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 $LiNi_{1/2}Mn_{1/2}O_2$ and $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$, or more generally $LiCo_{x/3}Ni_{(3-x)/6}Mn_{(3-x)/6}O_2$ 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 $Li[Li_{1/3}Ti_{5/3}]O_4$ 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 $P4_332$ or $P4_132$. According to the analytical results, $Li[Ni_{1/2}Mn_{3/2}]O_4$ has a superlattce 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 $\square_{1/2}Li_{1/2}[Ni_{1/2}Mn_{3/2}]O_4$ via 8.09 Å for $\square[Ni_{1/2}Mn_{3/2}]O_4$ 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

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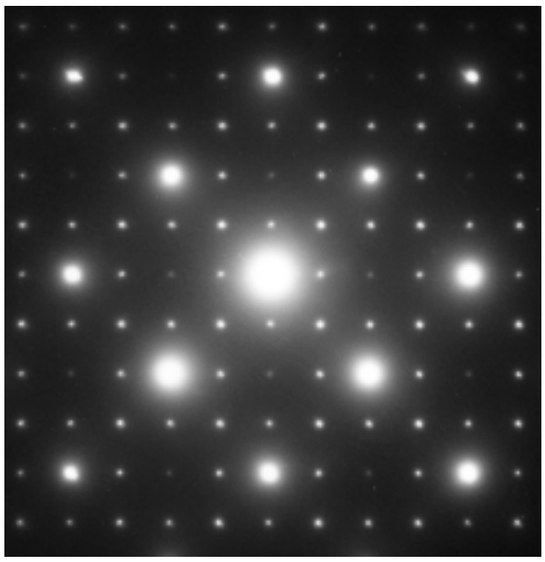

Fig. 1 Electron diffraction pattern of $Li[Ni_{1/2}Mn_{3/2}]O_4$ prepared by a two-step solid-state reaction taken along a [100] zone axis.

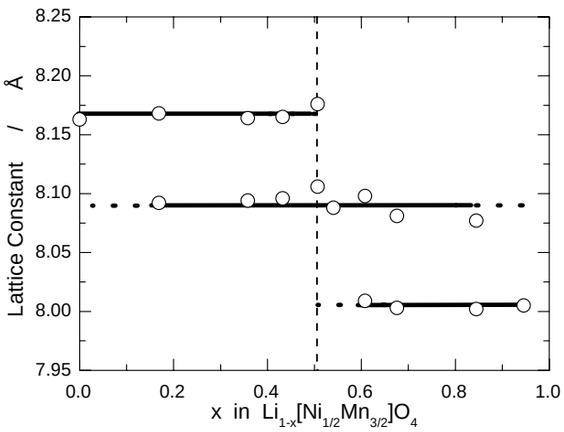

Fig. 2 Cubic lattice constant as a function of x in $Li_{1-x}[Ni_{1/2}Mn_{3/2}]O_4$.

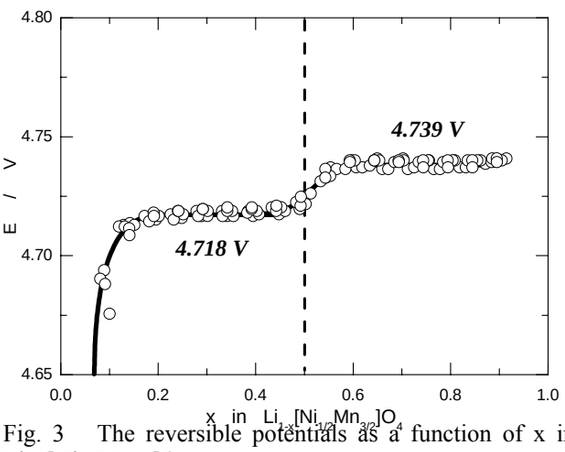

Fig. 3 The reversible potentials as a function of x in $Li_{1-x}[Ni_{1/2}Mn_{3/2}]O_4$.

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