Lithium nickel manganese oxides have been investigated to advance lithium insertion materials for lithium-ion batteries[1-4]. Of these, LiNi1/2Mn1/2O2 shows anomalous behaviors in both structure and electrochemistry. In order to identify the structure, a systematic study has been undertaken. In the previous paper[4], we have shown that LiNi1/2Mn1/2O2 consists of Ni2+ and Mn4+ ions distributed in a cubic-close packed oxygen array. In this paper, we report detailed crystal structure analysis and electrochemistry of LiNi1/2Mn1/2O2.

LiNi1/2Mn1/2O2 was prepared by heating a reaction mixture of LiOH and nickel manganese double hydroxide at 1000 °C in air. Figure 1 shows the XRD pattern of thus prepared LiNi1/2Mn1/2O2. This material is battery-active, i.e., about 200 mAh/g of rechargeable capacity in 2.5 – 4.5 V. The XRD pattern is similar to that of LiNiO2 having a space group R3m. However, about 9 % of displacement between lithium and transition metal ions at the 3(a) and 3(b) sites is required to give a reasonable fit between the experimental and the calculated pattern (Rwp = 11.28, R = 1.95). For LiNiO2, about 9 % of displacement with a longer c-axis dimension than 14.25 Å meant inactive form for battery application. In other words, when the integrated intensity of the (003) line was stronger than that of (001), we could not expect battery-active materials for LiNiO2-based materials.

In order to examine whether or not such a highly concentrated rock-salt domain is contaminated in our active samples, HRTEM and SAED observations were carried out. Figure 2 shows an example of the HRTEM images for a single domain of LiNi1/2Mn1/2O2. From this direct observation, we have convinced that we need other structure models to describe LiNi1/2Mn1/2O2. Since XRD cannot help so much speculate structural models, electron diffraction measurements are carried out from several incident angles. An example is shown in Fig. 3. Although a [√3 x √3]R30° superlattice formation was not expected because of the composition, extra spots are clearly seen in this figure in addition to fundamental spots based on α-NaFeO2-type structure.

From these experimental and analytical results, we will discuss structural chemistry and electrochemistry of LiNi1/2Mn1/2O2 for advanced lithium-ion batteries.

References

Fig. 1 Rietveld analysis on the XRD pattern of LiNi1/2Mn1/2O2 assuming a space group R3m (a0 = 2.893 Å, c0 = 14.310 Å in hexagonal setting ). The R-values are obtained to be Rwp = 11.28, R = 1.95, and s = 1.98 for ca. 9% of displacement between Ni2+ and Li+ ions at the 3(a) and 3(b) sites by RIETAN-2000.

Fig. 2 HRTEM image of single domain of LiNi1/2Mn1/2O2. Layered structure with a cubic-closest packed oxygen is directly seen in this figure.

Fig. 3 Electron diffraction pattern of LiNi1/2Mn1/2O2 along a [1 -1 -1] zone axis. Extra spots corresponding to [√3 x √3]R30° superlattice can be seen in addition to fundamental spots based on a space group R3m.

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