OXYGEN NONSTOICHIOMETRY IN PEROVSKITE-TYPE OXIDE, UNDOPED AND Sr-DOPED LaMnO₃

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ABSTRACT

The oxygen nonstoichiometry of a perovskite-type oxide, undoped LaMnO₃+d and Sr-doped La₁₋ₓSrₓMnO₃+d (x = 0 - 0.5) was examined at temperatures between 600 and 1000°C in oxygen pressure between 1 and 10⁻²⁸ atm by thermogravimetry and coulometric titration. The oxygen content, 3+d, in the oxide series La₁₋ₓSrₓMnO₃+d is changed from hyperstoichiometric region (d > 0), to hypostoichiometric region (d < 0), through stoichiometric region (d = 0). The oxide of x = 0 and 0.1 are decomposed into the component oxides, La₂O₃, SrO and MnO. The oxides of x > 0.2 is decomposed through (La,Sr)₂MnO₄ to the component oxides. The partial molar enthalpy and entropy of La₁₋ₓSrₓMnO₃+d (x = 0 - 0.5) were calculated.

INTRODUCTION

Perovskite-type oxide, especially Sr-doped LaMnO₃, La₁₋ₓSrₓMnO₃+d or denoted as (La,Sr)MnO₃, is used as a cathode material in solid oxide fuel cells (SOFCs). Currently, SOFCs are operated at temperatures as high as 1000°C. The surface of the cathode is placed in an air stream, and oxygen pressure within a porous cathode decreases toward electrolyte from the surface. The oxygen pressure at the interface between cathode and electrolyte is reduced to 10⁻³ or 10⁻⁴ atm when high current density is applied.

The undoped mother oxide, LaMnO₃, and the Sr-doped, La₁₋ₓSrₓMnO₃ (x = 0.1 - 0.5), have a wide range of oxygen nonstoichiometry [1,2,3]. Knowledge of the crystal structure, phase relations, thermodynamic stability and thermal expansion coefficient of undoped and doped LaMnO₃ with oxygen nonstoichiometry is required as a function of temperature and oxygen pressure. These properties at high temperatures in various oxygen pressures, however, have not been systematically studied, as described by Minh [4] and Mizusaki [5].

We have been interested in the relationships among crystal structure, phase relations and thermodynamic properties, nonstoichiometry, chemical reactivity and electrical properties of perovskite-type oxides, undoped and doped LaMBO₃ (M = Cr, Mn, Fe, Co), because the oxides are used as components in SOFCs. All of the perovskite-type oxides, (La,AE)MO₃ (AE = Mg, Ca, Sr; M = Cr, Mn, Fe, Co) have a wide range of...
oxygen nonstoichiometry, which governs crystal structure, phase stability, physicochemical and electrical properties.

For the crystal structure of undoped and doped (La,AE)MnO₃, the crystal structure has different modifications under different oxygen nonstoichiometry [6,7]. Although measurements of the nonstoichiometry have been performed by some workers [1,8,9], there is little systematic study as a function of dopant content. Oxygen superstoichiometry of undoped and Sr–doped (La,Sr)MnO₃ of x = 0 – 0.5 are only reported at temperatures between 600 and 1000°C in oxygen pressure higher than 10⁻¹⁰ atm [10].

In the present work, oxygen nonstoichiometry of undoped and Sr–doped LaMnO₃, La₁₋ₓSrxMnO₃+x (x = 0 – 0.5), was examined as a function of temperature and oxygen pressure to clarify the stability as a cathode material under SOFC operating conditions.

EXPERIMENTAL

Precursors of undoped and Sr–doped LaMnO₃ were prepared from mixtures of aqueous acetate solutions of component metals, La, Sr, and Mn by freeze–drying method [2]. The resultant dried and mixed acetates were calcined into oxides at 1000°C for 24hrs, then again fired at 1200°C for 4 hrs in air after well mixed. The metal contents in the precursors and the resultant oxides were analyzed by inductively coupled plasma atomic emission spectrometer (ICP, Seiko Instruments Inc., Japan). All of the oxides were examined by X–ray diffraction (XRD) and confirmed to be a single phase.

Oxygen nonstoichiometry in undoped and doped LaMnO₃ was determined in high–temperature thermogravimetry as a function of temperature and oxygen pressure. An electrobalance (Cahn, Type–2000, USA) was used as a thermal balance. A powder sample in a Pt crucible, hung from the one end of the arm of the balance in a closed vessel, was placed in flowing gas of controlled oxygen pressures between 1 and 10⁻²⁸ atm. Oxygen pressure was changed in different flow rates between oxygen and argon, or in different H₂O/H₂ mixing ratios in flowing hydrogen saturated with water vapor, and monitored by an electrochemical zirconia oxygen sensor at the outlet of the thermal balance. Temperature was kept constant by a thermocouple placed in the vicinity of sample in a reaction tube.

Coulometric titration was also performed to determine the oxygen nonstoichiometry in the oxide below 10⁻³ atm O₂. The data obtained were connected with the result by the thermal balance above 10⁻⁵ atm O₂. A sample was contained and sealed in a YSZ tube closed at one end, where porous Pt electrodes were fixed by painting on inside and outside walls. The oxygen content was varied by the procedure that direct current was applied from inside to outside or vice versa. The equilibrium oxygen pressure was determined by EMF measurements between both the electrodes.

The oxygen contents obtained by coulometric titration were compared with those by using the thermal balance. The contents by the former were in good agreement with those by the latter within one order of oxygen pressure for any oxide with the same oxygen nonstoichiometric composition.
RESULTS AND DISCUSSION

The oxygen nonstoichiometry in \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) \((x = 0 - 0.4)\) was measured by the thermal balance at temperatures between 600 and 1000°C in an argon stream of different oxygen partial pressures between 1 and \(10^{-5}\) atm, or in \(10^{-8} - 10^{-28}\) atm \(\text{O}_2\) of a humidified hydrogen stream. Coulometric titration was carried out at 600 - 1000°C below \(10^{-3}\) atm \(\text{O}_2\), where 1 atm. is exactly equal to \(1.013\times10^5\) Pa in SI unit.

Results obtained by the thermogravimetry and the coulometric titration were depicted as nonstoichiometry curves between oxygen content, \(3+d\), and logarithm of oxygen pressure, \(\log p(\text{O}_2)\), at a temperature between 600 and 1000°C. The results obtained by the thermogravimetry and coulometric titration were connected to make one curve in the oxygen pressure range between \(10^{-3}\) and \(10^{-5}\) atm, and to make the oxygen content of the plateau region the stoichiometry of \(d = 0\).

The oxygen content at the plateau is determined from the standpoint of perovskite-type structure. The perovskite-type structure does not have any interstitial site for excess oxygen ions in the hyperstoichiometric region \((d > 0)\) in \(\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+d}\), although the structure can produce defects in oxygen sites in the hypostoichiometric region \((d < 0)\). In the hyperstoichiometric region, oxygen atoms fill the oxygen lattice points, therefore metals become deficient in A or A and B lattice sites, as \(\text{La}_{w(1-x)}\text{Sr}_x\text{Mn}_w\text{O}_3\) or \(\text{La}_{w(1-x)}\text{Sr}_x\text{La}_w(\text{Mn})\text{O}_3\), where \(w = 3/(3+d)\). In the hypo stoichiometric region, oxygen atoms are deficient in the lattice sites. When oxygen nonstoichiometry is measured by the thermal balance, it is observed that time for attaining the equilibrium in excess oxygen region \((d > 0)\) is longer than that in deficient oxygen region \((d < 0)\). Thus, the existence of deficiency in metal sites, especially deficiency in A lattice sites, will be supported or interstitial oxygen atoms, although it is difficult to experimentally detect defects in the hyperstoichiometric region by X-ray (XRD) and neutron diffractions because of small amounts of defects.

Figures 1 - 5 show the relationship between oxygen content and \(\log p(\text{O}_2)\) for undoped and Sr-doped \(\text{LaMnO}_3\) of \(x = 0 - 0.4\), respectively, at temperatures between 600 and 1000°C in \(1 - 10^{-28}\) atm \(\text{O}_2\). When oxygen pressure is reduced from 1 atm, the oxygen content in the oxides decreases to a constant value, then is kept constant to make a plateau for some decades of oxygen pressure, and again goes down to the decomposition pressure. As seen in the figures, these phenomena show that the curves are divided into three regions from the oxygen content: hyperstoichiometric region \((d > 0)\), stoichiometric \((d = 0)\) and hypostoichiometric \((d < 0)\).

Fig. 1 shows the nonstoichiometry curve of \(\text{LaMnO}_3\). Kuo and Anderson's data are also depicted. The oxygen content, \(3 + d\), in undoped \(\text{LaMnO}_{3+d}\) is 3.17. The content decreases with increase of Sr content. For \(\text{La}_{0.35}\text{Sr}_{0.65}\text{MnO}_3\), oxygen hyperstoichiometric region was hardly observed.

The results obtained using thermal balance by Kuo, et al. [1] are also shown in Fig. 2. Their data show little lower oxygen content than ours at 1000°C when the oxygen content is compared at a constant oxygen pressure. As they used 30g of the oxide in the determination, it is thought that the measurements were carried out by not attaining equilibrium. This discrepancy is also observed for the oxide of \(x = 0.2\), as shown in Fig. 3.

When Sr is doped in \(\text{LaMnO}_3\), similar nonstoichiometric curves are obtained.
Figure 2 shows oxygen content vs. log $p(O_2)$ curves in the oxygen nonstoichiometric La$_{0.9}$Sr$_{0.1}$MnO$_3$ at 600 – 1000°C. In the figure, Kuo and Anderson's data are also shown. As already described in Fig. 1, their data slightly shift toward higher oxygen pressure. The shape of the nonstoichiometric curves is similar to that for LaMnO$_3$, but the oxygen content in 1 atm $O_2$ becomes slightly lower than that for LaMnO$_3$ by doping Sr.

The oxygen nonstoichiometry in La$_{0.8}$Sr$_{0.2}$MnO$_3$ is shown in Fig. 3. The shape of the curve of La$_{0.8}$Sr$_{0.2}$MnO$_3$ is similar to that of undoped LaMnO$_3$. For La$_{0.8}$Sr$_{0.2}$MnO$_3$, however, two phase region is observed in the oxygen deficient region of $d<0$. The decomposition to the component oxides occurs at the lower oxygen pressure beyond the two-phase region at any temperature. It was shown by XRD that the oxide in the two-phase region is a mixture of (La,Sr)MnO$_3$ and (La,Sr)$_2$MnO$_4$. It is thought that the following reaction occurs as

$$2 (\text{La}, \text{Sr})\text{MnO}_3 = (\text{La}, \text{Sr})_2\text{MnO}_4 + \text{MnO} + 1/2 \text{O}_2 \quad (1)$$

$$ (\text{La}, \text{Sr})_2\text{MnO}_4 = \text{La}_2\text{O}_3 + \text{MnO} + 1/2 \text{O}_2 \quad (2)$$

Oxygen pressure over two phase region is the equilibrium pressure in Eq.(1). The two phase region is seen in Kuo's data [1] for the oxides of $x = 0.2$.

Figure 4 shows the nonstoichiometry curve of La$_{0.7}$Sr$_{0.3}$MnO$_3$. The oxygen content in the hyperstoichiometric region is lower than that in La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0, 0.1, 0.2$). Two phase region over (La,Sr)MnO$_3$ and (La,Sr)$_2$MnO$_4$ is also clearly seen in the curve in Fig. 4.

The oxygen nonstoichiometry in La$_{0.6}$Sr$_{0.4}$MnO$_3$ is shown in Fig. 5. When coulometric titration is applied to this oxide, electric resistance suddenly increased and electric current was stopped at near the oxygen pressure over the two phase region. This may be due to the formation of (La,Sr)$_2$MnO$_4$, which is an electric insulator. A measurement at 800°C in $10^{-18}$ atm $O_2$ by the thermal balance gives that the oxygen content, as $3+d$ in La$_{0.6}$Sr$_{0.4}$MnO$_{3+d}$, is 2.48, which is little larger than the total oxygen content, 2.30 and a composition on the way to decompose to the component oxides.

Figure 6 shows the nonstoichiometry curves for the oxides, La$_{1-x}$Sr$_x$MnO$_3$ ($x = 0$ – 0.5) at 800°C. The oxygen content, $3+d$, in oxygen hyperstoichiometric region has a tendency to decrease, already shown in ref. (10), and the curves in the hypostoichiometric region move toward higher oxygen pressure with increase of Sr content.

Figure 7 shows the relationship between oxygen pressure in the two phase region and decomposition pressure and doped Sr content at 800 and 1000°C. Both the oxygen pressure in the two phase region, (La,Sr)MnO$_3$ and (La,Sr)$_2$MnO$_4$, and the decomposition pressure slightly increase with doped Sr content. That is, the stability of the oxide decreases with doping Sr. Both the oxygen pressure in the two phase region and the decomposition pressure slightly increase with doped Sr content. The slopes give the heat of decomposition.

Figure 8 shows the temperature dependence of the oxygen pressure in the two phase region, (La,Sr)MnO$_3$ and (La,Sr)$_2$MnO$_4$, and the decomposition pressure, (La,Sr)MnO$_3$ and (La,Sr)$_2$MnO$_4$. The heat of decomposition of (La,Sr)MnO$_3$ to (La,Sr)$_2$MnO$_4$, depicted as the first stage in Fig. 8, is 151.9, 145.8, 145.6, and 128.6 kcal mol$^{-1}$ for $x = 0.2$, 0.3, 0.4, and 0.5, respectively. The heat of decomposition of
(La,Sr)MnO₃ to the components or of (La,Sr)₂MnO₄ to the components, denoted as the second stage in Fig. 8, is 172.6, 162.1, 159.5, and 154.9 kcal mol⁻¹ for x = 0, 0.1, 0.2, 0.3, respectively. The decomposition of the oxide, La₁₋ₓSrₓMnO₃₊d (x = 0 - 0.5; d < 0), becomes easy with the increase of doped Sr content.

Figures 9 and 10 show the partial molar enthalpy, Hₒ, and the entropy, Sₒ, for La₁₋ₓSrₓMnO₃₊d (x = 0 - 0.5) as a function of oxygen content, 3+d. The figures show that sharp changes in both the enthalpy and entropy occur at the oxygen stoichiometry (d = 0). The difference between above and below d = 3 comes from the formation of different lattice vacancies, in A or A and B sites and oxygen sites. In the oxygen deficient region of d<0 in Fig. 10, partial molar enthalpy has a tendency to remain constant regardless of oxygen content. From the partial molar entropy, Sₒ, vs. oxygen content, 3+d, it is known that oxygen vacancies randomly distribute in the oxygen deficient region of the oxide series, La₁₋ₓSrₓMnO₃₊d (x = 0 - 0.5; d < 0), as pointed out by Kuo, et al.(1) and Mizusaki, et al (2).

ACKNOWLEDGEMENTS

The authors wish to thank NEDO for financial support of an International Joint Research Grant for performing this work. A part of this work has been also carried out as a research project of the Japan Petroleum Institute commissioned by the Petroleum Energy Center with the subsidy of the Ministry of International trade and Industry of Japan.

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Fig. 1. Relationship between oxygen content, $3 + d$, and log $p(O_2)$ for LaMnO$_3$ at 600 - 1000°C. Open symbols: this work, closed symbols: after Kuo, et al. [1].

Fig. 2. Relationship between oxygen content, $3 + d$, and log $p(O_2)$ for La$_{0.5}$Sr$_{0.1}$MnO$_3$ at 600 - 1000°C. Open symbols: this work, closed symbols: after Kuo, et al. [1].
Fig. 3. Relationship between oxygen content, $3 + d$, and log $p(O_2)$ for La$_{0.8}$Sr$_{0.2}$MnO$_3$ at 600 – 1000°C. Open symbols: this work, closed symbols: after Kuo, et al. [1].

Fig. 4. Relationship between oxygen content, $3 + d$, and log $p(O_2)$ for La$_{0.7}$Sr$_{0.3}$MnO$_3$ at 600 – 1000°C.
Fig. 5. Relationship between oxygen content, $3 + d$, and log $p(O_2)$ for $La_{0.6}Sr_{0.4}MnO_3$ at 600 – 1000°C.

Fig. 6. Relationship between oxygen content, $3 + d$, vs. log $p(O_2)$ curves for the oxide, $La_{1-x}Sr_xMnO_3$ ($x = 0 – 0.5$), at 800°C.
Fig. 7. Relationship between equilibrium oxygen pressure over the two phase region, (La,Sr)MnO$_3$ + (La,Sr)$_2$MnO$_4$, and decomposition pressure into the components at 800 and 1000°C. The decomposition of (La,Sr)MnO$_3$ to (La,Sr)$_2$MnO$_4$ is denoted as the first stage with open symbols, and of (La,Sr)MnO$_3$ to (La,Sr)$_2$MnO$_4$ as the second stage with closed symbols.

Fig. 8. Temperature dependence of the oxygen pressure over the two phase region, (La,Sr)MnO$_3$ and (La,Sr)$_2$MnO$_4$, and the decomposition pressure into the components. The decomposition of (La,Sr)MnO$_3$ to (La,Sr)$_2$MnO$_4$ is denoted as the first stage, and of (La,Sr)MnO$_3$ to (La,Sr)$_2$MnO$_4$ as the second stage.
Figs. 9. Partial molar enthalpy, $\tilde{H}_0$, for $La_{1-x}Sr_xMnO_{3+d}$ ($x = 0 - 0.5$) as a function of oxygen content, $3+d$, in the temperature range between 600 and 1000°C.

Figs. 10. Partial molar entropy, $\tilde{S}_0$, for $La_{1-x}Sr_xMnO_{3+d}$ ($x = 0 - 0.5$) as a function of oxygen content, $3+d$, in the temperature range between 600 and 1000°C.