

Oxygen nonstoichiometry of spinel $\text{LiMn}_2\text{O}_{4-\delta}$

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Abstract

Oxygen nonstoichiometry δ has been determined for a spinel $\text{LiMn}_2\text{O}_{4-\delta}$ sample as a function of oxygen partial pressure P_{O_2} in the temperature range between 873 and 1123 K, using a thermogravimetric analysis and a chemical titration analysis. The maximum oxygen deficiency of $\text{LiMn}_2\text{O}_{4-\delta}$ was found to be $\delta_{\text{cr.}} \sim 0.2$. For the samples obtained at 1023 K, as δ increased from zero, the tetragonal spinel phase appeared around $\delta = 0.07$, while only the cubic spinel phase was observed for the samples with $\delta \leq 0.07$. Partial molar enthalpy $\Delta\bar{H}_{\text{O}_2}$ and entropy $\Delta\bar{S}_{\text{O}_2}$ of oxygen in the $\text{LiMn}_2\text{O}_{4-\delta}$ samples with $0.05 \leq \delta \leq 0.2$ were estimated to be -208 to -277 kJ mol^{-1} and -168 to -219 $\text{J K}^{-1} \text{mol}^{-1}$ respectively. The dependence of δ on P_{O_2} was expressed as $\delta \sim P_{\text{O}_2}^{(-0.67 \pm 0.06)}$; to explain this relation, we employed a defect cluster model. In contrast, the sample with $\delta = 0.67$ was found to decompose to LiMnO_2 and Mn_3O_4 . The change in standard enthalpy for the decomposition ΔH^0 was estimated to be 84 kJ mol^{-1} .

Keywords: Oxygen nonstoichiometry; Thermogravimetric analysis; LiMn_2O_4 ; Spinel

1. Introduction

Various kinds of ternary oxide which contain a transition metal element and lithium have been investigated as cathode materials for rechargeable lithium batteries [1–3]. Among them, LiMn_2O_4 spinel is considered to be one of the most promising candidates [4]. At room temperature, the crystal structure of LiMn_2O_4 belongs to $Fd\bar{3}m$ space group [5] of a cubic system. The distribution of cations in LiMn_2O_4 is represented by the following ionic formula: $(\text{Li}^+)_{8a}[\text{Mn}^{3+}\text{Mn}^{4+}]_{16d}\text{O}_4^{2-}$ [6], where 8a and 16d refer to the tetrahedral and octahedral sites of the cubic spinel structure. Furthermore, the Mn_2O_4 spinel skeleton remains during the insertion of excess lithium into LiMn_2O_4 , as well as during lithium extraction from the stoichiometric material [4,7–9]. However, lithium insertion into $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ induces a structural phase transition from a cubic spinel phase to a tetragonal $I4_1/amd$ phase around $x = 0$ [10]. This phase transition is caused by a cooperative Jahn–Teller distortion of Mn^{3+} ions. Consequently, the average valence of Mn ions in $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ plays a significant role in determining not only the total amount of Li ions removed or restored, but also the crystal structure.

Recently, Tarascon et al. [11] reported that LiMn_2O_4 lost oxygen at temperatures above 873 K in an Ar gas flow. Thus, the composition of the sample annealed in a reducing atmosphere can be represented as $\text{LiMn}_2\text{O}_{4-\delta}$. In order to balance the charge in $\text{LiMn}_2\text{O}_{4-\delta}$, the average valence of Mn ions should decrease in proportion to oxygen nonstoichiometry δ . As a result, δ is considered to be one of the essential factors controlling the structural and electronic properties of $\text{LiMn}_2\text{O}_{4-\delta}$. Nevertheless, to the authors' knowledge, δ of $\text{LiMn}_2\text{O}_{4-\delta}$ has not been investigated in detail, except in the report [11] mentioned above. In particular, there is no data on the relationship between δ of $\text{LiMn}_2\text{O}_{4-\delta}$ and oxygen partial pressure P_{O_2} . Here, we report δ of $\text{LiMn}_2\text{O}_{4-\delta}$ with respect to P_{O_2} and temperature and discuss the mechanism for formation of oxygen defects using a defect cluster model.

2. Experimental

A powder sample of LiMn_2O_4 was synthesized by a solid state reaction technique using reagent-grade Li_2CO_3 and MnO_2 powders. The powders were thor-

oughly mixed by a planetary ball mill using ethanol as solvent. After drying, the mixture was pressed into a pellet with 30 mm diameter and about 5 mm thick. The pellet was calcined three times at 1073 K for 8 h in air. The sample was furnace-cooled to room temperature with a rate of about 4 K min⁻¹. Powder X-ray diffraction (XRD) analysis indicated that the sample was single phase and of a cubic spinel structure with lattice parameter $a \sim 0.824$ nm.

Oxygen nonstoichiometry δ was measured using a thermogravimetric technique. A powder sample of about 100 mg was placed in a platinum crucible and accurately weighed. The crucible was suspended in a furnace tube by a platinum wire at temperatures between 873 and 1123 K for 24 h in an O₂-Ar gas mixture flow. In order to quench the sample to 273 K, the crucible was downed onto the glass wool, which was placed at the bottom of the tube, within a few seconds; the bottom of the tube was immersed in ice-water. Then, the crucible was weighed again to obtain the change in the weight of the sample. Oxygen partial pressure P_{O_2} of the mixed gas was checked by measuring conductivity of CoO in the furnace tube [12].

For the samples annealed in a 20%O₂-Ar gas mixture flow at temperatures between 873 and 1123 K and then quenched, the absolute values of δ were determined by an induction coupled plasma analysis and a chemical titration analysis using KMnO₄. For each series of the samples obtained at the same temperature (T_O) but for the different values of P_{O_2} , the values of δ were calculated using the change in the weight from the sample obtained in a 20%O₂-Ar gas mixture flow at T_O . The measurement accuracy of δ was estimated to be ± 0.005 .

3. Results

3.1. Oxygen nonstoichiometry

Fig. 1 shows the relationship between oxygen nonstoichiometry δ and $\log P_{O_2}$ at temperatures between 873 and 1123 K for LiMn₂O_{4- δ} . There were no marked differences between the data obtained on decreasing or increasing P_{O_2} . Thus, formation of oxygen deficiency in LiMn₂O₄ is found to be a reversible reaction with respect to P_{O_2} . For the data obtained at 873 and 973 K, $4 - \delta$ decreased monotonically with decreasing P_{O_2} . In contrast, for the data obtained at 1023 K, as P_{O_2} decreased, $4 - \delta$ decreased monotonically down to $4 - \delta \sim 3.6$, suddenly decreased from 3.6 to 3.33 at $\log P_{O_2} = -3.6$, and then $4 - \delta$ leveled off to a constant value, $4 - \delta = 3.33$ in the P_{O_2} range below $10^{-3.6}$ atm. The $\log P_{O_2}$ vs. T curves

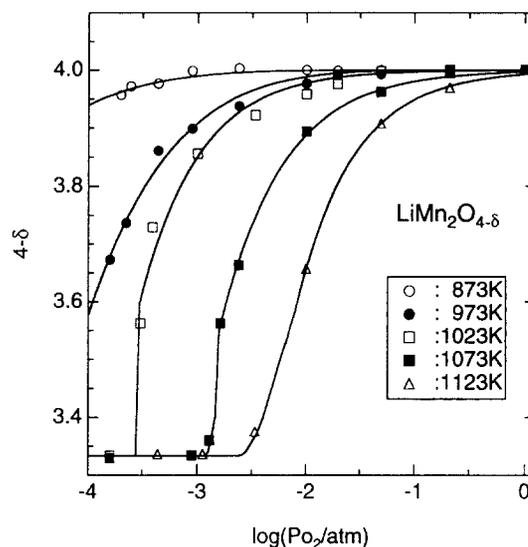


Fig. 1. The relationship between oxygen nonstoichiometry $4 - \delta$ and oxygen partial pressure $\log(P_{O_2}/\text{atm})$ for LiMn₂O_{4- δ} obtained at temperatures between 873 and 1123 K.

obtained at 1073 and 1123 K were parallel to that obtained at 1023 K, though the sudden decreases in $4 - \delta$ were observed around $\log P_{O_2} = -2.9$ at 1073 K and $\log P_{O_2} \sim -2.0$ at 1123 K. According to a powder XRD analysis, the samples with $4 - \delta > 3.85$ were assigned to be a single phase of a cubic spinel structure or to consist of cubic and tetragonal spinel phases, while the samples with $3.33 < 4 - \delta \leq 3.75$ were a mixture of LiMn₂O_{4- δ} , LiMnO₂ and Mn₃O₄. Therefore, the maximum oxygen deficiency was found to be $\delta_{cr.} \sim 0.2$. Furthermore, the sample with $4 - \delta = 3.33$ consisted of LiMnO₂ and Mn₃O₄; that is, LiMn₂O₄ decomposed as follows:



For this reaction, a change in weight due to vaporization of oxygen is calculated to be -5.90%; this value was in good agreement with those obtained by thermogravimetric measurements; that is, the weight of the sample with $4 - \delta = 3.33$ reduced by about 5.9% compared with that of the stoichiometric material.

3.2. Formation of oxygen deficiency

The partial molar enthalpy $\Delta\bar{H}_{O_2}$ and entropy $\Delta\bar{S}_{O_2}$ of the formation of oxygen deficiency are given by

$$\Delta\bar{G}_{O_2} = RT \ln P_{O_2} = \Delta\bar{H}_{O_2} - T\Delta\bar{S}_{O_2} \quad (2)$$

where $\Delta\bar{G}_{O_2}$ is the partial molar free energy, R is the gas constant and T is the absolute temperature. Using thermodynamic relations in equilibrium states, $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ can be represented as follows:

$$\Delta\bar{H}_{O_2} = \left[\frac{\partial(R \ln P_{O_2})}{\partial(1/T)} \right]_{\delta}$$

$$\Delta\bar{S}_{O_2} = - \left[\frac{\partial(RT \ln P_{O_2})}{\partial T} \right]_{\delta} \quad (3)$$

Fig. 2(a) shows $\log P_{O_2}$ as a function of $1/T$ for different values of δ , and Fig. 2(b) $T \log P_{O_2}$ as a function of T . For each set of data obtained for different values of δ , linear relationships were clearly observed. Using Eqs. (3) and each of the values of the slope, we can obtain $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$. Fig. 3 shows the $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ as a function of δ . As δ increased from zero, both $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ decreased monotonically up to $\delta = 0.15$, and then $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ increased with further increasing δ . The values of $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ for the $\text{LiMn}_2\text{O}_{4-\delta}$ samples with $0.05 \leq \delta \leq 0.2$ were estimated to be -208 to -277 kJ mol^{-1} and -168 to $-219 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. The mechanism of the formation of oxygen defects will be discussed later.

3.3. Nonstoichiometry and lattice constants

Fig. 4 shows the lattice constants a , c and c/a as a function of δ for the samples obtained at 1023 K. The samples with $4 - \delta > 3.95$ were assigned to be a single

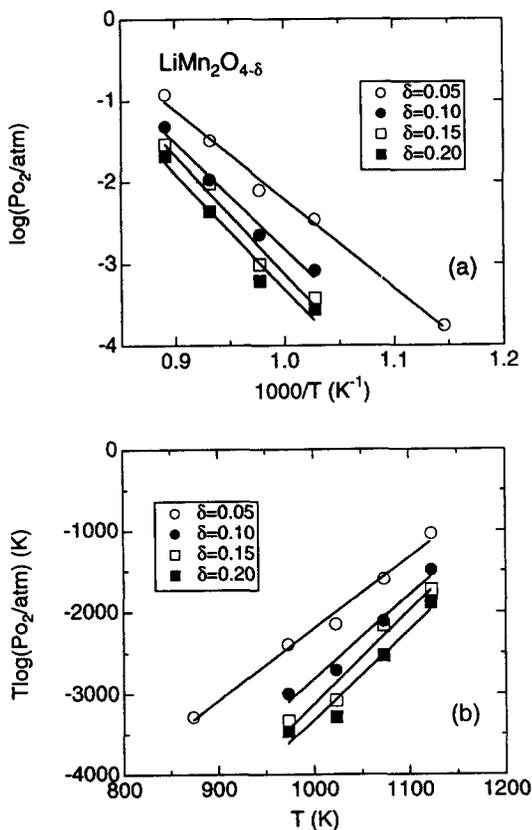


Fig. 2. The dependences of (a) $\log P_{O_2}$ on reciprocal temperature T^{-1} and (b) $T \log P_{O_2}$ on T for $\text{LiMn}_2\text{O}_{4-\delta}$ with different values of δ ($0.05 \leq \delta \leq 0.2$).

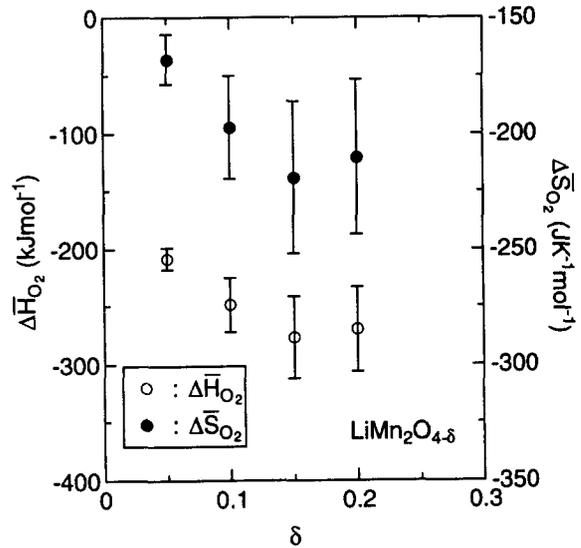


Fig. 3. Partial molar enthalpy $\Delta\bar{H}_{O_2}$ and entropy $\Delta\bar{S}_{O_2}$ of oxygen in $\text{LiMn}_2\text{O}_{4-\delta}$ as a function of δ .

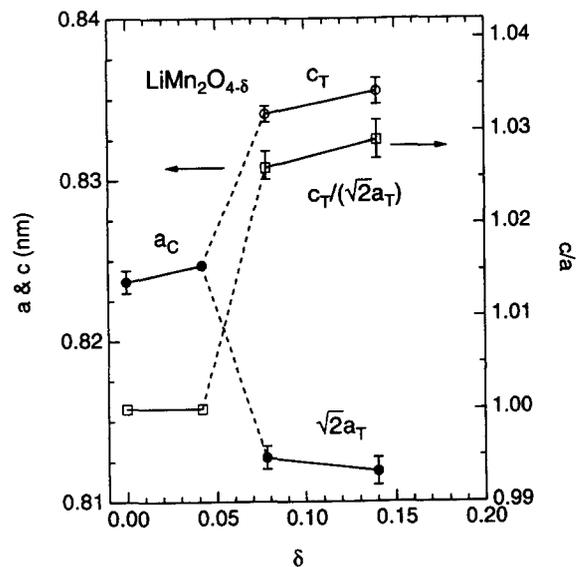


Fig. 4. Lattice constants a , c and c/a as a function of δ for the $\text{LiMn}_2\text{O}_{4-\delta}$ samples obtained at 1023 K; the lattice constants of the tetragonal phase a_T and c_T are expressed as $a_T = a_c/\sqrt{2}$ and $c_T = a_c$, in which a_c is the lattice constant of the cubic phase.

phase of a cubic spinel structure, while both the cubic and the tetragonal spinel phases coexisted in the samples with $3.85 < 4 - \delta < 3.93$. In addition, the tetragonal phase was found to be predominant in the samples with $3.85 < 4 - \delta < 3.93$; in other words, as δ increased from zero, the cubic phase partially transformed into the tetragonal phase around $\delta = 0.07$. According to a geometrical relationship between both spinel phases, the lattice constants of the tetragonal phase a_T and c_T are expressed as $a_T = a_c/\sqrt{2}$ and $c_T = a_c$, in which a_c is the lattice constant of the cubic phase [10]. As seen in Fig. 4, both values of a_c and c_T

increased with increasing δ , while that of a_T decreased. The average valence of Mn ions in $\text{LiMn}_2\text{O}_{4-\delta}$ is expected to decrease from 3.5 as δ increases from zero. Since the ionic radius of the Mn^{3+} ion ($r = 0.0645$ nm [13]) is larger than that of the Mn^{4+} ion ($r = 0.0530$ nm [13]), the increases in the length of both a_c and c_T due to the loss of oxygen are in accordance with the decrease in the average valence of Mn ions. In contrast, the decrease in the length of a_T with increasing δ indicates the decrease in the unit-cell volume due to oxygen defects. Furthermore, the tetragonal distortion c/a increased with increasing δ : for the sample with $\delta = 0.14$, the value of c/a was estimated to be 1.029. This value was rather small compared with that for $\text{LiMn}_2\text{O}_{3.84}$, i.e. $c/a = 1.06$ [11], which had been reported by Tarascon et al. The discrepancy between both values of c/a is probably due to the difference in the temperatures (T_O) from which the samples were quenched; that is, the present result was obtained for a sample annealed at 1023 K, while that of Tarascon et al. was obtained for a sample at 1178 K. According to their result, as T_O was increased, the XRD peaks from the tetragonal phase became intense and sharp [11] because the volume of tetragonal phase increased and/or the homogeneity of the sample was improved. As a result, it is considered that the value of c/a seemed to increase with increasing T_O .

For $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, as x varies from -1 to 1 , a structural phase transition from a cubic $Fd3m$ phase to a tetragonal $I4_1/amd$ phase occurs at $x = 0$ owing to a cooperative Jahn–Teller distortion of Mn^{3+} ions [10]. In contrast, the $\text{LiMn}_2\text{O}_{4-\delta}$ sample with $\delta = 0.042$ was assigned to be a cubic spinel phase, though the average valence of Mn ions was $+3.458$. In the case of $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$, the tetragonal phase should appear, if the average valence of Mn ions is $+3.458$. Assuming that only the average valence of Mn ions is a predominant factor for the cubic to tetragonal phase transition, the cubic symmetry of the $\text{LiMn}_2\text{O}_{3.958}$ sample indicates the possibility that the cooperative Jahn–Teller distortion of Mn^{3+} ions is suppressed by the oxygen deficiency; this is probably because oxygen vacancies weaken the long-range interaction between Mn^{3+} ions. On the contrary, this result may suggest that the excess Li^+ ions in $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ play a significant role in determining the crystal structure.

3.4. Decomposition of LiMn_2O_4

In order to investigate the decomposition process of LiMn_2O_4 , the relationship between $\log P_{\text{O}_2}$ and $1/T$ of the decomposition reaction is shown in Fig. 5. Although $\text{LiMn}_2\text{O}_{4-\delta}$ partially decomposed into LiMnO_2 and Mn_3O_4 around $\delta = 0.2$ and completely decom-

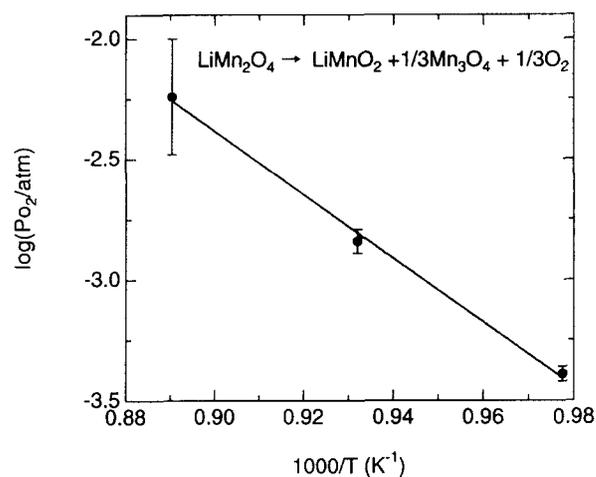


Fig. 5. The relationship between the decomposition P_{O_2} and $1/T$ at temperatures above 1023 K.

posed at $\delta = 0.67$, the decomposition reaction would be approximately represented by Eq. (1). Therefore, the changes in standard free energy ΔG^0 , enthalpy ΔH^0 , and entropy ΔS^0 are given by

$$\Delta G^0 = -RT \ln P_{\text{O}_2}^{1/3} = \Delta H^0 - T\Delta S^0 \quad (4)$$

Using the slope of the $\log P_{\text{O}_2}$ vs. $1/T$ curve and Eq. (4), we obtain $\Delta H^0 = 84$ kJ mol $^{-1}$ in the temperature range between 1023 and 1123 K. This value of ΔH^0 is about a half that of perovskite LaMnO_3 [14]; i.e. $\Delta H^0 = 152.8$ kJ mol $^{-1}$ for the reaction



The crystal structure of LiMnO_2 is an orthorhombic NaCl-type structure with ordering of Li^+ and Mn^{3+} ions [15]. In contrast, the crystal structure of Mn_3O_4 is a tetragonal spinel structure [6] (hausmannite) and the distribution of cations can be represented by $(\text{Mn}^{3+})_{8a}[\text{Mn}^{2+}\text{Mn}^{3+}]_{16d}\text{O}_4$ using an ionic formula. Therefore, it is worth noting that not only Li ions but also Mn ions change their positions in the lattice during the decomposition.

4. Discussion

Now, we discuss the mechanism of the formation of oxygen deficiency in $\text{LiMn}_2\text{O}_{4-\delta}$. Fig. 6 shows the dependences of $\log \delta$ on $\log P_{\text{O}_2}$ for the $\text{LiMn}_2\text{O}_{4-\delta}$ samples with $\delta \leq 0.20$ obtained at temperatures between 873 and 1123 K. Since five $\log \delta$ vs. $\log P_{\text{O}_2}$ curves seem to be approximately parallel each other, it is considered that oxygen deficiency is formed through the same process. The average value of the slope of the five $\log \delta$ vs. $\log P_{\text{O}_2}$ curves was estimated to be -0.67 ± 0.06 . In order to explain the relationship between $\log \delta$ and $\log P_{\text{O}_2}$, we employ a cluster model

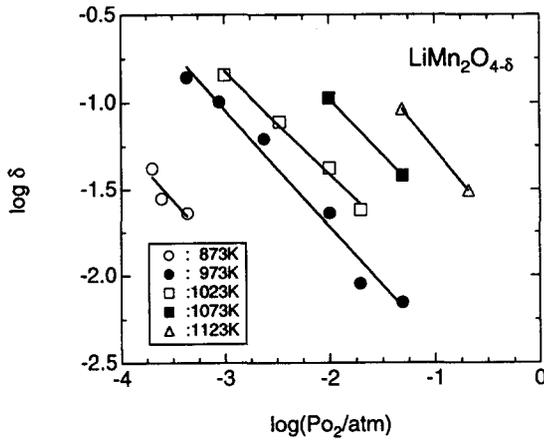
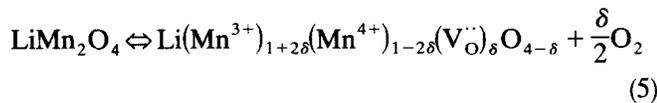


Fig. 6. The dependences of $\log \delta$ on $\log P_{O_2}$ for $\text{LiMn}_2\text{O}_{4-\delta}$ obtained at temperatures between 873 and 1123 K.

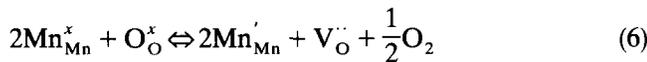
proposed for perovskites $\text{LaMnO}_{3-\delta}$ and $\text{LaCoO}_{3-\delta}$ by Roosmalen and Cordfunke [16]. However, every oxygen ion of spinel LiMn_2O_4 has four nearest neighbors, i.e. three Mn ions and one Li ion. In addition, the connection between MnO_6 octahedra in spinel is characterized as edge-sharing, while that in perovskite as corner-sharing. Furthermore, we assume that only the valence of the Mn ions in $\text{LiMn}_2\text{O}_{4-\delta}$ alters caused by the formation of oxygen deficiency. Therefore, their cluster model could be modified as follows: (1) point defect model; (2) simple cluster model; (3) more complicated cluster model.

(1) *The point defect model.*

At first, we assume that there is no interaction among oxygen defects and between oxygen defects and Mn ions; in other words, both oxygen vacancies and Mn^{3+} ions are randomly distributed on the spinel lattice sites. We will abbreviate this model hereafter as Model 1. The equilibrium reaction for the loss of oxygen from LiMn_2O_4 by Model 1 can be expressed as



or

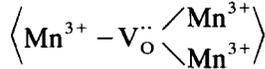


in which Mn'_{Mn} means Mn^{4+} on the Mn sites, Mn_{Mn} Mn^{3+} in place of Mn^{4+} , $\text{V}_\text{O}^{\cdot\cdot}$ O^{2-} vacancy with +2 charge. The equilibrium constant for this reaction K_1 is given by

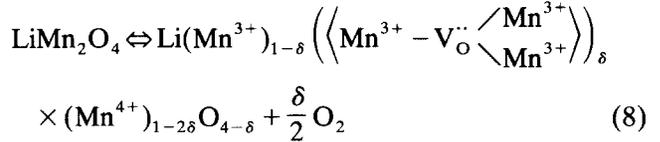
$$K_1 = \frac{[\text{Mn}'_{\text{Mn}}]^2 [\text{V}_\text{O}^{\cdot\cdot}] P_{\text{O}_2}^{1/2}}{[\text{Mn}_{\text{Mn}}^x]^2 [\text{O}_\text{O}^x]} = \frac{4\delta^3 P_{\text{O}_2}^{1/2}}{(1-2\delta)^2(4-\delta)} \quad (7)$$

(2) *The simple cluster model.*

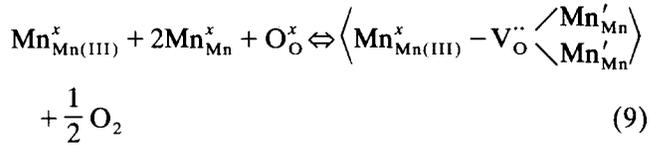
Assuming that there is an interaction between oxygen defects and Mn^{3+} ions, a defect cluster



may be formed to minimize an electrostatic repulsion. We will abbreviate this model hereafter as Model 2. For Model 2, the equilibrium reaction can be expressed as



or

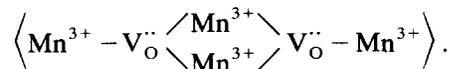


where $\text{Mn}_{\text{Mn(III)}}^x$ means Mn^{3+} on the Mn sites in LiMn_2O_4 ; in order to distinguish from Mn^{3+} replacing Mn^{4+} caused by the formation of oxygen defects, i.e. Mn'_{Mn} , we use this symbol in Eq. (9). The equilibrium constant for this reaction K_2 is given by

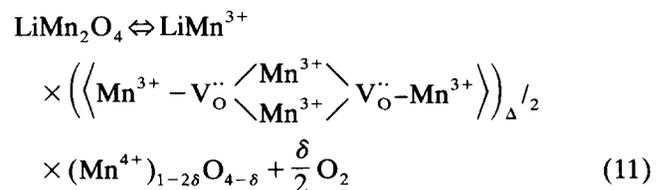
$$K_2 = \frac{\left[\left\langle \text{Mn}_{\text{Mn(III)}}^x - \text{V}_\text{O}^{\cdot\cdot} \left\langle \text{Mn}'_{\text{Mn}} \right\rangle \right\rangle P_{\text{O}_2}^{1/2} \right]}{[\text{Mn}_{\text{Mn(III)}}^x][\text{Mn}_{\text{Mn}}^x]^2 [\text{O}_\text{O}^x]} = \frac{\delta P_{\text{O}_2}^{1/2}}{(1-\delta)(1-2\delta)^2(4-\delta)} \quad (10)$$

(3) *The more complicated cluster model.*

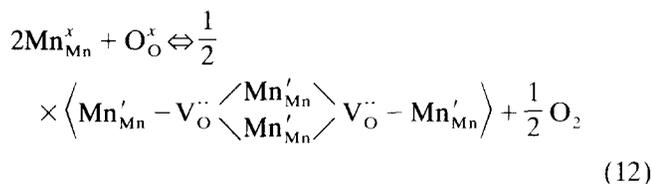
If we assume a strong interaction between oxygen defects, the more complicated cluster is also available for the spinel lattice containing oxygen defects; that is, a cluster which consists of four Mn^{3+} ions and two oxygen defects,



We will call this Model 3 hereafter. The equilibrium reaction can be expressed as



or



The equilibrium constant for this reaction K_3 is given by

$$K_3 = \frac{\left[\left\langle \text{Mn}'_{\text{Mn}} - \text{V}_{\text{O}}^{\cdot\cdot} \left\langle \text{Mn}'_{\text{Mn}} \right\rangle \text{V}_{\text{O}}^{\cdot\cdot} - \text{Mn}'_{\text{Mn}} \right\rangle \right]^{1/2} P_{\text{O}_2}^{1/2}}{[\text{Mn}_{\text{Mn}}^x]^2 [\text{O}_{\text{O}}^x]} \\ = \frac{\delta^{1/2} P_{\text{O}_2}^{1/2}}{(1 - 2\delta)^2 (4 - \delta)} \quad (13)$$

Fig. 7 shows the dependences of $\log P_{\text{O}_2}$ on δ ; the solid circles represent the experimental data obtained at 973 K, the broken line represents the calculated dependence using Model 1, the dotted line Model 2 and the solid line Model 3. The calculated result using Model 3 seems to fit in with the experimental data compared with those using the other two models. Fig. 8 shows the temperature dependence of the equilibrium constant K_3 estimated using Eq. (13) and the present experimental data. The molar enthalpy ΔH_{V}^0 and entropy ΔS_{V}^0 of the formation of the defect cluster are given by

$$RT \ln K_3 = -\Delta H_{\text{V}}^0 + T\Delta S_{\text{V}}^0 \quad (14)$$

On the basis of a linear fit (see Fig. 8), we obtain $\Delta H_{\text{V}}^0 = (116 \pm 9) \text{ kJ mol}^{-1}$ and $\Delta S_{\text{V}}^0 = (31 \pm 4) \text{ J K}^{-1}$

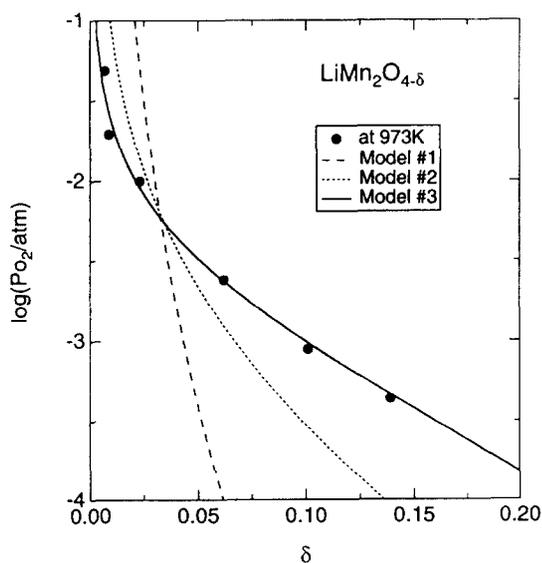


Fig. 7. The dependences of $\log P_{\text{O}_2}$ on δ ; the solid circles represent the experimental data obtained at 973 K, the broken line the calculated dependence using Model 1, the dotted line Model 2 and the solid line Model 3.

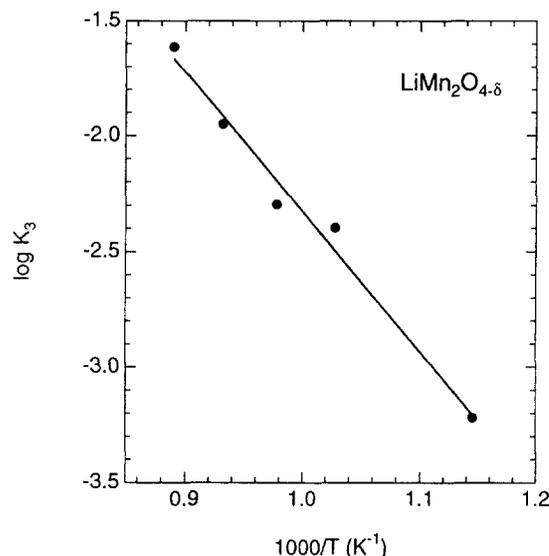


Fig. 8. Temperature dependence of equilibrium constant K_3 ; K_3 was estimated by fitting the experimental data using Model 3.

mol^{-1} in the temperature range between 873 and 1123 K. These values are rather small compared with the values of the formation of the defect cluster, $\langle \text{Mn}^{2+} - \text{V}_{\text{O}}^{\cdot\cdot} - \text{Mn}^{2+} \rangle$, in $\text{LaMnO}_{3-\delta}$ [17], i.e. $\Delta H_{\text{V}}^0 = (349 \pm 6) \text{ kJ mol}^{-1}$ and $\Delta S_{\text{V}}^0 = (96.4 \pm 4.9) \text{ J K}^{-1} \text{ mol}^{-1}$. This implies the possibility that the defect cluster in $\text{LiMn}_2\text{O}_{4-\delta}$ is more easily formed than in $\text{LaMnO}_{3-\delta}$.

Nevertheless, there is no evidence that such a complicated cluster exists in $\text{LiMn}_2\text{O}_{4-\delta}$. Since such defect clusters give rise to a strong local distortion in the lattice, a structural analysis of $\text{LiMn}_2\text{O}_{4-\delta}$ would be useful to investigate the defect structure; in particular, it may be useful to carry out an extended X-ray absorption fine structure (EXAFS) and/or an X-ray absorption near-edge structure (XANES) study on the Mn K-edge. Furthermore, measurements of transport properties for LiMn_2O_4 as a function of P_{O_2} must provide us with significant information on the formation of oxygen defects.

Finally, it should be pointed out that we ignored the role of the Li^+ ions in the present discussion; that is, we assumed that not only the valence state but also the position of the Li^+ ions in $\text{LiMn}_2\text{O}_{4-\delta}$ remained unchanged during the formation of oxygen defects. Considering the mass difference between electrons and Li^+ ions, this assumption looks to be appropriate within a first approximation. However, there is a possibility that Li^+ ions change position from the tetrahedral 8a site to the other vacant sites in $\text{LiMn}_2\text{O}_{4-\delta}$, as had been reported for $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ [9]. Since the distribution of Li^+ ions should alter to minimize electrostatic repulsion, the defect cluster is expected to be stabilized due to the movement of Li^+ ions. Unfortunately, to the authors' knowledge, there

have been no data on the distributions of Li^+ ions and oxygen vacancies in $\text{LiMn}_2\text{O}_{4-\delta}$. In order to further understand the defect structure, it is necessary to carry out a neutron diffraction analysis for $\text{LiMn}_2\text{O}_{4-\delta}$.

5. Summary

We investigated oxygen nonstoichiometry δ for a spinel $\text{LiMn}_2\text{O}_{4-\delta}$ sample as a function of oxygen partial pressure P_{O_2} in the temperature range between 873 and 1123 K using thermogravimetric analysis and a chemical titration analysis. The maximum oxygen deficiency of $\text{LiMn}_2\text{O}_{4-\delta}$ was found to be $\delta_{\text{cr}} \sim 0.2$. For the samples obtained at 1023 K, as δ increased from zero, the tetragonal spinel phase appeared around $\delta = 0.07$, while only the cubic spinel phase was observed for the samples with $\delta \leq 0.07$. Partial molar enthalpy $\Delta\bar{H}_{\text{O}_2}$ and entropy $\Delta\bar{S}_{\text{O}_2}$ of oxygen in the $\text{LiMn}_2\text{O}_{4-\delta}$ samples with $0.05 \leq \delta \leq 0.2$ were estimated to be -208 to -277 kJ mol^{-1} and -168 to $-219 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. The dependence of δ on P_{O_2} was expressed as $\delta \sim P_{\text{O}_2}^{(-0.67 \pm 0.06)}$; in order to interpret this relation, we employed a defect cluster, which consists of two oxygen defects and four Mn^{3+} ions, on the bases of the defect equilibrium. The molar enthalpy ΔH_{V}^0 and entropy ΔS_{V}^0 of formation of the defect cluster was estimated to be $116 \pm 9 \text{ kJ mol}^{-1}$ and $31 \pm 4 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively.

In contrast, the sample with $\delta = 0.67$ decomposed to LiMnO_2 and Mn_3O_4 . The change in standard enthalpy ΔH^0 for the decomposition was estimated to be 84 kJ mol^{-1} in the temperature range between 1023 and 1123 K.

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Note added in proof

Just after our original submission, we found that Yamada et al. had reported a relationship between δ in $\text{LiMn}_2\text{O}_{4-\delta}$ and P_{O_2} . Their result seems to be consistent with ours. (A. Yamada, K. Miura, K. Hinokuma and M. Tanaka, *J. Electrochem. Soc.*, **142**, (1995) 2149.)