

Structural Chemistry and Electrochemistry of  
LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> for Advanced Lithium Batteries

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Lithium nickel manganese oxides have been investigated to advance lithium insertion materials for lithium-ion batteries[1-4]. Of these, LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> 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 LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> consists of Ni<sup>2+</sup> and Mn<sup>4+</sup> ions distributed in a cubic-close packed oxygen array. In this paper, we report detailed crystal structure analysis and electrochemistry of LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub>.

LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> 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 LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub>. 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 LiNiO<sub>2</sub> 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 ( R<sub>wp</sub> = 11.28, R<sub>B</sub> = 1.95 ). For LiNiO<sub>2</sub>, 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 (104) line was stronger than that of (003), we could not expect battery-active materials for LiNiO<sub>2</sub>-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 LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub>. From this direct observation, we have convinced that we need other structure models to describe LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub>. 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-NaFeO<sub>2</sub>-type structure.

From these experimental and analytical results, we will discuss structural chemistry and electrochemistry of LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> for advanced lithium-ion batteries.

## References

- [1] Y. Makimura and T. Ohzuku, Abstract No. 2D20 – 2D21, 41<sup>st</sup> Battery Symposium, Nagoya (2000).
- [2] T. Ohzuku and Y. Makimura, *Chemistry Letters*, 642, 744 (2001).
- [3] Y. Makimura and T. Ohzuku, Abstract No. 117, 11<sup>th</sup> IMLB, Monterey, California (2002).
- [4] Y. Makimura, N. Terada, T. Ohzuku, Y. Koyama, I. Tanaka, and H. Adachi, Abstract No. 2I01 – 2I02, 43<sup>rd</sup> Battery Symposium, Fukuoka (2002).

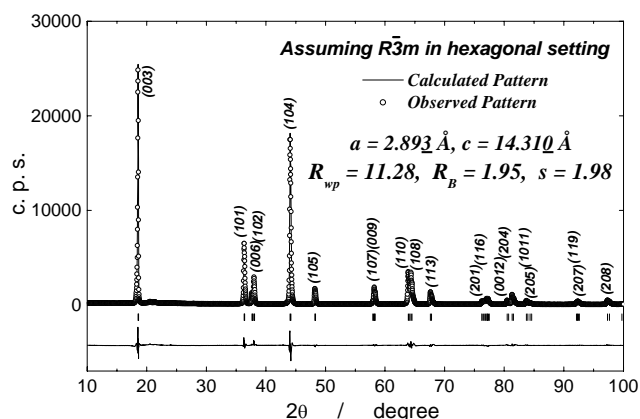


Fig. 1 Rietveld analysis on the XRD pattern of LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> assuming a space group R3m ( a<sub>h</sub> = 2.893 Å, c<sub>h</sub> = 14.310 Å in hexagonal setting ). The R-values are obtained to be R<sub>wp</sub> = 11.28, R<sub>B</sub> = 1.95, and s = 1.98 for ca. 9% of displacement between Ni<sup>2+</sup> and Li<sup>+</sup> ions at the 3(a) and 3(b) sites by RIETAN-2000.

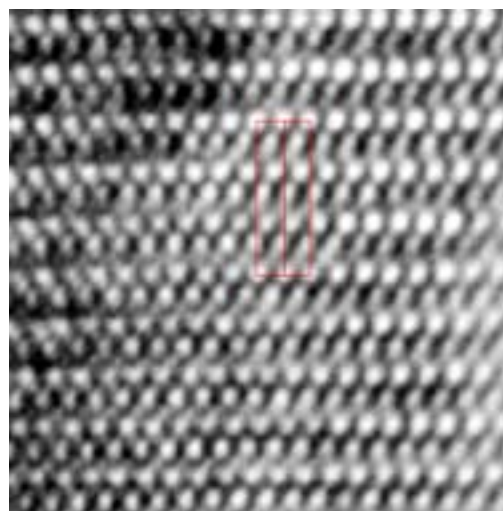


Fig. 2 HRTEM image of single domain of LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub>. Layered structure with a cubic-closest packed oxygen is directly seen in this figure.

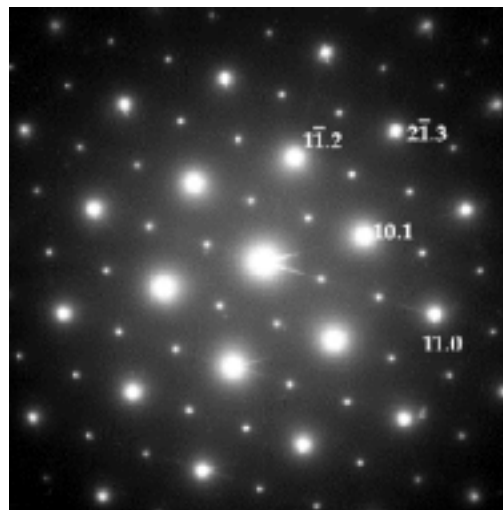


Fig. 3 Electron diffraction pattern of LiNi<sub>1/2</sub>Mn<sub>1/2</sub>O<sub>2</sub> along a [ 1 -1 -1 ] zone axis. Extra spots corresponding to [ √3 x √3 ]R30° superlattice can be seen in addition to fundamental spots based on a space group R3m.

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