Magnetic and Electrochemical Studies on Li-Mn-Ni Spinel Oxides

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ABSTRACT

Ni^{2+}-substituted Li-Mn spinel oxide, $LiMn_{2-x}Ni_xO_4$ (X<0.5), were prepared by the sol gel method using nitrate and acetate salts. For a fixed annealing temperature of 700°C, the lattice constant almost linearly decreased with an increase in X. Simultaneously, the asymptotic Curie temperature which was estimated from high-temperature magnetic susceptibility shifted toward positive direction : it changed its sign from negative to positive around X=0.2. In the case that x=0.5 and the annealing temperature was varied between 500 and 850°C, the lattice constant had a minimum at the annealing temperature of 700°C, where both the saturation magnetization at 5K and the Curie temperature took maximum values. The variation of the magnetic properties was attributed to the electronic state of transition metals in the spinel oxide, and it was also reflected in the electrochemical properties as the cathode active material.
Key words: Spinel oxide, Curie temperature, Magnetization, Cathode material.

1. INTRODUCTION

Cathode materials for lithium ion secondary batteries contain transition metal ions with high valence state, which strongly affects the magnetic properties in these compounds. It is known that the electrochemical properties of these cathode materials are very sensitive to the preparation conditions [1-3]. It is likely that the compounds have non-stoichiometric features, which is influenced by the preparation conditions. It was also reported that the non-stoichiometry had great influence on the magnetic properties at low temperature [4,5].

Recently, high-voltage cathode materials have been extensively studied [6-9], since their application enables us to attain the secondary battery with high energy density, and makes it possible to select various anode materials. Here, we focus Ni^{2+}-substituted Li-Mn spinel oxide as one of the high-voltage cathode materials. In the compounds, the magnetic properties as well as the electrochemical property are discussed.

2. EXPERIMENTAL PROCEDURES

2.1. Sample preparation

The powder samples $LiMn_{2-x}Ni_xO_4$ with X<0.5 were prepared by the sol gel method. Reagent grade Li-nitrate, Mn-acetate tetrahydrate and Ni-acetate tetrahydrate were used as raw materials. The stoichiometric amount of them were dissolved in distilled water and the aqueous solution was evaporated at temperature approximately 80°C using the rotary evaporator until a transparent and viscous gel was obtained. The resulting gel precursors were thermally decomposed at 300°C in air. The obtained powders were ground by dry milling and press-compacted into pellets. And they were annealed at temperature between 500 and 850°C in an oxygen flow for 10hr, followed by furnace cooling down to room temperature.

2.2. Material evaluation

The Rietveld refinement was carried out for the powder X-ray diffraction patterns, and the generated phases were identified and the lattice constants were determined. The magnetic susceptibility was measured using the magnetic balance on heating process in temperature range from 4.2 to 300K under the external applied field less than 10kOe. It was certified that the temperature-dependent susceptibility above 200K was fitted to the Curie-Weiss expression in order to numerically evaluate the asymptotic Curie temperature Θ. Only for the specimen with X=0.5, the magnetic hysteresis curve under the maximum field of 10kOe was taken at 5K and the saturation magnetization was also measured as a function of temperature (<200K).

The electrochemical Li^+ insertion/extraction reactions were made with Li^+ ion battery cell. The powder sample (20mg) was mixed thoroughly with acetylene black (5mg) and organic binder PTFE (1mg), and pressed into composite pellet, which was used as the cathode electrode. Using Li foil as the counter electrode and 1.0M-$LiPF_6$/PC-DME solution as organic electrolyte solution, the Li^+ ion battery performance was evaluated by galvanostatically charging and discharging at the constant current (the current rate of C/10), where the upper and lower voltage limit was adjusted at 4.9 and 3.0V, respectively.

3. RESULTS AND DISCUSSION

3.1. Ni^{2+} substitution degree

First, in order to examine the effect of the Ni^{2+}-substitution degree, the annealing temperature was fixed at 700°C. The obtained specimen consisted of only cubic spinel oxide phase in the whole composition range. The variations of the lattice constant and the asymptotic Curie temperature with the substitution degree were shown in Fig. 1. As the substitution degree was increased, the lattice constant almost linearly decreased and the Θ value shifted toward positive direction. The Θ values of two end members were close to the previously reported values [5,10]. The Θ value took negative values at X<0.2, changed its sign around X=0.2 and then had positive values at X>0.2. It indicated the transformation from antiferromagentic to ferrimagnetic material with the substitution.
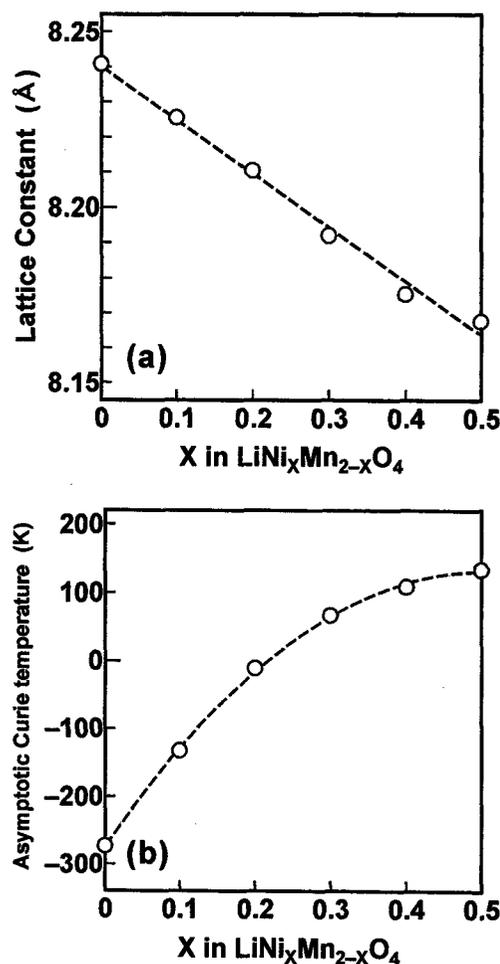
Fig. 1. Variations of the lattice parameter (a) and the asymptotic Curie temperature (b) with the Ni^{2+}-substitution degree.

It is known that, in the Ni^{2+}-substituted Li-Mn spinel oxides, Li^+ ions are located only at 8a tetrahedral site and the other cations (Ni^{2+}, Mn^{3+} and Mn^{4+}) have strong preference for the 16d octahedral site. It was also confirmed that the 8a site contained only Li^+ ions and the transition metal ions were located in 16d site in our Rietveld refinement. Therefore, the cation distribution is

expected as follow :

$$(Li^+)[Mn^{3+}_{1-2x}Mn^{4+}_xNi^{2+}_x]O_4$$
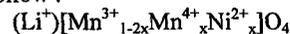
Here, the brackets () and [] denote the 8a and 16d sites, respectively. The linear variation of the lattice constant, influenced with the ionic radius difference, implied the formation of homogeneous solid solution.

Considering the above cation distribution, only the super-exchange interaction with the coupling angle of $\pi/2$ exists. The Kanamori-Goodenough rules enable us to estimate the super-exchange interactions between these cations [11,12]. In the specimen with low substitution degree, the antiferromagnetic Mn^{3+}-Mn^{4+} coupling is dominant and then the asymptotic Curie temperature is expected to be negative. In the case of high substitution degree, the ferromagnetic Mn^{4+}-Mn^{4+} grows and becomes a dominant contribution, and consequently the asymptotic Curie temperature has a positive value. Therefore, it was found that the variation of the asymptotic Curie temperature was explained according to the super-exchange interactions.

Figure 2 shows potential profiles in the galvanostatic measurement. It was seen that there were two potential plateaus around 4.0 and 4.7V. The total capacity remained almost constant (approximately 135mAh/g). The capacity at 4.7V range became larger with an increase in X, while that at 4.0V range decreased. It was explained that the capacity at 4.0V region was related to the Mn^{4+}/Mn^{3+} redox reaction and that at 4.7V region was attributed to the Ni^{2+}/Ni^{4+} redox couple, as discussed in the previous report [7].
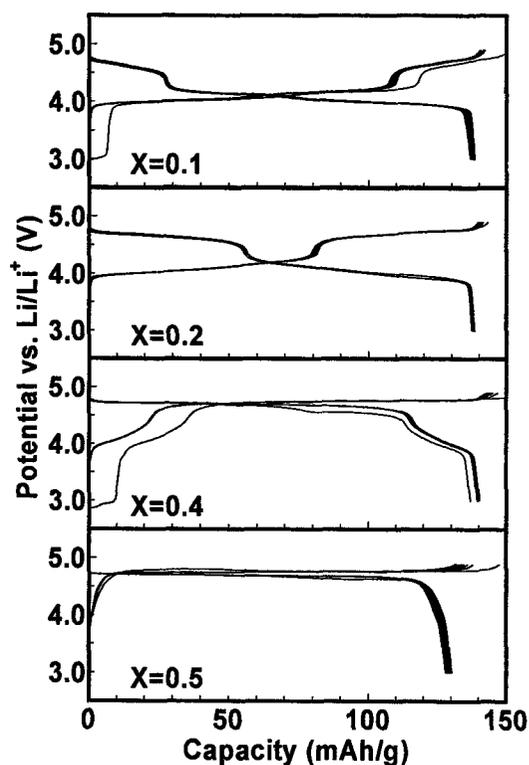
Fig. 2. Charge-discharge curves of $LiMn_{2-x}Ni_xO_4$ spinel oxide cathode with Li metal anode.

3.2. The annealing temperature

Next, we examined the effect of the annealing temperature for a fixed substitution degree X=0.5. The powder X-ray diffraction analysis showed that the specimens prepared below 700℃ consisted of only cubic spinel oxide, however, those annealed above 750℃ had a main phase of cubic spinel oxide with a trace amount of NiO rock-salt. The variation of the lattice constant of the cubic spinel oxide with the annealing temperature is shown in Fig. 3. The lattice constant slightly decreased with an increase in the annealing temperature upto 700℃, and took a minimum. Further increase in the annealing temperature caused the elongation of the lattice constant. It was seen from the X-ray diffraction that, in high-temperature annealing, the precipitation of NiO occurred as a separated phase. Subsequently, the NiO separation generated the spinel oxide containing less Ni^{2+} and Mn^{4+} amounts, that is, the spinel oxide with larger lattice constant.
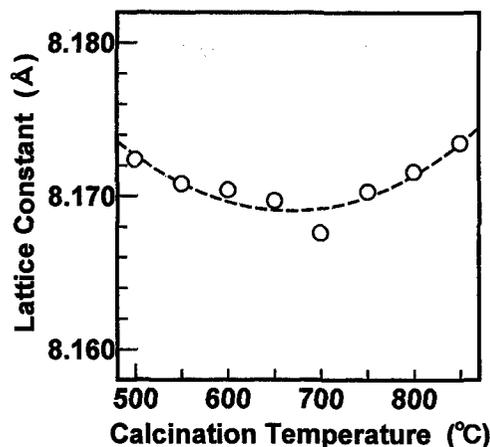
Fig. 3. Variation of the lattice parameter with the calcination temperature.

Fig. 4. The saturation magnetization at 5K (a) and the Curie temperature (b) versus the annealing temperature.

From the magnetic measurement, all the compounds with X=0.5 were ferromagnetic materials with the Curie temperature higher than 100K and exhibited typical magnetic hysteresis loops at low temperature. The magnetic saturation was easily attained and the values at 5K were plotted as a function of the preparation temperature in Fig. 4(a). In addition, the temperature dependence of the saturation magnetization enabled us to determine the Curie temperature, which was plotted in Fig. 4(b). Both two gradually increased as the preparation temperature was raised upto 700℃, and had maximum values (approximately 105emu/g and 145K). They were reduced, as the annealing temperature was higher than 750℃. It was possible that the lowering of both the magnetization and the Curie temperature at high preparation temperature was also attributed to the formation of spinel oxide containing less Ni^{2+} and Mn^{4+}, which had smaller magnetization and lower Curie temperature. Furthermore, the maximum value of the saturation magnetization coincided well with the expected one (108emu/g), in which the magnetic moments of Mn^{4+} ($3\mu_B$) were assumed to be anti-parallel to those of Ni^{2+} ($2\mu_B$).

The electrochemical charge-discharge curves are shown in Fig. 5. It was clear from the potential profiles that the redox curves consisted of mainly the plateau at 4.7V region. However, a small anomaly at 4.0V region was detected for the cathode material prepared below 700℃ and above 700℃, and the capacity at 4.0V region was negligible for only the specimen annealed at 700℃. Considering the above results, the spinel oxide prepared at 700℃ had no Mn^{3+} ion as the constituent, but the other specimen had a small amount of Mn^{3+} ions. In addition, the cathode material prepared at 700℃ had the redox capacity at 4.7V region of approximately 130mAh/g, which was almost 90% of the theoretical value. The facts obtained from these electrochemical results were consistent with those from the magnetic studies. They implied that it was necessary to adjust the preparation conditions in order to obtain the spinel oxide with the correct composition and stoichiometry. There existed an optimum annealing temperature, which was about 700℃ in our preparation method. The optimum preparation condition brought about the material with the smallest lattice constant, the greatest magnetization and the highest Curie temperature. Consequently, it was thought that the magnetic properties were good indices

of the spinel oxide cathode material.

Potential vs. Li/Li$^+$ (V)

500°C

600°C

700°C

800°C

Capacity (mAh/g)
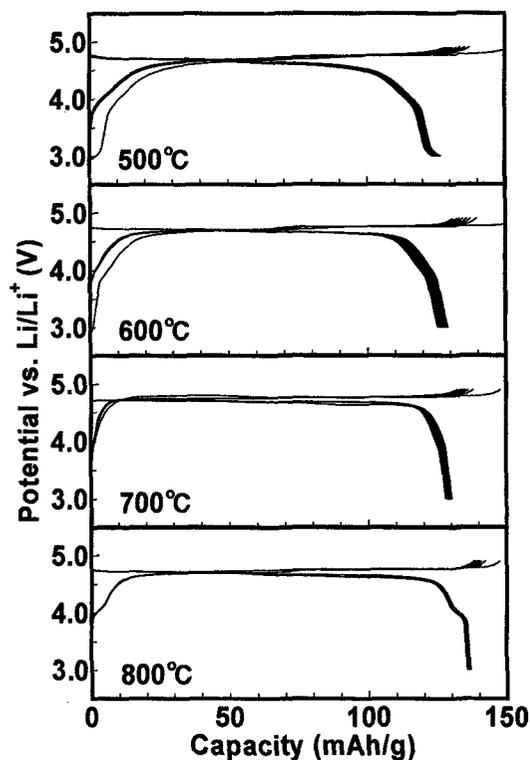
Fig. 5. Charge-discharge curves of $LiMn_{1.5}Ni_{0.5}O_4$ spinel oxide cathode with Li metal anode.

4. CONCLUSION

We have investigated the synthesis, magnetic and electrochemical properties of Ni^{2+}-substituted Li-Mn spinel oxide. The increase in the substitution degree brought about the linear decrease in the lattice parameter and the magnetic transformation from antiferromagnetic to ferrimagnetic material. In the electrochemical aspect, the capacity at 4.7V region grew with an expense of the capacity at 4.0V region. For the annealing temperature, there existed an optimum temperature, where the lattice constant took a minimum, both the low-temperature magnetization and the Curie temperature had maximum values (145K and 105emu/g), and no redox signal at 4.0V was detected. It was found that the redox capacity at 4.7V region reached approximately 130mAh/g.

REFERENCES
[1] W. Li and J. C. Currie, J. Electrochem. Soc., **144** (1997) 2773.
[2] A. Yamada, S. C. Chung and K. Hinokuma, J. Electrochem. Soc., **148** (2001) 224.
[3] Y. Xia and M. Yoshio, J. Electrochem. Soc., **144** (1997) 4186.
[4] K. Yamaura, N. Takano, A. Hirano and R. Kanno, J. Solid State Chem., **127** (1996) 109.
[5] Y. Jang, B. Huang, F. C. Chou, D. R. Sadoway and Y. M. Chiang, J. Appl. Phys., **87** (2000) 7382.
[6] C. Sigala, D. Guyomard, A. Verbaere, Y. Piffard and M. Tournoux, Solid State Ionics, **81** (1995) 167.
[7] Q. Zhong, A. Banakdarpour, M. Zhang, Y. Gao and J. R. Dahn, J. Electrochem. Soc., **144** (1997) 205.
[8 H. Kawai, M. Nagata, H. Tsukamoto and A. R. West, J. Mater. Chem., **8** (1998) 837.
[9] H. Shigemura, M. Tabuchi, H. Kobayashi, A. Hirano and H. Kageyama, J. Mater. Chem., **12** (2002) 1882.
[10] G. Blasse, J. Phys. Chem. Solids, **27** (1966) 383.
[11] J. B. Goodenough, *Magnetism and the Chemical Bond* (Wiley, New York, 1963).
[12] J. Kanamori, J. Phys. Chem. Solids, **10** (1959) 87.