

Crystal Structural Change during Charge-Discharge Process of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ as a Cathode Active Material for 5V Class Lithium Secondary Battery

Y. Idemoto,^a H. Sekine,^a K. Ui,^a N. Koura,^a

^a Department of Pure and Applied Chemistry,
Faculty of Science and Technology,
Tokyo University of Science
2641 Yamazaki, Noda, Chiba 278-8510, Japan

INTRODUCTION

$\text{LiMn}_{2-x}\text{M}_x\text{O}_4$ has an ca. 5V plateau when part of the Mn-site is substituted for the 3d-transition metals (M=Cr, Co, Ni, Fe, Cu). $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ is easy to prepare, and has been shown to have a high capacity, and good cycle performance. However, this material has a different cathode performance, which appears in the 4V-region, charge-discharge behavior, and cycle performance, by changing the synthesis method^{1,2}. The authors reported that $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ synthesized by the sol-gel method has a good cycle performance with the increasing oxygen content³. On the other hand, the lower cycle performance for $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ is due to the coexistence of several phases in this potential region⁴. The crystal structural change of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, accompanying the intercalation-deintercalation of lithium, is important, and yet there are few reports about the stability of the (Mn,Ni)- O_6 octahedral site, which is the frame of the spinel structure.

In this study, $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, as a 5V cathode material was synthesized by the sol-gel method, in which the calcination temperature was changed, and the lithium content of $\text{Li}_{1-x}\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ ($x=0.5, 0.7, 1.0$) was controlled by an electrochemical treatment. We investigated the crystal structural change, which includes the (Mn,Ni)- O_6 octahedral site, during the charge-discharge process by Rietveld analysis with powder neutron diffraction, and the relations between the structure and the cycle performance.

EXPERIMENTAL

$\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ was prepared by the sol-gel method using the LiNO_3 , $\text{Mn}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor and PVA with subsequent decomposition at 150°C. The resulting solids were heated at 600°C for 24h in O_2 , then calcined at (700 °C, 680 °C) for 24h in O_2 ³. The lithium content was controlled by an electrochemical treatment. A three-electrode electrochemical cell composed of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ as the working electrode, a lithium metal anode as the counter electrode and lithium film as the reference electrode was used for controlling the lithium content. The cathodes were prepared by mixing the active material, acetylene black, and polytetrafluoroethylene at a weight ratio of 5:2:1 by pressing them onto an aluminum mesh current collector. The electrodes were dried at 150 °C in a vacuum atmosphere, and pressed at 40MPa. The electrolyte was 1M LiPF_6 in an ethylene carbonate / diethyl carbonate (1:1) solution. All procedures were carried out in a dry box containing an argon atmosphere.

The crystal structures of $\text{Li}_{1-x}\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ were studied by neutron powder diffraction using HERMES. The data were refined with the Rietveld technique using the Rietan-2000 program. The Madelung energy was calculated by the attached software MADEL of FATRIETAN. The bond valence sum was calculated by the

VICS program, and the nuclear densities were calculated by the maximum entropy method using the PRIMA program.

RESULTS AND DISCUSSION

The electrode characteristics of the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ were examined by CV and charge-discharge tests. The CV data showed that the redox reaction occurred only in the 5V region. These results suggested that the obtained sample does not exist as Mn^{3+} . The Mn valence of the samples was in good agreement with about 4.0 by chemical analysis, assuming that the Ni valence was 2.0. The sample, which was calcined at 700°C, showed a good cycle performance with the maximum discharge capacity of 125.3mAh/g, and the capacity after 100 cycles was 95.1% of the maximum capacity. On the other hand, the sample, which was calcined at 680 °C, showed the maximum discharge capacity of 122.6mAh/g, and the capacity after 100 cycles was 90.5% of the maximum capacity⁵.

The crystal structure was determined by Rietveld analysis using powder neutron diffraction. As a result, all samples consisted of three phases (space group: $\text{P4}_3\text{32}$) of different lattice constants and Ni valences. The main phase, which has the maximum percentage, was shifted to a phase with a lower lattice constant with the decreasing lithium content, and then finally $\text{Li}_{1-x}\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ ($x=1.0$) was almost oxidized to Ni^{4+} by a charging process. We clarify that the Ni-doped spinel oxide, $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, with a 5V class cathode material is oxidized from Ni^{2+} ($a=0.816\text{nm}$) to Ni^{4+} ($a=0.800\text{nm}$) via Ni^{3+} ($a=0.809\text{nm}$) with the deintercalation of Li based on a crystal structure analysis. The oxidation process of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ is slightly different from the synthesis temperature. Moreover, the Ni,Mn(4b) octahedral site, which has a high Ni, shrunk during the deintercalation of Li, and the Mn,Ni(12d) octahedral site, which has a high multiplicity, was the most distorted for the Ni^{3+} phase. The crystal structure became unstable for the Ni^{3+} phase and stable for the Ni^{4+} phase based on the results of the distortion of octahedral-site, nuclear density and Madelung energy. It was suggested that these factors should provide an effective cycle performance.

From these results, it is important for improvement of the cycle performance of this material to investigate the crystal structure and reaction mechanism, for which the oxidation-reduction reaction from Ni^{3+} and the reduction reaction from Ni^{4+} to Ni^{3+} easily occur.

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REFERENCES

1. Q. Zhong, A. Bonakdarpour, M. Zhang, Y. Gao, and J. R. Dahn, *J. Electroanal Chem.*, **144**, 205 (1997).
2. T. Ohzuku, S. Takeda, and M. Iwanaga, *J. Power Sources*, **81-82**, 90 (1999).
3. Y. Idemoto, H. Narai and N. Koura, *J. Power Sources*, **119-121**, 125 (2003).
4. T. Yasuko, K. Yasaka, F. Nishikawa, T. Konishi, M. Yoshio, I. Nakai, *J. Solid State Chem.*, **156**, 286 (2001).
5. Y. Idemoto, H. Sekine, K. Ui, N. Koura, *Electrochemistry*, in press.