EFFECT OF OXYGEN NON-STOICHIOMETRY ON La$_{1.5}$A$_x$MnO$_{3-x/2}$ CATHODE AT ELECTRODE POLARIZED STATE

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ABSTRACT

Lanthanum manganite, an air electrode material of solid oxide fuel cells, is well known for its complicated non-stoichiometry, which depends upon oxygen partial pressure. This non-stoichiometry has relationship with electrode activity at its exchange current state as it affects oxygen activation step and/or oxide ion sink, etc. This paper aims to elucidate the effect of oxygen non-stoichiometry on cathode activity at its polarized state. Thus far, electrode activity was usually studied for its exchange current density character, in other words, at its non-polarized (equilibrium) state. Complex-impedance was measured on Ar-O$_2$/porous La$_{0.95}$Sr$_{0.05}$MnO$_{3-x/2}$/YSZ at oxygen partial pressure in the range of $10^{-2}$-$10^{2}$Pa and temperature between 873~1273K. The results suggest that oxygen non-stoichiometry affects cathode activity both at polarized and non-polarized state through the exchange current density.

INTRODUCTION

Solid oxide fuel cells (SOFCs) are candidates for new power generation devices of near future. Alkali earth doped lanthanum manganite has been recognized as the most reliable cathode material for SOFCs at 1073~1273K. Detailed elucidation of cathode mechanism is not yet available. It is well known that this lanthanum manganite has complicated lattice defect depending upon oxygen partial pressure (1, 2). On the surface of lanthanum manganite these defects may work as active sites of electrode, such as oxygen adsorption/dissociation, surface diffusion, or incorporation into bulk electrolyte sites, and so forth (3, 4). The cathode activity, $\sigma_E$, is defined as follows

$$\sigma_E = 1/(A R_E).$$  

(1)
where $A$ is electrode area and $R_e$ is electrode resistance. Based on detailed studies on non-stoichiometry (1, 2), we had compared non-stoichiometry, $\delta$, and $\sigma_e$, and found that $\delta$ affects $\sigma_e$ at its rate constant, $\alpha$, as follows (3, 4).

$$
\sigma_e^0 = \alpha \times (F/RT) \times (P_{O_2}^0)^{1/2}
$$

(2)

Here, $\sigma_e^0$ is $\sigma_e$ at non-polarized state and $P_{O_2}^0$ is oxygen partial pressure. In this report, we aim to clarify the relation between non-stoichiometry and cathode activity at electrode polarized state.

**EXPERIMENTAL**

The powder of cathode material La$_{0.5}$Sr$_{0.5}$MnO$_3$ (coded as LSM-1) was synthesized by the Pechini method (5, 6). The prepared powder was calcined at 1473K for 3h in air and was shown to be single phase of the perovskite type by powder X-ray analysis. To obtain the electrode paste, LSM-1 and YSZ (8 mole percent Y$_2$O$_3$, Tosoh Ltd.) powders were mixed together in the molar ratio 4:6 and were milled with a dispersant in ethanol. The YSZ powder was pressed and sintered in air at 1673K into the pellet of about 20mm in diameter and about 1 mm in thickness with relative density of more than 95%. The electrode paste was painted as WE on one side of the YSZ disk and as CE on other side of the YSZ disk, and the disk was fired at 1473K for 3h in air. Then, the Pt paste was painted as RE on disk side, and the disk was fired at 1323K for 3h in air.

Electrochemical measurement for LSM-1/YSZ was made using a three-terminal method. Four lead wires from a potentiostat were connected to the respective electrodes using Pt wires and Pt mesh attached to the surface of the respective electrode, the current and the potential lead to WE, the reference lead to RE, and the counter lead to CE. The complex impedance measurements at electrode polarized state were made over the frequency range of 100kHz~1mHz using a frequency analyzer (NF, Type FRA-NF-S-5720C), a potentiostat (Toho, Type 2000), and a personal computer (EPSON, PC-286VF). Measurements were made in Ar/O$_2$ atmosphere of $P_{O_2}^0 = 10^2$~$10^5$ Pa at temperatures of 873~1273K.

**RESULTS AND DISCUSSION**

AC impedance showed two or three arcs. At 873K and at 1073K except for $10^2$Pa, the arcs showed grain boundary and cathode electrode resistances. At $10^2$Pa in 1073K, the arcs showed grain boundary, cathode, and gas diffusion resistances. At 1273K, the arcs showed cathode and gas diffusion resistances. The cathode resistance, $R_e$, was defined as cathode conductivity, $\sigma_e$, according to Eq. (1).

Figure 1 and 2 summarize the relation between $\sigma_e$ and $\eta_{int}$ and between $\sigma_e$ and $\eta_{E}$. Here, the $\eta_{int}$ is defined as

$$
\eta_{int} = \eta_{PO_2}^E + \eta_{E}
$$

$$
P_{O_2}^{ext} = P_{O_2}^0 + P_{O_2}^E
$$

(3)
\[ \eta_{\text{POZ}} = RT / 4F \cdot \ln(P_{\text{OZ}}^0), \]
\[ \eta_{\text{act}} = RT / 4F \cdot \ln(P_{\text{OZ}}^{\text{ads}}). \]  

Here, \( P_{\text{OZ}}^0 \) is the oxygen partial pressure of atmosphere, and \( \eta_{\text{E}} \) is the over-potential. Thus, \( \eta_{\text{act}} \) means the actual oxygen partial pressure on the cathode.

Using Figs. 1 and 2, we looked for the relation between \( \sigma_{\text{E}} \) and oxygen non-stoichiometry, \( \delta \), of cathode, \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_{3.6} \). However, we could not observe clear relation between \( \delta \) and \( \sigma_{\text{E}} \) because these results were affected by polarized state, oxygen partial pressure, and so forth. The \( \sigma_{\text{E}} \) is influenced by polarized states. In other words, \( \sigma_{\text{E}} \) varies with \( \eta_{\text{E}} \) itself as Butler-Volmer relation indicates. Therefore, we re-arranged the \( \sigma_{\text{E}} \) at the same over-potential with respective \( P_{\text{OZ}}^0 \) from Fig. 2 as shown in Fig. 3.

Figure 3 shows the observed \( \sigma_{\text{E}} \) for 873–1273K as a function of \( P_{\text{OZ}}^0 \) for different electrode over-potential. LSM-1 shows non-stoichiometry of \( \delta>0 \) in the \( P_{\text{OZ}}^0 \) region of \( 10^2-10^5 \text{Pa} \), and \( \delta \) decreases with \( P_{\text{OZ}}^0 \) (1, 2). The characteristics of the relation between \( \sigma_{\text{E}}, \delta, \text{ and } P_{\text{OZ}}^0 \) can be summarized as follows:

1. The dependency of the \( \sigma_{\text{E}} \) on \( P_{\text{OZ}}^0 \) is roughly \( (P_{\text{OZ}}^0)^{1/2} \).
2. However, the dependency on \( P_{\text{OZ}}^0 \) frequently becomes lower than \( 1/2 \).
3. When \( \delta \) increases, the \( \sigma_{\text{E}} \) increases and saturates at \( \eta_{\text{E}} = +100 \text{mV} \) in 873K.

As summarized above, it is thought that both \( P_{\text{OZ}}^0 \) in the gas phase and the non-stoichiometry, \( \delta \), of \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_{3.6} \) electrode influenced \( \sigma_{\text{E}} \). Since \( \delta \) also depends on \( P_{\text{OZ}}^0 \), the apparent \( P_{\text{OZ}}^0 \) dependence on \( \sigma_{\text{E}} \) becomes complicated. We adopted the following procedure to separate these two effects of \( P_{\text{OZ}}^0 \), i.e., the direct effect of oxygen chemical potential, and the indirect effect through the variation of \( \delta \).

Because \( \sigma_{\text{E}} \) depends on \( (P_{\text{OZ}}^0)^{1/2} \), firstly we assume that \( (P_{\text{OZ}}^0)^{1/2} \) dependency represents the direct effect of \( P_{\text{OZ}}^0 \) on \( \sigma_{\text{E}} \). Then, the direct effect of \( P_{\text{OZ}}^0 \) on \( \sigma_{\text{E}} \) can be expressed by

\[ \sigma_{\text{E}} = \beta \times (F/RT) \times (P_{\text{OZ}}^0)^{1/2} \]  

where \( \beta \) (mA/cm\(^2\)) is proportional to the exchange current density, \( \eta_{\text{E}} \), at given (or constant) \( \eta_{\text{E}} \), respective electrode over-potential, but varies according to \( \eta_{\text{E}} \). \( F \) (C/mol) is the Faraday constant, \( R \) (J/K mol) is gas constant, and \( T \) (K) is temperature.

The gas phase oxygen affects the reaction rate through a term such as \( (P_{\text{OZ}}^0)^{1/2} \) independently from the state of electrode. In addition, the reaction rate is also affected by the state of electrode, such as non-stoichiometry, electrode geometry, and so forth. When we represent the electrode reactivity by Eq. (5), these factors may appear in the variation of the rate constant, \( \beta \). In summary, it is considered that the interaction between electrode and oxygen gas follows \( (P_{\text{OZ}}^0)^{1/2} \), and that the rate constant, \( \beta \), follows the state of electrode.

The results obtained in Fig. 3, however, showed some deviation from Eq. (5). When we rearrange the obtained \( \sigma_{\text{E}} \) using Eq. (5), this deviation will appear in the reaction rate constant, \( \beta \), and the dependency of \( \beta \) on \( \delta \) will explain the effect of non-stoichiometry of \( \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_{3.6} \). Figures 4 and 5 show the relation between \( \beta \) and \( \delta \) from the \( \eta_{\text{act}} \), and that between \( \beta \) and \( \delta \) from...
the $\eta_{\text{PO}2}$ calculated using Eq. (5) from the observed data in Fig. 3. From Fig. 4 and 5, we can summarize that $\beta$ increases linearly with decrease in $\delta$. However, we can attribute this linear relation to both $\delta$ derived from $\eta_{\text{po}}$ and $\eta_{\text{PO}2}$. We observed a hysteresis at increase and decrease of $\eta_{\text{po}}$. This effect appeared as dispersion of data-points in Figs. 1 and 2. Therefore, this hysteresis suggests that non-stoichiometry induced by $\eta_{\text{po}}$, that is shown Fig. 4.

Because the cation vacancies are formed at oxygen excess region, it shows that $\beta$ decreased according to the increase of $\delta$. Thus, the increase of the cation vacancies relates to the decreased active site of electrodes.

In conclusion, the results suggest that oxygen non-stoichiometry affects cathode activity at not only the non-polarized state but also at the polarized state.

The detailed mechanism of how oxygen non-stoichiometry contributes, for example, to adsorption/dissociation or diffusion will be studied in the future.

SUMMARY

Complex-impedance measurements at polarized state were analyzed in relation to $P_{\text{O}2}$, the reaction rate constant, $\beta$, and non-stoichiometry, $\delta$. When we assume the reaction rate, $\alpha_{\text{po}}$, follows $P_{\text{O}2}^{1/2}$ dependency, the deviation from $P_{\text{O}2}^{1/2}$ can be expressed as the effect of the non-stoichiometry, $\delta$, on the reaction rate constant, $\beta$. This $\beta$ becomes smaller with increase in oxygen deficiency, $\delta$. Because the cation vacancies are formed at oxygen excess region, it shows that $\beta$ decreases with increase in $\delta$. Thus, the increase of the cation vacancies relates to the decreased active site of electrodes. The results suggest that oxygen non-stoichiometry affects cathode activity at not only the non-polarized state but also the polarized state.

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Figure 1. $\eta_{\text{act}}$ dependence on $\sigma_E$ for O$_2$, La$_{0.9}$Sr$_{0.1}$MnO$_3$/YSZ electrode.
Figure 2. $\eta E$ dependence on $\sigma E$ for O$_2$, La$_{0.9}$Sr$_{0.1}$MnO$_{3+x}$/YSZ electrode.
Figure 3. \( P_{O_2}^0 \) dependence on \( \sigma_E \) for \( O_2, \text{La}_0.9\text{Sr}_0.1\text{MnO}_3/\text{YSZ} \) electrode. \( P_{O_2}^0 \): See Eq. (3).
Figure 4. log$\beta$ dependence on 3$\pm$δ obtained from PO$_2^{\text{act}}$ for O$_2$, La$_{0.9}$Sr$_{0.1}$MnO$_{3+\delta}$/YSZ electrode. PO$_2^{\text{act}}$: See Eq. (3).
Figure 5. $\log(\beta)$ dependence on $3\delta$ obtained from $P_{O_2}^0$ for $O_2$, $La_0.9Sr_0.1MnO_3\delta$/YSZ electrode. $P_{O_2}^0$: See Eq. (3).