Solid State Chemistry and Electrochemistry of Five-Volt Lithium Insertion Material of Li[Ni_{1/2}Mn_{3/2}]O_4

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In our laboratory, we have been studying a series of lithium nickel manganese oxides with or without cobalt, such as LiNi_{1/2}Mn_{3/2}O_4 and LiCo_{0.3}Ni_{1/2}Mn_{3/2}O_4 or more generally LiCo_{x}Ni_{1/3-x}Mn_{3/2}O_4 in which Ni^{2+} and Mn^{4+} ions play an interesting role in the solid-state electrochemical reactions. Li[Ni_{1/2}Mn_{3/2}]O_4 having a spinel-framework structure also consists of Ni^{2+} and Mn^{4+} ions distributed in a cubic-close packed oxygen array. Combination of this material and graphite gives a five-volt lithium ion battery or with Li[Li_{1/3}Ti_{1/3}]O gives a three-volt battery[1, 2]. In this study, we report the structural chemistry and electrochemistry of Li[Ni_{1/2}Mn_{3/2}]O_4.

Li[Ni_{1/2}Mn_{3/2}]O_4 was prepared by the two-step solid-state reaction [3] and characterized and examined by XRD, FT-IR, HRTEM & SAED, SEM, and electrochemical methods. From the XRD pattern of Li[Ni_{1/2}Mn_{3/2}]O_4, crystal structure was primarily identified as a spinel-framework structure (a = 8.17 Å). The well-defined 8 absorption bands were observed in FT-IR spectrum. In the electron diffraction pattern of Li[Ni_{1/2}Mn_{3/2}]O_4 in Fig. 1, many extra spots can be seen in addition to fundamental spots based on a spinel-framework structure. Powdered XRD was performed and analyzed by assuming a space group of P4_{3}2 or P4_{3}32. According to the analytical results, Li[Ni_{1/2}Mn_{3/2}]O_4 has a superlattice based on a spinel-framework structure, in which nickel and manganese ion ordering can be seen at the octahedral sites.

A Li / Li[Ni_{1/2}Mn_{3/2}]O_4 cell shows flat operating voltage at 4.7 V and rechargeable capacity of about 135 mAh/g. In order to characterize the solid-state redox reaction, ex-situ X-ray diffraction measurements were carried out. During charge, all diffraction lines can be indexed assuming a cubic lattice over the entire range. Figure 2 shows the change in lattice constant as a function of x in Li_{1-x}Ni_{1/2}Mn_{3/2}O_{4}. The a-axis dimension decreased from 8.17 Å for Li[Ni_{1/2}Mn_{3/2}]O_4 to 8.00 Å for Li_{1/2}Li_{1/2}Ni_{1/2}Mn_{3/2}O_4 via 8.09 Å for Li_{1/2}Ni_{1/2}Mn_{3/2}O_4 on charge.

In order to examine whether or not such a structural change reflected upon a potential curve, reversible potential measurements were performed. Figure 3 shows the reversible potentials as a function of x in Li_{1-x}Ni_{1/2}Mn_{3/2}O_{4}. Two voltage plateaus were clearly observed at 4.718 and 4.739 V. From these experimental and analytical results, we will discuss the reaction mechanism of Li[Ni_{1/2}Mn_{3/2}]O_4 in terms of topotactic two-phase reactions.

References

Fig. 1 Electron diffraction pattern of Li[Ni_{1/2}Mn_{3/2}]O_4 prepared by a two-step solid-state reaction taken along a [100] zone axis.

Fig. 2 Cubic lattice constant as a function of x in Li_{1-x}Ni_{1/2}Mn_{3/2}O_{4}.

Fig. 3 The reversible potentials as a function of x in Li_{1-x}Ni_{1/2}Mn_{3/2}O_{4}.

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