ELECTROCHEMICAL REACTION KINETICS OF MIXED CONDUCTING ELECTRODES ON CeO₂-BASED SOLID ELECTROLYTES

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ABSTRACT

Porous and dense Lao₃Sr₀₆CoO₃₋₄ layers were prepared as working electrodes on 10 mole % CaO doped CeO₂ electrolytes. Electrochemical measurements were made as a function of oxygen partial pressure at 500 to 900°C. The electrode interface conductivity and the steady-state polarization curve suggested that the reaction rates with porous electrodes are controlled by gas diffusion process at low P(O₂) and those with dense electrodes by surface reaction.

INTRODUCTION

For low temperature solid oxide fuel cells (SOFCs), ceria-based solid oxides are supposed to be used as the electrolyte(1-3). In this case, La₁₋ₓSrₓCoO₃₋₄ (LSCO) which has high oxide ion conductivity is a candidate for the cathode material(4-7). Though LSCO reacts with ZrO₂-based electrolytes at high temperature, it can make a stable interface with CeO₂-based electrolytes. Investigations on porous mixed conducting electrodes on ceria based electrolytes have been performed by several groups(8,15,16). Gödickermeier et al. concluded that the charge transfer controlled reaction with preceding dissociative adsorption is the Rate Determining Step, (RDS), from analysis of I-V characteristics(8). However, from investigation with only porous electrode, it is difficult to reach a definite conclusion for RDS.

The reaction at the cathode is generally considered to proceed mostly through Three Phase Boundary (TPB) of gas/electrode/electrolyte, as shown in Fig. 1(a). When the oxide ion conductivity in the electrode is large enough, the electrode reaction takes place also through the closely contacted interface of electrode/electrolyte as shown in Fig. 1(a). Both reaction paths
are possible with a porous LSCO electrode. When the electrode is dense, the reaction path is restricted to the latter one (Fig. 1(b)). In such a case, the oxygen incorporation reaction will proceed via the following steps: (a) gas diffusion, (b) dissociative adsorption reaction, (c) charge transfer reaction, (d) oxide ion diffusion in bulk electrode, (e) oxide ion transfer at the electrode/electrolyte boundary, as shown in Fig. 1(b)(9-11).

This work aims to make clear the electrode reaction mechanism by comparing the electrochemical properties of porous electrodes and dense electrodes.

**EXPERIMENTAL**

The electrolyte, 10 mole % CaO doped CeO$_2$, was prepared by solid reaction from CaCO$_3$ and CeO$_2$(1). The powders were mixed in an appropriate ratio and calcined at 1400°C for 2 hours twice. It was compacted using a cold isostatic press (CIP) and sintered at 1700°C for 4 hours. The relative density was higher than 98%. The surface of the pellet was polished with emery papers (#400).

Electrode material La$_{0.6}$Sr$_{0.4}$CoO$_{3+\delta}$ was prepared by coprecipitation method (12). To prepare the porous electrode, the powder was calcined at 1000°C for 2 hours and suspended in C$_2$H$_5$OH. It was placed on the electrolyte pellet surface and sintered at 1100°C for 2 hours. The dense electrodes were prepared by a laser ablation method (12). A sintered pellet of La$_{0.6}$Sr$_{0.4}$CoO$_{3+\delta}$ was used for the target. ArF laser beam of about 150 ~ 170 J cm$^{-2}$ was focused on the target with the incident angle at 40°. The repetition rate was 10 Hz. The substrate was heated at 600°C. The deposition atmosphere was kept at $10^{-2}$ torr oxygen to avoid reduction of La$_{0.6}$Sr$_{0.4}$CoO$_{3+\delta}$. The electrode thickness was controlled by changing the number of shot (3600 ~ 144000). The morphology of the electrode was observed by a Scanning Electron Microscope (SEM) and the thickness was measured by a surface profilometer (Sloan, DECTAC 3). The counter electrode (CE) and the reference electrodes (RE) were prepared on the back surface and on the side of the pellet, respectively, by printing Pt paste and firing at 800°C.

Electrochemical measurements were made by the use of a three terminal method with a potentiogalvanostat (Solartron 1286) and a Frequency Response Analyzer (FRA, Solartron 1260) under controlled oxygen partial pressures by using O$_2$-Ar gas mixtures at 500~900°C.
ELECTRODE REACTION PROCESS

The oxygen electrode reaction with a LSCO electrode is schematically explained in fig. 1(b). The characteristic feature of each reaction step is described as follows.

(a) gas diffusion. The gas diffusion overvoltage, $\eta$, is given by Nernst equation as represented by eq. [1]. If oxygen potential gradient is constant in the diffusion layer, the current density, $J$, is described by eq. [2].

\[
\eta = \frac{RT}{4F} \ln \frac{P_o}{P'_o} \tag{1}
\]

\[
J = 4FD_g \frac{P_o - P'_o}{LRT} \tag{2}
\]

where, $R$ is gas constant, $T$ is absolute temperature, $F$ is Faraday constant, $L$ is the thickness of diffusion layer, $D_g$ is diffusion coefficient (17) and $P(O_2)$ and $P'(O_2)$ are oxygen partial pressures at the inside and the outside boundaries across the diffusion layer, respectively. Using eq. [1] and [2], $J$ can be expressed as

\[
J = \frac{4FD_g}{LRT} P_o \left(1 - \exp\left(-\frac{4F\eta}{RT}\right)\right) \tag{3}
\]

Using eq. [3], the interface conductivity, $\sigma_{ef}$, is given by

\[
\sigma_{ef} = \frac{\partial J}{\partial \eta} \bigg|_{\eta = 0} = \frac{4^4 F^4}{LR^2 T^2} D_g P_o \tag{4}
\]

Eq. [4] shows that $\sigma_{ef}$ is proportional to $P(O_2)$. Since the diffusion coefficient in the gas phase is proportional to $T^{3/2}$ (18), the interface conductivity has a slightly negative dependence on temperature ($\sigma_{ef} \propto T^{-1/2}$).

(b) adsorption/desorption reaction. The motive force of the surface adsorption/desorption reaction is the oxygen potential difference between the gas phase and the electrode surface. Thus, the surface reaction overvoltage is determined by the deviation of the surface oxygen potential from the equilibrium. The current density is dependent on the oxygen partial pressure and the concentration of the adsorbed species.

(c) charge transfer reaction. In a dense LSCO electrode, charge transfer reaction occurs at the surface of the electrode layer. It causes the difference in the oxygen potential between the adsorbed species and the uppermost layer inside the electrode.
(d) oxide ion diffusion in electrode bulk. The current density, \( J (O^2^-) \), through layers of \( \text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3.\delta \) is described by the following equation [5].

\[
J_{O^{2-}} = -\frac{1}{L_e} \int_{P_{O_2}}^{P_{O_2}^0} \frac{RT}{4F} \sigma_{O^{2-}} \ln P(O_2)
\]

where, \( L_e \) is the electrode thickness, \( P \, \text{I} (O_2) \) and \( P \, \text{II} (O_2) \) are oxygen partial pressures at each side of the layer and \( \sigma (O^{2-}) \) is the oxide ion conductivity which is described by

\[
\sigma_{O^{2-}} = \frac{4F^2 D_V \delta}{RT V_m}
\]

where, \( D_V \) is the self diffusion coefficient of \( O^{2-} \) vacancy, \( V_m \) is the molar volume and \( \delta \) is the oxygen nonstoichiometry in \( \text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3.\delta \). The current density \( J(O^{2-}) \) is represented by

\[
J_{O^{2-}} = -\frac{FD_V}{L_e V_m} \int_{P_{O_2}}^{P_{O_2}^0} \frac{\rho_{O_2}}{P_{O_2}^0} \ln P(O_2)
\]

Fig. 2 shows the \( J(O^{2-}) \) calculated using eq. [7] with varying \( P \, \text{II} (O_2) \) and fixed \( P \, \text{I} (O_2) \) (1 atm), where \( D_V \) was assumed to be the same as that of \( \text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3.\delta \) reported by Fueki et al., \((D_V=10^{-5.4} \text{ cm}^2\text{s}^{-1}) \) (13), and \( \delta \) was estimated from the data obtained by Mizusaki et al. with \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3.\delta \) \((x = 0, 0.1, 0.2, 0.3, 0.5) \) (5). The molar volume, \( V_m \), of \( \text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3.\delta \) is assumed to be independent of the nonstoichiometry.

(e) oxide ion transfer at the electrode/electrolyte boundary. When oxide ion is transferred between the oxides, there can be a gap in its electrochemical potential. This also may cause the overvoltage.

Pseudocapacitance due to the nonstoichiometry in the electrode material

If the concentration of \( O^{2-} \) vacancy in bulk electrode varies with the applied potential, it will cause pseudocapacitance, \( C \), which is described by the following equation,

\[
C = \frac{\partial Q}{\partial \eta} = \frac{\partial}{\partial \eta} \int_{x=0}^{x=\delta} \left( \frac{2F}{V_m} \delta \right) dx
\]
where, $\eta$ is the overpotential and $Q$ is the electric charge per unit area. When the gas diffusion or the surface reaction is RDS, $\delta$ is constant inside the electrode layer, and oxygen potential in the electrode is expressed as a function of $\eta$ using Nernst law equation (eq. [1]). Thus, $C$ can be calculated as a function of oxygen partial pressure by using the $\delta$ vs. $P(O_2)$ dependence (5). This pseudocapacitance is proportional to the electrode thickness. When the bulk diffusion is RDS, oxygen potential gradient is established inside the electrode and the pseudocapacitance will be smaller than that in eq. [8] (about half if thermodynamic factor is neglected).

RESULTS AND DISCUSSION

Dense electrode

Fig. 3 shows SEM pictures of the membranes fabricated by laser ablation. Though some cracks were observed in the 2.5 $\mu$m thick membrane, most part of the membrane was closely filled with grains of nano meter order. Considering the high oxide ion diffusivity in the membrane, these are able to be regarded as dense electrodes without effective TPB. Fig. 4 shows typical complex impedance plots with a dense electrode at 800°C. Two semicircles appeared in almost all $P(O_2)$ region. The semicircles of the lower frequency region depended on $P(O_2)$. The high frequency semicircles varied little. In this paper, the discussion will focus on the lower frequency semicircles. The semicircle can fit well with a parallel connection of a resistance, $R$, and a capacitance, $C$. $R$ is considered to be due to the electrochemical process at the electrode. Electrode interface conductivity $\sigma_E$ is defined as,

$$\sigma_E = \frac{1}{AR} \quad [9]$$

where, $A$ is the area of the electrode/electrolyte interface. Fig. 5 shows $P(O_2)$ dependence of the calculated $\sigma_E$ for 500-800°C. As shown in Fig. 5, $\sigma_E$ of the dense electrodes is proportional to $P(O_2)$ in low $P(O_2)$ region and becomes constant in high $P(O_2)$ region at each temperature. $\sigma_E$ has temperature dependence in all $P(O_2)$ regions. Since the gas phase diffusion process would have different temperature dependence (eq. [4]), it can not be RDS with the dense LSCO electrode. Fig. 6 shows the effect of thickness on steady-state polarization of the dense electrodes at 800°C. As shown in Fig. 6, the polarization curves are almost the same in all $P(O_2)$ regions, and independent of the electrode thickness. This result suggests that the oxide ion diffusion in the electrode bulk is fast enough. It is consistent with the high diffusion current density expected from the calculation (eq. [7] and Fig. 2).
The capacitance values calculated from the lower frequency semicircles are plotted as a function of oxygen partial pressure in Fig. 7. They were quite high (0.1-1 F) and had a dependence on electrode thickness and temperature. The lines in Fig. 7 are the pseudocapacitance $C$ calculated using eq. [8] for each condition. They are comparatively close to the experimental data. Because no other reaction can explain such a large capacitance, this electrode capacitance is attributed to the $O^{2-}$ going in and out of the electrode. This suggests that the RDS is a process which gives rise to the oxygen potential shift in the electrode layer. Thus, the oxide ion transfer at the electrode/electrolyte is not likely to be the RDS.

Consequently, the surface reaction of oxygen, (b) (c) is most likely to be the RDS in the dense electrode.

Porous Electrode

Fig. 8 shows typical complex impedance plots for a porous electrode at 800°C. Two semicircles appeared in almost all $P(O_2)$ region like dense electrode. Fig. 9. shows $P(O_2)$ dependence of the calculated $\sigma E$ for 500-900°C. In low $P(O_2)$, high temperature region, $\sigma E$ was proportional to $P(O_2)$ and almost independent of temperature. The capacitance calculated for the lower frequency semicircle was in the range of 0.1~1 F. In this region, the oxygen gas diffusion process, (a), is most likely to be RDS. The $L$ calculated using eq. [4] with $D_g$ (16) and experimental data is about 1 mm. This is about 100 times as long as the electrode thickness. These suggest that the RDS is oxygen gas diffusion not in the pores in the electrode but in the gas phase above the electrode layer. In high $P(O_2)$-low temperature region, $\sigma E$ is independent on $P(O_2)$ and depends on temperature. $C$ is around 0.001 F, which means the RDS does not involve the change of $\delta$. Therefore, the gas/electrode surface reaction, (b) and (c) is not the RDS. The electrode/electrolyte interface reaction, (d) and reaction at TPB seems to be RDS. Further examination must be carried out to make this clear.

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Fig. 1 Schematics of the possible reaction path at mixed conductor electrodes. (a) porous, (b) dense electrode.

Fig. 2 The oxygen permeation current density through a 2 μm layer of La$_{0.6}$Sr$_{0.4}$CoO$_3$ as a function of oxygen potential.

Fig. 4 Typical impedance plot of a dense electrode with varying $P$(O$_2$) at 800°C.

Fig. 5 Interface conductivity $\sigma$ of a dense electrode as a function of oxygen potential.
Fig. 3  SEM pictures of the LSCO membranes fabricated by laser ablation. $L_E$ is the thickness of LSCO.
Fig. 6 Effect of thickness on steady-state polarization curve of dense electrodes at 800°C.

Fig. 7 Capacitance as a function of oxygen potential. Lines are calculated from equ. [8] for each condition.

Fig. 8 Typical impedance plot of a porous electrode with varying P(O2) at 800°C.

Fig. 9 Interface conductivity σ of a porous electrode as a function of oxygen potential.