 120°C for 24 h, a two-electrode type metal cell (Hohsen Corp.) was assembled in an argon-filled glove box. Lithium metal was used for counter electrode. The electrolyte was 1 mol·dm$^{-3}$ LiPF$_6$, in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) solution (3:7 v/v, Kishida chemical Corp., Ltd.).

2.2 Electrochemical Li extraction

For the preparation of electrochemically lithium extracted sample, the cell was charged to achieve the amount of lithium as $x = 0.1$ and 0.2 in terms of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ at a constant current of 0.3 C. A typical charge curve is represented in Fig. 1. After the termination of lithium extraction, we opened the circuit and immediately took the working electrode out of the cell in an argon-filled glove box to avoid the local cell reaction between the active material and the current collector. Thereafter we washed the working electrode in EC/EMC (3:7 v/v, Kishida chemical Corp., Ltd.) and EMC (Kishida chemical Corp., Ltd.) and then dried the working electrode in argon atmosphere.

2.3 X-ray diffraction (XRD) measurement

The sample was set in a sealed holder (Rigaku Corp., Ltd.) with beryllium window in an argon-filled glove box. The sealed holder was set to a diffractometer with Bragg-Brentano geometry for XRD measurement (UltimaIV, Rigaku Corp., Ltd.). XRD patterns were measured from 10 to 100° in 2θ at a rate of 2° per min with 0.04° step width by using CuKα radiation. The tube voltage and current were set to 40 kV and 40 mA, respectively. In order to investigate the structure change during relaxation precisely, XRD measurements were repeatedly carried out at various relaxation times after termination of lithium extraction.

2.4 The Rietveld analysis

The XRD profiles were analyzed by the Rietveld method using RIEVEC code.18 We summed five continuous patterns to improve...
S/N ratio for the Rietveld analysis. We selected the space group of LNMO sample as Fd3m, since characteristic Mn$^{3+}$/Mn$^{4+}$ plateau for disordered LNMO is observed at 4.1 V in the charging process as shown in Fig. 1. For the structure refinement, Mn and Ni ions are placed at 16d site and oxide ion is at 32e site, and the contribution of lithium was ignored. Occupancies for all the ions except for lithium are fixed as unity. The contribution of the aluminum collector and sample additives to the XRD patterns was evaluated as the background intensity. The Rietveld analysis has been carried out assuming coexistence of two spinel phases to determine the structure of each spinel phase and mole fractions.

3. Results and Discussion

Figure 2 represents the X-ray diffraction patterns of Li$_{x}$Ni$_{0.5}$Mn$_{1.5}$O$_{4}$ (x = 0.1 and 0.2), which has been measured after 68 hours from the termination of lithium extraction. As observed in the insets, a smaller diffraction peak appears at the lower angle side of each main peak of spinel-type structure, indicating that two spinel-type structured materials are coexisted. These phases would be nominally assigned as Li$_{x}$Ni$_{0.5}$Mn$_{1.5}$O$_{4}$ (larger unit cell) and Ni$_{0.5}$Mn$_{1.5}$O$_{4}$ (smaller one). We refer the former and the latter phases as Li-rich and Li-lean phases, respectively according to the previous study since we discuss on the phase change during the relaxation accompanied by the lithium transfer between these two phases. The Rietveld refined patterns assuming coexisting two spinel phases agree well with the measured plots yielding sufficiently small $R_{wp}$ values. Some structure parameters after refinement is listed in Table 1 for initial and 68 hours of relaxed sample. Figure 3 shows the relaxation time variation of the lattice parameters of Li-rich and lean phases. Although the obtained data in Li-rich phase are a little scattered especially for $x = 0.1$, the lattice parameters of both phases remains almost constant values during the relaxation time. Nevertheless, mole fraction of Li-lean phase gradually decreases with the relaxation time as observed in Fig. 4, indicating that a slight part of Li-lean phase transforms into the Li-rich phase. Such a behavior is more apparent for $x = 0.1$ rather than $x = 0.2$. Figure 5 shows the relaxation time dependence of the interatomic distances between lithium ion in tetrahedral site and bonding oxide ion, $d_{Li-O}$. For both compositions, the interatomic distance in Li-lean phase is larger than that of Li-rich phase, presumably because the nominal negative charge of lithium vacancy would expand the size of oxygen tetrahedron. Although $d_{Li-O}$ of Li-rich phase is considerably scattered due to its very small fraction, the interatomic distances in Li-lean phase seems to grow slightly larger with relaxation time. In addition, interatomic distances between metal (octahedral site of Ni/Mn) and oxide ions ($d_{M-O}$) are shown in Fig. 6. Focusing on the $d_{M-O}$ of Li-rich phase, the interatomic distance seems to slightly decrease with the relaxation in $x = 0.1$. This also support the decrease in the lithium concentration in the Li-lean phase, since the valence of nickel ion would increase to decrease the ionic radius for the charge compensation.

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**Figure 1.** Charging curves of (a) Li$_{0.1}$Ni$_{0.5}$Mn$_{1.5}$O$_{4}$ and (b) Li$_{0.2}$Ni$_{0.5}$Mn$_{1.5}$O$_{4}$ at the rate of 0.3 C.

**Figure 2.** (Color online) Measured and refined XRD patterns of (a) Li$_{0.1}$Ni$_{0.5}$Mn$_{1.5}$O$_{4}$ and (b) Li$_{0.2}$Ni$_{0.5}$Mn$_{1.5}$O$_{4}$ with 68 hours of relaxation time after the lithium extraction. Observed and the Rietveld refined patterns are shown by dots and the red solid line, respectively. The vertical lines in the middle part show the positions of peaks calculated for Bragg reflection. The trace ($\Delta Y$) in the bottom part represents the difference between observed and calculated patterns. Asterisk mark (*) indicates diffraction peaks of aluminum foil collector.
Table 1. Structure parameters after refinement for initial and 68 hours of relaxed samples.

<table>
<thead>
<tr>
<th>Mole fraction</th>
<th>Lattice parameter/Å</th>
<th>Oxide ion coordinates</th>
<th>( B/\text{Å}^2 )</th>
<th>( R_{WP} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li-rich</td>
<td>Li-lean</td>
<td>Li-rich</td>
<td>Li-lean</td>
</tr>
<tr>
<td>( x = 0.1 )</td>
<td>3 h</td>
<td>0.211(9)</td>
<td>0.789(9)</td>
<td>8.08311(12)</td>
</tr>
<tr>
<td></td>
<td>68 h</td>
<td>0.240(9)</td>
<td>0.760(9)</td>
<td>8.08947(12)</td>
</tr>
<tr>
<td>( x = 0.2 )</td>
<td>3 h</td>
<td>0.272(8)</td>
<td>0.728(8)</td>
<td>8.08892(8)</td>
</tr>
<tr>
<td></td>
<td>68 h</td>
<td>0.304(8)</td>
<td>0.696(8)</td>
<td>8.09125(8)</td>
</tr>
</tbody>
</table>

Figure 3. Lattice constant variation of (a) \( \text{Li}_{0.1}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) and (b) \( \text{Li}_{0.2}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) during the relaxation time. □ Li-rich phase, □ Li-lean phase, and the error bars were also plotted.

Figure 4. Obtained mole fraction change of (a) \( \text{Li}_{0.1}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) and (b) \( \text{Li}_{0.2}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) during the relaxation time. □ Li-rich phase, □ Li-lean phase.

Figure 5. Change in distance between lithium ion in tetrahedral site and bonding oxide ion of (a) \( \text{Li}_{0.1}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) and (b) \( \text{Li}_{0.2}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) during the relaxation time. □ Li-rich phase, □ Li-lean phase. The solid lines represent the least-squares linear approximation of Li-lean phase.

Figure 6. Change in distance between Mn/Ni ion in octahedral site and bonding oxide ion of (a) \( \text{Li}_{0.1}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) and (b) \( \text{Li}_{0.2}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) during the relaxation time. □ Li-rich phase, □ Li-lean phase. The solid lines represent the least-squares linear approximation of Li-lean phase.
Accordingly, lithium concentration in the Li-lean phase is supposed to decrease with the relaxation time, presumably because lithium ions in the Li-lean phase are consumed to form Li-rich phase during the relaxation. At the lithium extraction, Li-lean phase should be favorable due to lower lithium concentration in Li site as well as larger size of LiO$_4$ tetrahedron, which allows the formation of excess amount of Li-lean phase in comparison with the equilibrium ratio of Li-rich and lean phases. The enhanced molar ratio of Li-lean phase gradually varies toward the equilibrium ratio in the relaxation time.

4. Conclusion

We have performed the relaxation analysis on 5 V class Li$_{1-x}$Ni$_{0.5}$Mn$_{1.5}$O$_4$ ($x=0.1$ and 0.2) cathode materials after lithium extraction assuming Li-rich and lean spinel-type structured phases. It is found that the mole fraction of Li-lean phase decreases with slightly expanding the LiO$_4$ tetrahedron in the Li-lean phase. This indicates that the Li-lean phase with smaller lithium concentration and with larger size of LiO$_4$ tetrahedron is preferred for lithium diffusion, and excess amount of Li-lean phase would be created in the lithium extraction process. During the relaxation, excessively formed Li-lean phase partly changes into the Li-rich phase by decreasing the lithium concentration in remaining Li-lean phase.

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References