IN-SITU OXYGEN POTENTIAL MEASUREMENT ON (La,Sr)CoO$_3$$_8$ ELECTRODES

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ABSTRACT

A dense film of La$_{0.6}$SrCoO$_3$$_8$ was fabricated on a Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$
electrolyte pellet by a laser ablation method. Electrochemical
measurements were performed using a three-terminal cell, and at the
same time, the oxygen potential on the electrode surface was monitored
by a potentiometric method. A porous ceria pellet with a platinum
electrode on one side (porous oxygen sensor: POS) was put on the
electrode surface as a surface oxygen potential probe. The ac response of
POS was analyzed as pseudo impedance in a complex impedance plane.
Although the impedance of the three-terminal cell had two kinds of
responses, i.e. high frequency response due to the grain boundary
impedance and a low frequency response due to the electrochemical
impedance, POS responded only in the frequency range of the
electrochemical impedance. The magnitude of the POS response was
close to that of the three-terminal impedance in that frequency range,
suggesting that the electrode overvoltage is mostly due to the slow
dissociative adsorption of oxygen and the resulting non-equilibrium
oxygen potential at the electrode surface.

INTRODUCTION

Solid oxide fuel cells (SOFCs) are expected to be used not only for a large scale
energy system but also for a small size application such as a domestic generator or a
power source for an electric vehicle. Reduced temperature operation will be necessary
for a small system, which requires frequent start up and shut down. Since the electrode
overvoltages usually have high activation energies, improvement of the electrode
material is important especially for a reduced temperature system. As for the cathode,
LaCoO$_3$ based perovskites are the most promising materials when they are used on an
electrolyte of doped ceria or stabilized zirconia with a ceria interlayer. Thermodynamic
and electrochemical studies have been reported on (La,Sr)CoO$_3$ and related materials (1-
8). In our previous works (7, 8), the electrode surface reaction was found to be the most
important process to determine the overvoltage. In order to study further details, more
information is necessary on the “working” electrode surface. Several years ago, Kawada
et al. (9) reported the use of a potentiometric method for in-situ observation of oxygen
potential on noble metal electrodes. They used a porous zirconia pellet which has a
reference Pt electrode on one side (POS: porous oxygen sensor) as a surface oxygen potential probe. It was put on the working electrode surface, and the voltage over POS was detected. The surface oxygen potential was calculated by using the Nernst’s equation. In this paper, POS measurement has been applied to study the oxygen reaction on a dense La$_{0.6}$Sr$_{0.4}$CoO$_{3.5}$ film electrode. The reliability of the method is discussed.

EXPERIMENTAL

Sample Preparation

The electrolyte material powder, Ce$_{0.6}$Gd$_{0.4}$O$_{1.95}$, was prepared from an aqueous nitrate solution by co-precipitation with oxalic acid. The powder was pressed and sintered into a pellet of 16 mm in diameter and 2 mm in thickness. The surface of the pellet was polished by diamond paste (1 µm). The electrode material, La$_{0.6}$Sr$_{0.4}$CoO$_{3.5}$, was prepared by drying and firing the mixed nitrate together with citric acid. A dense electrode film was deposited on the electrolyte by a laser ablation method. The detail of the film deposition is in Ref. (7). The resulting electrode film was 1.8 µm thick and 6 mm in diameter. A counter and a reference electrodes were prepared by a platinum paste on the opposite side and on the periphery of the pellet, respectively.

Porous Oxygen Sensor (POS)

In order to fabricate a porous oxygen sensor, Ce$_{0.6}$Gd$_{0.4}$O$_{1.95}$ powder was once fired at 1400°C, and then, ground, pressed, and sintered at 1400°C. The porosity of the obtained pellet was higher than 40%. It was easily shaped by a polishing paper to be a small piece of 4 mm in diameter and 1 mm in thickness. A POS-reference electrode (PRE) was formed on one side of the porous pellet with a platinum paste.

Surface Oxygen Potential Measurement

Arrangement for the surface oxygen potential measurement is schematically shown in Figure 1. The three electrodes, WE, CE and RE, were connected to a potentiostat (Solartron 1287) in the usual manner. The potential difference between WE and PRE, $\Delta E_{ WE-PRE }$, was monitored by an electrometer (Toho Technical Research, PS-14). When POS is porous enough not to impede gaseous transport, the oxygen potential is almost identical all around POS except for the point where POS is in contact with the surface of WE. Since electrode potential on a solid electrolyte is determined by the oxygen potentials at the electrode contacts, the oxygen potential at WE surface, $\mu_{O_2}$, is calculated

Figure 1. Schematic diagram of the measurement of surface oxygen potential using porous oxygen sensor (POS).
from $\Delta E_{\text{WE-PRE}}$ as

$$\mu_{O_2,g} = \mu_{O_2,g} \exp \left( \frac{4F \Delta E_{\text{WE-PRE}}}{RT} \right)$$

where $\mu_{O_2,g}$ is oxygen potential in the gas phase. The ac response of the working electrode was monitored by using a potentiostat (Solartron 1287) and a frequency response analyzer (FRA, Solartron 1260). For the measurement of the three-terminal cell impedance, the “voltage” output signal from the potentiostat, $\Delta E_{\text{WE-PRE}}$, was connected to the input channel-1 of FRA, and compared with the “current” signal, $I$, connected to the channel-2. For the ac response analysis of POS, the 1:1 analog output of the electrometer, $\Delta E_{\text{WE-PRE}}$, instead of $\Delta E_{\text{WE-PRE}}$, was connected to the channel-1. The “pseudo impedance” of the POS response was defined as $\Delta E_{\text{WE-PRE}} / I$, and analyzed in the similar method as the “impedance” in the normal meaning.

![Figure 2. Schematic diagram of the connection for the measurement of the three-terminal cell impedance and POS pseudo impedance.]

**RESULTS AND DISCUSSION**

**Possible Reaction Pathway and Oxygen Potential Profile**

Electrochemical oxygen reduction on a dense mixed conductor electrode takes place through the following serial processes.

1. gas phase diffusion
2. desorptive adsorption of oxygen
3. ionization and incorporation
4. bulk diffusion
5. transfer at electrode / electrolyte boundary

Our previous results with the electrodes of various thickness showed the possible rate limiting steps are <2> and/or <3>. Other processes are fast enough and can be
Figure 3. Reaction pathway and possible oxygen potential profile across the electrode disregarded. Figure 3 shows the schematic drawing of the oxygen potential profile around the electrode during the oxygen incorporation reaction. The potential gaps, $E_2$ and $E_3$, are the motive forces to promote the reaction $\langle 2 \rangle$ and $\langle 3 \rangle$, respectively. When the adsorption process is the rate-determining step, oxygen potential gap will be built between the gas phase and the electrode surface in order to provide a motive force for the adsorption reaction. The magnitude of the gap will be detected with POS. On the other hand, when the ionization / incorporation reaction is rate limiting, the potential gap will be generated between the surface and the sub-surface of the electrode (i.e. certain atomic layers below the surface in the electrode layer). Then, the surface oxygen potential will remain in equilibrium with that in the gas phase. In that case, the POS will not show any signal.

**AC Responses**

Figures 4 and 5 show examples of the ac responses of the electrode. The impedance of the three-terminal cell (open symbols) and the pseudo impedance of the POS (closed symbols) are compared. In the complex plane (Figure 4), two semicircles appeared in the both responses. From our previous results, the impedance in the three-terminal cell is described by the serial connections of the grain boundary impedance and the electrochemical reaction impedance. It is roughly represented by an equivalent circuit as shown in Figure 6. The higher frequency arc corresponds to the grain boundary impedance, $Z_{gb}$. It should be noted that POS showed no response in the frequency range where $Z_{gb}$ appeared. It is because POS detects the surface state of the electrode, which is not affected by any voltage loss in the electrolyte layer. This result confirms that POS can be used as the probe for the surface oxygen potential. In the higher frequency region (around 100 kHz), however, another small arc appeared only in the POS response. This small pseudo impedance has not been identified yet. It might have been due to an error in the measurement since the frequency range is close to the maximum frequency where the equipment can work correctly. The highest frequency intercept of the pseudo impedance arc did not go to zero although the high frequency limit of the POS response must be zero. It is because the measured voltage includes the resistance of the Pt lead.
wire and in-plane resistance of the electrode film. The highest frequency resistance had positive temperature dependency, which is consistent with the temperature dependence of the resistivity of Pt and highly doped lanthanum cobaltites.

**Figure 4.** Complex plane plot of the three-terminal impedance (open symbol) and the POS pseudo impedance (closed symbol) for the dense $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ electrode.

**Figure 5.** Real and imaginary parts of the three-terminal impedance (open symbol) and the POS pseudo impedance (closed symbol) shown in Figure 4.
The lower frequency arc of the three-terminal impedance is attributed to the electrochemical reaction impedance. As is mentioned above, the electrochemical reaction is rate limited solely by the surface reactions. Thus, the resistance $R_E$ can be written with the two serial resistances, $R_2$ and $R_3$, which corresponds to the reaction <2> and <3> in Fig. 3, respectively. The capacitance, $C_E$, represents the oxygen nonstoichiometry in the electrode layer. The three-terminal impedance is thus written as,

$$Z_T = \frac{(R_2 + R_3)}{1 + \omega^2 (R_2 + R_3) C_E^2} - j \frac{\omega (R_2 + R_3)^2 C_E}{1 + \omega^2 (R_2 + R_3)^2 C_E^2}$$

where $\omega$ is the frequency. In an ideal situation, the voltage over POS is the same as that across $R_2$ in Fig. 6. From the definition of the pseudo impedance, it should be written as

$$Z_p = \frac{R_2}{1 + \omega^2 (R_2 + R_3)^2 C_E^2} - j \frac{\omega R_2^2 C_E}{1 + \omega^2 (R_2 + R_3)^2 C_E^2}$$

Comparing the equations [2] and [3], the pseudo impedance of POS is described by a parallel connection of the resistance, $R_2$, and a capacitance, $C_E (R_2 + R_3)/ R_2$, which has the same relaxation time as the impedance of the three-terminal cell. Actually, in the POS response in Figures 4 and 5, a similar but slightly smaller arc appeared in the same frequency range. This means that the oxygen potential on the electrode surface shifted under the current flow in order to promote the reaction <2>. Comparing the magnitude of the three-terminal impedance and the POS response, it can be concluded that the most part of the electrode impedance is due to the dissociative adsorption of oxygen (reaction <2>). The contribution of the oxygen incorporation reaction (reaction <3>) appears to remain in a certain amount. It is, however, still to be studied since it is not clear yet if the POS contact is in an ideal condition; i.e. possible existence of local oxygen transport around the POS/WE contacts, for example, may have affected the POS response.

**Figure 6** Equivalent circuit for the impedance of the three terminal cell and the pseudo impedance of POS. $R_2$ and $R_3$ are the resistances for the dissociative adsorption of oxygen (reaction <2>) in Fig.3) and the oxygen incorporation reaction (reaction <3> in Figure 3), respectively.
A typical result of the dc polarization experiment is shown in Figure 7. The polarization curve obtained by the three-terminal method is shown with the open symbols. The IR-free electrode potential is plotted against the voltage in equilibrium with 1 bar oxygen. The surface oxygen potential was calculated from the POS response using equation [1], and plotted in the closed symbols. When the current increased in both the anodic and the cathodic directions, the electrode polarization increased, and at the same time, the surface oxygen potential shifted from the equilibrium. The magnitude of the surface oxygen potential shift was close to the electrode polarization especially in the cathodic direction. The ratio of the polarization and the surface oxygen potential shift is similar to that of the three-terminal impedance and the POS pseudo impedance around the equilibrium potential. It should be noted that the surface oxygen potential become higher than 1 bar when the electrode was highly polarized to the anodic direction. Those results suggest the most overvoltage is consumed for the oxygen adsorption reaction (reaction <2> in Figure 3) making an inequilibrium surface state of oxygen. The remaining part of the polarization may be due to the oxygen incorporation (reaction <3>). However, further experimental studies are necessary for the quantitative discussion on the contributions of the reactions <2> and <3>.

Figure 7. Direct current polarization and surface oxygen potential on the dense La$_{0.6}$Sr$_{0.4}$CoO$_{3-δ}$ electrode film (1.8 μm).
ACKNOWLEDGEMENTS

This study was performed through Special Coordination Funds of the Science and Technology Agency of the Japanese Government. A part of the work was supported by NEDO international joint research program.

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