Thermodynamic Stability and Cathode Performance of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ as Cathode Active Material for the Lithium Secondary Battery

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To improve the cycle performance of the 4 V class lithium manganese oxide positive electrode material for the lithium secondary battery, we have been investigated the partial substitution of an another metal for Mn. In this study, the quaternary spinel, $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$, in which a part of the Mn is replaced by Mg is prepared. The Mn valence was determined by chemical analysis. The heats of dissolution of the samples were measured by the solution calorimetry method. The standard enthalpy of formation, $\Delta_f H^\circ$, and the change in the enthalpy of the reaction, ΔH , were calculated from the heat of dissolution. The $\Delta_f H^\circ$ and ΔH decreased and the Mn valence increased with increasing Mg content. The effect of the electrode characteristics on these properties of the positive electrode active materials was investigated in the 4 V range. The discharge capacity decreased with increasing Mg content. On the other hand, the cycle performance was improved by increasing the Mg content. We investigated the relation between the cathode performance and the thermodynamic stability of the quaternary spinel, $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ ($x = 0-0.2$).

Key Words : Li Secondary Battery, Positive Electrode, Thermodynamic Stability, Substitution Effect

1 Introduction

The stoichiometric lithium manganese oxide as a positive electrode active material for the lithium secondary battery has advantages of low cost and low toxicity, but it has been shown to exhibit poor cycling behavior.¹⁾ This poor cycling behavior has been attributed to several factors. The main factor suggested (1) dissolution of Mn^{3+} in the electrolyte, (2) instability of the spinel structure during the charge-discharge cycle that caused the appearance of two phases (cubic spinel and $\lambda\text{-MnO}_2$). (3) Jahn-Teller effect at the end of the discharge especially at the grain surface, etc.²⁻⁴⁾ The approach to improve the cycle performance is to change of Li and Mn composition, $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$,⁵⁾ and to partially replace Mn by other transition metals, $\text{Li}_x\text{Mn}_{2-y}\text{M}_y\text{O}_4$ ($\text{M} = \text{Ti, Ge, Fe, Co, Zn, Ni, Ga, Cu, Mg, Cr}$),⁶⁻¹⁷⁾ and $\text{LiMn}_{2-\delta}\text{M}_{\delta/2}\text{O}_4$ ($\text{M} = \text{Mg, Zn}$).²⁾ Kock *et al.* demonstrated the cycle performance of the oxygen-rich spinel $\text{LiMn}_{2-x}\text{Mg}_{x/2}\text{O}_{4+\delta}$ ($x = 0.02, 0.05, 0.10$),¹⁸⁾ and Hayashi *et al.* have evaluated the density, the cycle performance, and the chemical diffusion coefficient of Li^+ in the $\text{LiMg}_{1/6}\text{Mn}_{11/6}\text{O}_{4-\delta}$.¹⁹⁾ We have been reported that the preparation of a quaternary spinel, $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$, in which a part of Mn is replaced by Mg ($x = 0-0.2$: single phase) improves the cycle performance. The lattice parameter, a , decreases and the Mn valence increases with increasing Mg content. Partial substitution of Mn with Mg improves the cycling performance in spite of some decrease in the initial capacity.²⁰⁾ We also investigated the relation between the structural phase transition and the electrode characteristics of the $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$.²¹⁾

The calorimetric measurement is important for obtaining information on the thermodynamic energy changes with various changes in the chemical and physical

states.²²⁾ The chemical and physical changes essentially involve heat transfer, which provides useful information on the stability and the processing conditions. The authors have conducted a thermodynamic measurement using the solution calorimetric method and by the EMF method using a solid-state electrochemical cell. For example, the enthalpy change in the reaction and the standard enthalpy of formation were determined by measuring the heat of dissolution for the superconducting complex oxide $\text{Bi}_2\text{Sr}_2(\text{Ca}_x\text{Y}_{1-x})\text{Cu}_2\text{O}_7$ and its related oxides of varying x values as substituted by Ca and by varying the oxygen content at a constant x . The enthalpy change of the formation reaction of the superconducting $(\text{La}_{1-x}\text{Ba}_x)_2\text{CuO}_{4-\delta}$ oxide from simple oxides has revealed that the solid solution is unstable in the composition range $0.04 < x < 0.08$ where a remarkable decrease in T_c , which is called the 1/8 anomaly, is observed.²³⁾ These are examples of useful information obtained by measuring the heat quantity. In this study, $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ ($x = 0-0.2$) were measured for the heat of dissolution to obtain thermodynamic data and to study the thermodynamic stability. We investigated the relation between the properties, cathode performance, and the thermodynamic stability of the quaternary spinel, $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$.

2 Experimental

2.1 Sample preparation

$\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ powders ($x = 0, 0.05, 0.1, 0.15, 0.2$) were prepared by reacting a stoichiometric mixture from $^7\text{Li}_2\text{CO}_3$ powder (99.99% purity and 99.9% ^7Li isotopic substitution, supplied by Tomiyama's high Purity Chemical Ind., Ltd.), MnO_2 powder (99.5% purity, supplied by Wako Pure Chemical Ind., Ltd.), and MgO powder (99.9% purity, also supplied by Wako Pure Chemical

Ind., Ltd.). The mixtures were preheated at 600°C for 24 h in air, then heated at 700°C for 24 h in oxygen.²⁰⁾

2. 2 Structural analysis

The phase identification and the evaluation of the lattice parameters of the products were carried out by powder X-ray diffractometry (XRD) using Cu-K α radiation ($\lambda = 1.54178 \times 10^{-10}$ m, RAD-C, Rigaku Co., Ltd.) in the 2θ range from 10.0 to 70.0°.²⁰⁾

2. 3 Chemical analysis

The single phase samples were subjected to chemical analysis. A quantity of the sample was dissolved in a HCl solution and diluted with water. The total amount of Mn + Mg was determined with a standard solution of EDTA (ethylenediaminetetraacetic acid) using BT (Eriochrome Black T) as an indicator. The total amount of Mn was determined from the total amount of (Mn + Mg) and the Mn to Mg ratio obtained by ICP (inductively coupled plasma atomic emission spectroscopy, Seiko Instruments Co., Ltd, SPS-7000) method. The average valence of the manganese ion was determined by iodometry and chemical analysis.^{20, 21)}

2. 4 Measuring heat of dissolution

The heat of dissolution was measured by a twin-type multicalorimeter (Tokyo Riko MMC-5111),²⁴⁾ where the sample was vacuum-sealed in a glass ampoule. The sample and empty ampoules were placed in the sample and reference containers and placed in a 1.53 mol dm⁻³ HClO₄ solution containing 1×10^{-4} mol of Fe(ClO₄)₂. The solution was stirred until equilibrium was reached, and the ampoule was broken by a hammer to dissolve the sample in the solvent, and changes over time in differential temperature caused by the ampoule breaking and stirring was corrected in order to only measure the heat from the dissolution. A given current was supplied at a constant voltage to the heater to produce the differential temperature-time curves and determine the heat of dissolution by comparing curves.²⁵⁾

2. 5 Electrochemical measurement

The electrochemical cell was a three-electrode cell consisting of the Li film (C. E. and R. E.) and a LiMn_{2-x}Mg_xO₄ ($x = 0, 0.05, 0.1, 0.15, 0.2$) cathode (10 × 10 mm²) (W. E.). The cathodes were prepared by pressing a blend of active material (30 mg), acetylene black (10 mg) and PTFE (10 mg) onto a Ni mesh (Taiyo Kanaami Co., Ltd.) at 400 kgf cm⁻². The cathodes were then dried at 150°C for 12 h under vacuum. The anodes were prepared by pressing a lithium sheet onto a Ni mesh. The electrolyte used was 1 mol dm⁻³ LiClO₄ - propylene carbonate

(PC)/dimethyl carbonate(DMC) (1 : 1) solution. All procedures were carried out in a Ar box.

Constant-current charge-discharge studies were controlled by a battery cyler (Hokuto Denkou, HJR-110 mSM6). Cycling of the test material was performed in a sealed laboratory cell. Charge-discharge tests were performed at a constant current density (0.2 mA cm⁻²) with cutoff potentials of 3.5 to 4.3 V vs. Li/Li⁺. The specific capacity values were calculated from the value of the current, the mass of the active material in the cathode, and the elapsed time.²⁰⁾

3 Results and Discussion

3. 1 Sample characterization

The powder X-ray diffraction profiles of the LiMn_{2-x}Mg_xO₄ ($x = 0, 0.05, 0.1, 0.15, 0.2$) were identified as a single phase cubic spinel with a space group Fd3m. The cubic lattice parameters obtained from the XRD of LiMn_{2-x}Mg_xO₄ and the lattice parameter a decreased with increasing Mg content below $x = 0.2$. The boundary for a single phase solid solution of LiMn_{2-x}Mg_xO₄ was estimated to be $x = 0.2$.²⁰⁾ Hence, measurements of the other properties were made for the single phase samples. The metal compositions of these samples, which were determined by Inductively Coupled Plasma(ICP), are shown in Table 1.²⁰⁾ The resulting metal composition is the same as the nominal composition. Next, the Mn valence was determined by chemical analysis and the oxygen content was evaluated by metal composition and Mn valence using electroneutral conditions. The Mn valence, oxygen content and Mg content are shown in Table 1.²⁰⁾ The Mn valence increases with increasing Mg content. We may also consider how the Mg substitution affects the lithium storage capacity of LiMn₂O₄. The substitution of Mg²⁺ into the Mn-site is accompanied by the oxidation of Mn³⁺ to Mn⁴⁺, resulting in an increase in the average valence of Mn, and hence a suppression of the Jahn-Teller distortion. On the other hand, the oxygen content was almost constant at about 4.03 below $x = 0.2$.²⁰⁾

3. 2 Calculation of the standard enthalpy of formation, ΔH^0 , and the enthalpy change of reaction, ΔH

The thermodynamic stability of the oxide is usually evaluated by the Gibbs free energy, ΔG . ΔG consists of an enthalpy term, ΔH , and an entropy term, $T\Delta S$. Since the entropy term, $T\Delta S$, is negligible for the solid-phase at room temperature, confirmed by measuring the electromotive forces (EMF) of several oxides to determine their ΔS values. Thus the tendency of the enthalpy

Table 1 Results of composition. Mn valence, oxygen content, and lattice parameter of LiMn_{2-x}Mg_xO₄.

Mg substitution x	Composition Li : Mn : Mg				Mn valence	Oxygen content	Lattice parameter a (10 ⁻¹⁰ m)	
0	1.000	:	2.000	:	0	3.548	4.05	8.2358
0.05	1.000	:	1.948	:	0.052	3.556	4.02	8.2338
0.1	0.996	:	1.900	:	0.104	3.609	4.03	8.2356
0.15	1.005	:	1.850	:	0.145	3.674	4.04	8.2191
0.2	1.002	:	1.794	:	0.204	3.701	4.02	8.2154

The maximum errors of composition: ± 0.003

The maximum errors of Mn valence: ± 0.003

The maximum errors of oxygen content: ± 0.003

change of reaction, ΔH , which associates with the reaction to form $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ from simple oxides, was used instead of the ΔG tendency.^{23, 26, 27)}

ΔH and $\Delta_i H^0$ are predicted from heat of dissolution of the oxide. The enthalpy change of the reaction, ΔH , is calculated by applying Hess's law to oxides constituting $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ (Fig. 1). We determine the enthalpy changes of the reaction, ΔH , by subtracting the heat of dissolution of the complex oxide from the total heat of dissolution of the simple oxides constituting the complex oxide. Figure 2 shows the flow sheet for measuring the heat of dissolution, solution compositions, and sample quantities, where each simple oxide constituting the complex oxide is dissolved to stoichiometry in the complex oxide composition. Each heat of reaction was measured several times and the average reported. Its error bar was determined from the statistical error. For example, the heat of dissolution of the simple oxides and the

complex oxide $\text{Li}_{0.996}\text{Mn}_{1.900}\text{Mg}_{0.104}\text{O}_{4.03}$ ($x = 0.1$, Mn valence = 3.609), show in Fig. 2, are as follows:

These are substituted into

$$(0.996/2)\text{Li}_2\text{O} + (1/2) \{0.782(1.900/2)\} \text{Mn}_2\text{O}_3 + 1.218(1.900/2)\text{MnO}_2 + 0.104\text{MgO} = \text{Li}_{0.996}\text{Mn}_{1.900}\text{Mg}_{0.104}\text{O}_{4.03} \quad (1)$$

$$\text{Li}_2\text{O}(\text{s}) + \text{Soln.1} = \text{Soln.2} + Q_1; \quad Q_1 = 233.5 \pm 0.7 \text{ kJ/mol Li}_2\text{O} \quad (2)$$

$$\text{Mn}_2\text{O}_3(\text{s}) + \text{Soln.2} = \text{Soln.3} + Q_2; \quad Q_2 = 242.4 \pm 2.2 \text{ kJ/mol Mn}_2\text{O}_3 \quad (3)$$

$$\text{MnO}_2 + \text{Soln.3} = \text{Soln.4} + Q_3; \quad Q_3 = 173.84 \pm 0.09 \text{ kJ/mol MnO}_2 \quad (4)$$

$$\text{MgO}(\text{s}) + \text{Soln.4} = \text{Soln.5} + Q_4; \quad Q_4 = 141.1 \pm 0.8 \text{ kJ/mol MgO} \quad (5)$$

$$\text{Li}_{0.996}\text{Mn}_{1.900}\text{Mg}_{0.104}\text{O}_{4.03} + \text{Soln.1} = \text{Soln.5} + Q_5; \quad Q_5 = 350.9 \pm 0.5 \text{ kJ/mol Li}_{0.996}\text{Mn}_{1.900}\text{Mg}_{0.104}\text{O}_{4.03} \quad (6)$$

$$\Delta H \text{ is given from Eqs. (1) through (6):} \\ \Delta H = Q_5 - [(0.996/2)Q_1 + (1/2) \{0.782(1.900/2)\} Q_2 + 1.218(1.900/2)Q_3 + 0.104 Q_4] \\ = -71.3 \pm 1.0 \text{ kJ/mol} \quad (7)$$

Since the standard enthalpies of formation of Li_2O , Mn_2O_3 , MnO_2 and MgO are -597.94 , -959.0 , -520.03 and -601.70 kJ/mol,²⁸⁾ respectively, the standard enthalpies of formation of $\Delta_i H^0$ of $\text{Li}_{0.996}\text{Mn}_{1.900}\text{Mg}_{0.104}\text{O}_{4.03}$ is calculated as follows:

$$\Delta_i H^0 = (0.996/2)\Delta_i H^0(\text{Li}_2\text{O}) + (1/2) \{0.782(1.900/2)\} \Delta_i H^0(\text{Mn}_2\text{O}_3) + 1.218(1.900/2)\Delta_i H^0(\text{MnO}_2) + 0.104 \Delta_i H^0(\text{MgO}) + \Delta H \\ = -1389.5 \pm 1.0 \text{ kJ/mol} \quad (8)$$

Table 2 provides the enthalpy change, ΔH , of the formation reaction from simple oxides and the standard enthalpy of formation, $\Delta_i H^0$, of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ and the Mg

Table 2 Results of enthalpy changes for the reaction, ΔH , and standard enthalpies of formation, $\Delta_i H^0$, of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$.

$\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$	ΔH (kJ/mol)	$\Delta_i H^0$ (kJ/mol)
$x = 0$	$-66.1(10)$	$-1368.5(10)$
$x = 0.05$	$-70.5(10)$	$-1378.8(10)$
$x = 0.1$	$-71.3(10)$	$-1389.5(10)$
$x = 0.15$	$-73.0(8)$	$-1398.3(8)$
$x = 0.2$	$-72.5(6)$	$-1405.4(6)$

Fig. 3 Relation between enthalpy changes of reaction, ΔH , and Mg substitution x of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$.

Fig. 1 The calculation method of enthalpy change of reaction, ΔH , and its standard enthalpies of formation, $\Delta_i H^0$. The coefficients of p and q are determined by Mn valence.

Fig. 2 Flow sheet for the calorimetric measurement on the $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$

content. Figure 3 shows the relation between ΔH and the Mg content x in $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$. ΔH decreases with increasing Mg content. Thus, the $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ of higher Mg content x has a larger $|\Delta H|$ meaning it is thermodynamically stabler of the complex oxide.

3.3 Electrochemical studies

3.3.1 Galvanostatic charge-discharge curves

Figure 4 shows the charge-discharge curves during the first cycle of the $\text{Li} \mid \text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ cells for $x = 0, 0.05, 0.1, 0.15, 0.2$ at a current density of 0.2 mA cm^{-2} . The initial discharge capacity of the cells was reduced by increasing the Mg content and Mn valence. It suggests that even for the substituted spinel phases, only the amount of Mn^{3+} contributes to the charge capacity, because the deintercalation of Li^+ from the spinel structure must be electrically compensated by the oxidation of Mn^{3+} to Mn^{4+} . In terms of the capacity, the suitable dopant content should not be too large, especially for the divalent doping cations. The initial discharge capacity of the $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ electrodes drops with increasing Mg content from 121 mAh g^{-1} at $x = 0.05$ to 103 mAh g^{-1} at $x = 0.1$, and further decreased to 73 mAh g^{-1} at $x = 0.2$. We might also consider how the Mg substitution affects the lithium storage capacity of LiMn_2O_4 . The substitution of Mg^{2+} into the Mn-site is accompanied by an oxidation of Mn^{3+} to Mn^{4+} resulting in an increase in the average valence of the manganese ions,²⁰ and hence a suppression of the Jahn-Teller distortion.²¹ The electrochemical cycling of Mg substituted LiMn_2O_4 still involves two stages during the charge-discharge processes, but that the two plateaus are less distinct with increasing Mg content. This suggests that a single phase region of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ is maintained during the charge-discharge with increasing Mg content.

3.3.2 Cycle performance Figure 5 shows the discharge capacity with cycle number obtained between 3.5 and 4.3 V in $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ ($x = 0, 0.05, 0.1, 0.15, 0.2$).²⁰ The discharge capacity of the cell decreases with an increasing the Mg content. However, a drastic improvement in the cycle performance was observed with an increase in the Mg content of the spinel, and the Mg substitution causes an improved cycle performance.²⁰ The structural phase transition of LiMn_2O_4 from cubic to orthorhombic occurs at low temperature.^{21, 29} On the

Fig. 4 The galvanostatic charge-discharge curves at first cycle of $\text{Li} \mid \text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ cells (A: $x = 0$, B: $x = 0.05$, C: $x = 0.10$, D: $x = 0.15$, E: $x = 0.20$).

Fig. 5 Relation between discharge capacity and cycle number of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ at 25°C and 0.2 mA cm^{-2} . Cut-off voltage: 4.3–3.5 V ($\circ$: $x = 0$, $\square$: $x = 0.05$, $\triangle$: $x = 0.10$, ∇ : $x = 0.15$, $\diamond$: $x = 0.20$).

other hand, $\text{LiMn}_{1.8}\text{Mg}_{0.2}\text{O}_4$ almost retains a cubic phase down to 200 K. Hence, the crystal structure is more stable at low temperature by the substitution of Mg for Mn.²¹

3.4 Relation between thermodynamic stability and cycle performance

The relationship between the thermodynamic stability and cycle performance of quaternary $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ with respect to a partial substitution of Mn by Mg was investigated. The enthalpy change of the reaction, $|\Delta H|$, for $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ increased with increasing Mg content to make the complex oxide thermodynamically stable. On the other hand, the charge-discharge curves shows that the two stages disappeared with increasing the Mg content. This means a single phase region of $\text{Li}_y\text{Mn}_{2-x}\text{Mg}_x\text{O}_4$ was maintained during the charge-discharge with increasing the Mg content. Moreover, the cycle performance was improved by increasing Mg content. These results mean stabilization of the spinel structure during the charge-discharge process. Consequently, the more thermodynamically stable complex oxide sample makes a more stable structure and suppresses destruction of the structure during the charge-discharge cycle. Based on these results, the cycle performance is improved.

4 Conclusion

- (1) The enthalpy changes, ΔH , of the formation reaction of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ from simple oxides and the standard enthalpy of formation, $\Delta_f H^\circ$, were determined as a function of x using the solution calorimetric method.
- (2) It was found that the enthalpy change of formation reaction $|\Delta H|$ of $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ increased with increasing Mg content x , indicating that the $\text{LiMn}_{2-x}\text{Mg}_x\text{O}_4$ species are more thermodynamically stable with increasing x .
- (3) The two plateaus on the charge-discharge curves disappeared, and the cycle performance was improved with increasing Mg content x .
- (4) The more thermodynamically stable complex oxide makes a stable crystal structure and suppressed destruction of the structure during the charge-discharge cycle. Based on these results, the cycle performance is improved.

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