

Effect of Structure Change of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ by Exposing to High Voltage on Battery Performance

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The change in the crystal structure of layered $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ espoused to high voltage was investigated by synchrotron X-ray diffraction (XRD) with Debye-Scherrer camera in SPring-8. It was first found that $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ ($x \approx 0$) prepared by charging to 5.3 V has a O3 phase monoclinic cell as a main phase, which is slightly distorted from an ideal rhombohedral cell, and O1 phase rhombohedral cell as a minor phase (less than 10 %) having hexagonal close-packed oxygen array. Rietveld analyses of XRD patterns revealed that nickel ions migrated from the lithium layer to transition metal layer via tetrahedral sites in the lithium layer upon cycling to 4.5 V. Increasing the charging voltage to 5.3 V appeared further amount of nickel ions were migrated from the tetrahedral sites in the lithium layer to the transition metal layer.

Background

O3 $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ having cubic close-packed oxygen array have been widely studied for the most promising high-energy and high-power positive electrode material for advanced lithium-ion batteries. A barrier to the practical use of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ is the unsatisfied rate-capability, because a pristine sample of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ has 10 – 11 % interlayer mixing of lithium and nickel ions. The nickel ions locating in the lithium layer impede lithium-ion migration in the solid matrix. Recently, our research group has found that the rechargeable capacity and rate capability of $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ are significantly improved by the high-voltage exposure upon 5.3 V. We examine the effect of high-voltage exposure to 4.5 V and 5.3 V

on the structural changes of $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ using synchrotron X-ray diffraction (XRD).

Experimental

$\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ samples were prepared by electrochemical oxidation up to 4.5 and 5.3 V vs. Li metal and the compositions corresponds to $x = 0.22$ and $x \approx 0$, respectively. XRD measurements were carried out using the synchrotron irradiation of BL02B2, in SPring-8. The wavelength used was 0.501 Å, which was calibrated with CeO_2 .

Results and Discussion

Figure 1a shows the synchrotron XRD pattern of $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ sample ($x = 0.22$). The crystal

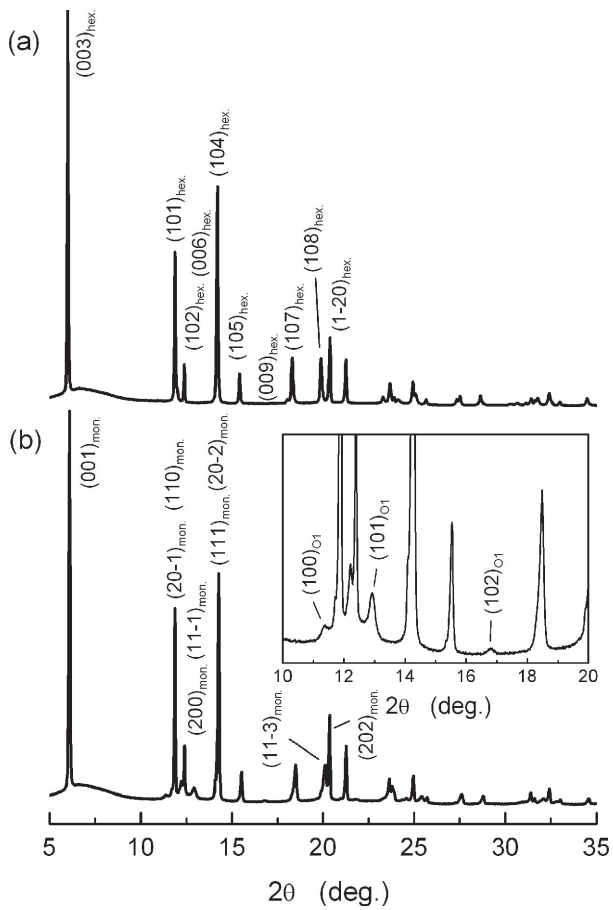


Figure 1. Synchrotron XRD pattern of $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ samples; (a) $x = 0.22$ ($R\bar{3}m$; $a_{\text{hex.}} = 2.833$, $c_{\text{hex.}} = 14.373$ Å) and (b) $x \approx 0$, which has two phases – monoclinic O3 ($C2/m$; $a_{\text{mon.}} = 4.914$, $b_{\text{mon.}} = 2.834$, $c_{\text{mon.}} = 4.984$ Å, $\beta = 108.92^\circ$), and O1 phase ($P\bar{3}1a_{O1} = 2.91$, $c_{O1} = 4.68$ Å).

structure was indexed as a rhombohedral-type unit cell with space group $R\bar{3}m$. When the sample was exposed to 5.3 V, pronounced broadening was found for the $(10l)_{\text{hex.}}$ peaks as the hexagonal unit cell setting while the $(00l)_{\text{hex.}}$ and $(1-20)_{\text{hex.}}$ peaks remained sharp (Figure 1b). This indicates monoclinic distortion from the rhombohedral cell. The lattice constants of monoclinic O3 phase were calculated to be $a_{\text{mon.}} = 4.914$, $b_{\text{mon.}} = 2.834$, $c_{\text{mon.}} = 4.984$ Å, and $\beta = 108.92^\circ$ with space group $C2/m$. In addition, we first confirmed O1 phase formation for $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ having hexagonal close-packed oxygen array with space group $P\bar{3}1$, though it was a minor phase (less than 10 %). The lattice constants of O1 phase were calculated to be a_{O1}

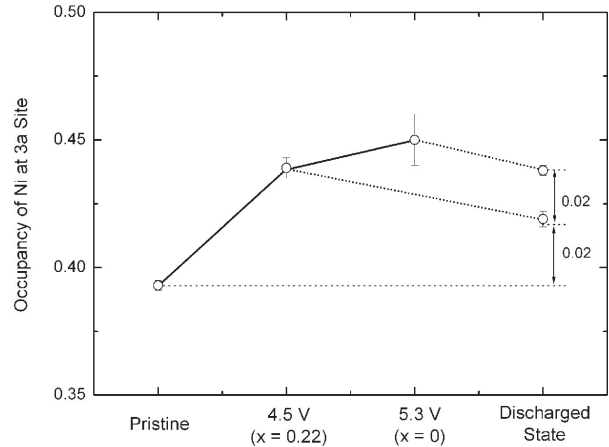


Figure 2. the change in the occupancy of Ni ions at octahedral 3a sites.

$$= 2.91, c_{O1} = 4.68 \text{ \AA}.$$

The change in the crystal structure including the cation migration in the close-packed oxygen array was examined by Rietveld refinement in further detail. Figure 2 shows the change in the occupancy of Ni ions octahedral 3a site. Approximately 5 % nickel ions migrated from the lithium layer to transition metal layer via tetrahedral sites upon charging to 4.5 V, and approximately 3 % nickel ions were confirmed at the tetrahedral site in the lithium layer. When the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ was exposed to 5.3 V, further amount of nickel ions were migrated from the tetrahedral sites in the lithium layer to the octahedral sites in the transition metal layer. It has been confirmed that, for the discharged state after exposure to 5.3 V, the occupancy of nickel ions at the lithium layer is approximately 2 % less than that of 4.5 V charged state, though some of these nickel ions migrates reversibly during charge and discharge cycling. From these results, we conclude that the permanently decreased interlayer mixing of lithium and nickel ions by exposing to high voltage improved the electrochemical reactivity of $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$ samples.