Transactions of the Materials Research Society of Japan 25 [1] 51-54 (2000)

Electrochemically Induced Non-equilibrium Oxygen on a Solid Oxide Electrolyte

Tatsuya Kawada, Satoshi Haga, Koichi Masuda, Kenichi Kawamura,
Yutaka Nigara, Atsushi Kaimai, Junichiro Mizusaki, Hiroo Yugami*
Research Institute for Scientific Measurements, Tohoku University
2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
Fax: 81-22-217-5341, e-mail: kawada@rism.tohoku.ac.jp
*Graduate School of Engineering, Tohoku University
Aoba01,Aramaki, Aoba-ku, Sendai 980-8579, Japan
Fax: 81-22-217-6924, email: yugami@cc.mech.tohoku.ac.jp

A potentiometric method has been applied to measure the local oxygen potential on the surface of a dense $(La,Sr)CoO_{3-\delta}$ electrode on a CeO_2 based solid electrolyte. While the oxygen electrode reaction proceeds, a porous ceria tip (Porous Oxygen Sensor, POS) with a platinum reference electrode on one side was pushed against the surface of the electrode. The surface oxygen potential was calculated from the observed voltage over POS. The surface oxygen potential increased under anodic polarization, and decreased under cathodic polarization. In some cases, the surface oxygen potential was higher than 1 bar under anodic polarization. An attempt was made to measure the distribution of the local oxygen potential by minimizing the size of POS. A small POS tip (micro-POS) was constructed by covering a thin platinum wire with zirconia electrolyte powders. The similar results were obtained with the micro-POS on the oxide electrode.

1. INTRODUCTION

Solid oxide ionic conductors are widely used for batteries, fuel cells, gas sensors, and catalysts, etc. By applying dc voltage on the oxide ion conductors, the oxide ions are transported through the solid, and at the same time, oxygen gas is released or incorporated at the electrode. When the electrode reaction proceeds, oxygen potential is accumulated or depleted where a kinetic barrier exists. If the electrode process is rate controlled by a chemical reaction between gas and a solid, it will result in the formation of a non-equilibrium oxygen on the electrode surface. In our previous studies[1-3], the oxygen incorporation / extraction reaction on a dense film electrode of a mixed electronic / ionic conductor, $(La,Sr)CoO_{3-\delta}$, was found to be controlled almost perfectly by the surface processes. With this electrode, the adsorbed oxygen on the surface can be in non-equilibrium state with the gas phase, which may affect the catalytic activity for gas reactions. This phenomenon was reported by Vaynus et al.[4] and named "NEMCA" effect (Non Faradaic Electrochemical Modification of Catalytic Activity) . Although several studies have been performed to characterize the surface species on the electrode, the thermodynamic properties have not been quantified.

The purpose of this study is to characterize the surface oxygen in terms of its oxygen potential. A potentiometric method which uses a "porous oxygen sensor" (POS)[5] is applied to measure the surface oxygen potential under current flow. The response of the sensor is analyzed under ac and dc polarization conditions. Attempts are made to develop a small surface oxygen probe in order to measure the two dimensional distribution of the oxygen potential on the surface.

2. EXPERIMENTAL

2.1 Sample Preparation

The electrolyte material powders, $Ce_{0.9}Ca_{0.1}O_{1.9}$ or $Ce_{0.9}Gd_{0.9}O_{1.95}$, were prepared from an aqueous nitrate solution by co-precipitation as oxalic salts. It was pressed and sintered into a pellet of 16 mm in diameter and 2 mm in thickness.

Dense films of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ were prepared by a laser ablation method. A sintered pellet of the oxide was used as a target. The substrate electrolyte pellet was heated to about 1000 K during the deposition. The oxygen pressure was controlled to be about 10^{-2} torr in order to avoid the reduction of the cobaltite. The resulting electrode film was 0.5 to 2 µm thick and 6 mm in diameter. The counter and the reference electrodes were prepared by a platinum paste on the opposite side and on the periphery of the pellet, respectively.

2.2 Porous Oxygen Sensor (POS)

A porous pellet of $Ce_{0.9}Ca_{0.1}O_{1.9}$ or $Ce_{0.9}Gd_{0.9}O_{1.95}$ was prepared to be used as the surface oxygen potential probe ("porous oxygen sensor", POS). The material powder was once fired at 1673 K, and then, ground, pressed, and sintered at 1673 K. The porosity of the obtained pellet was higher than 40%. A POS-reference electrode (PRE) was formed on one side of the porous pellet with a platinum paste.

2.3 Micro-POS

A smaller probe of the surface oxygen potential (micro-POS) was prepared by coating a thin platinum wire with a fine zirconia particles. A Pt / Pt-Rh(13%) thermocouple wire of 0.1 mm in diameter was used as the probe tip. It was fixed on the end of the thicker wires (0.3 mm) of Pt and Pt-Rh(13%). The wires were put in a small ceramic tubes and were fixed by an alumina base ceramic cement. The contact point of the thin thermocouple was soaked into the ethanol in which fine particles of yttria stabilized zirconia (8 mol% Y_2O_3 doped ZrO_2, Nissan Kagaku) was dispersed. It was, then, heated in a flame of CH_4-O_2 burner to sinter and fix the YSZ powder on the wire. The optical microscope image of the micro-POS probe is shown in Fig.1.

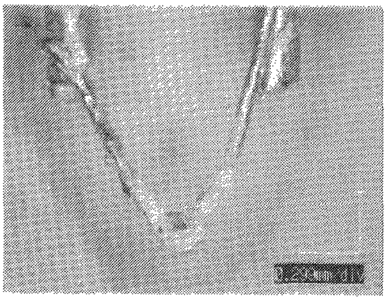

Fig. 1 The optical microscope photograph of the micro-POS tip. The white particles on the top of the probe is YSZ.

2.4 Electrochemical measurements

Figure 2 shows the arrangement of the electrodes for the surface oxygen potential measurement. The three electrodes, working (WE), counter (CE) and reference (RE), were connected to a potentio/galvano stat (Solartron 1287). The potential difference between WE and PRE was monitored with another potentiostat (Toho Technical Research, PS-14) in the electrometer mode.

Since the POS-reference electrode, PRE, is always in equilibrium with the gaseous oxygen, the oxygen potential on the surface of the working electrode, $\mu_{O,s}$ was calculated as follows,

$$\mu_{O_2,s} = \mu_{O_2,g} + 4F \cdot \Delta E_{WE-PRE} \quad [1],$$

where $\mu_{O,g}$ is the oxygen potential in the gas phase.

The ac response of the working electrode was monitored by using a frequency response analyzer (Solartron 1260), to which the potential and the current monitor signals from the potentio-stat 1287 were connected. The data obtained in this measurement will be called "three terminal cell impedance" in the following sections. In order to analyze the ac response of POS, the "pseudo impedance", Z_P, is defined as

$$Z_p \equiv \Delta E_{WE-PRE} / I. \quad [2]$$

where ΔE_{WE-PRE} is the POS signal, and I is the current through the cell. To measure the pseudo impedance, the output signal from the electrometer PS-14 was connected to 1260 instead of the potential signal from 1287. The measurements were done in O_2-Ar mixed gases of various oxygen partial pressures. Temperature was controlled from 873 K to 1073 K.

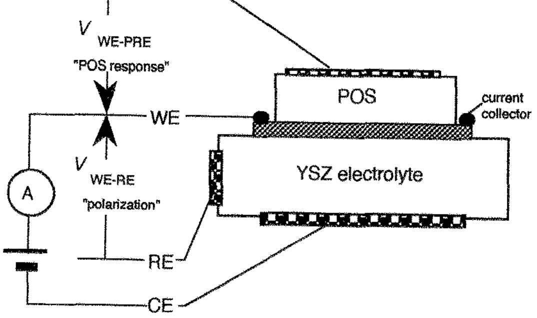

Fig. 2 The schematic drawing of the electrode arrangement for the in-situ surface oxygen potential measurement.

3. RESULTS AND DISCUSSION

3.1 AC Response

Figures 3 and 4 show typical ac responses of the $La_{0.6}Sr_{0.6}CoO_{3-\delta}$ electrode. The impedance of the three-terminal cell (open symbols) are compared with the "pseudo impedance" of the POS (closed symbols).

From our previous results, the electrochemical impedance can be represented by a parallel connection

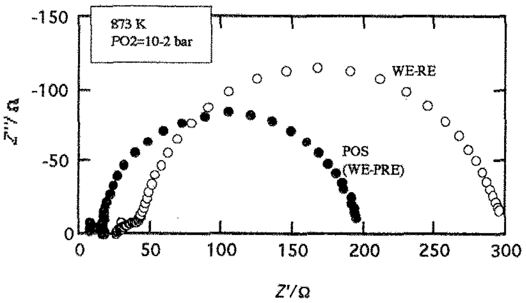

Fig. 3 A typical impedance of the three terminal cell and the pseudo impedance of POS plotted in a complex impedance plane.

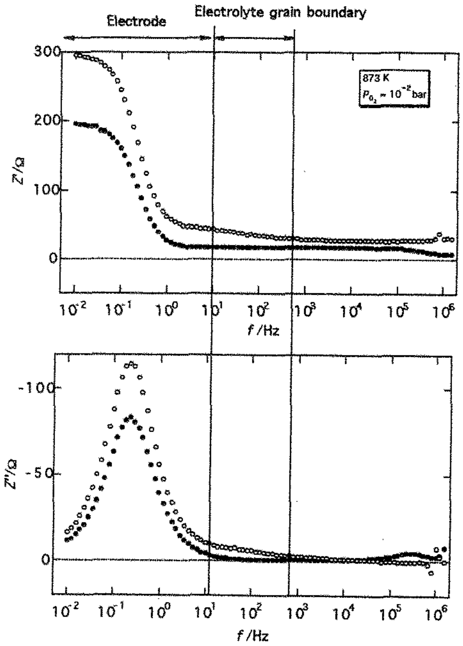

Fig. 4 Frequency dependence of the real (Z') and the imaginary (Z'') parts of the three terminal impedance and the pseudo impedance.

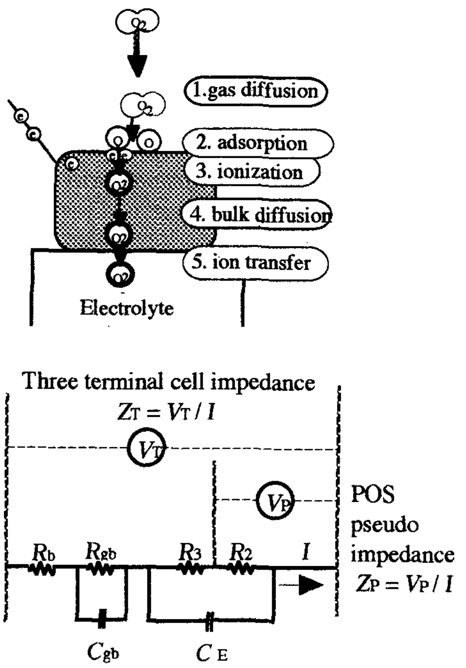

Fig.5 Schematic diagram of the oxygen reaction path and the equivalent circuit.

of the surface reaction resistance, R_2+R_3, and the chemical capacitance, C_E, which comes from the oxygen nonstoichiometry change in the electrode. The total impedance in the three-terminal cell is thus described by the equivalent circuit shown in Fig.5, and represented as,

$$Z_T = \frac{(R_2+R_3)}{1+\omega^2(R_2+R_3)^2 {C_E}^2} - j\frac{\omega(R_2+R_3)^2 C_E}{1+\omega^2(R_2+R_3)^2 {C_E}^2} + Z_{gb} \qquad [3]$$

From the definition (Eq.[2]), the POS "pseudo" impedance,Z_P, is written as

$$Z_P = \frac{R_2}{1+\omega^2(R_2+R_3)^2 {C_E}^2} - j\frac{\omega(R_2+R_3)R_2 C_E}{1+\omega^2(R_2+R_3)^2 {C_E}^2} \qquad [4]$$

The lower frequency arc in the three terminal cell impedance in Fig.3 corresponds to the electrochemical impedance. In the POS response, a similar but slightly smaller arc appeared in the same frequency region. On the other hand, the grain boundary impedance of the three terminal cell was observed in the higher frequency region, around 100 Hz, where no response was seen in the POS pseudo-impedance. This means that the electrode potential itself is not the direct reason of the POS response, but the change in the state of the electrode surface is detected.

Comparing the magnitude of the electrochemical impedance and the POS pseudo-impedance, a significant part of the electrode polarization is found due to the resistance of the surface adsorption/desorption reaction. Thus, the large oxygen potential gap between the gas phase and the electrode surface can be induced by applying the overvoltage to the electrode. The formation of the non-equilibrium oxygen may alter the catalytic activity of the electrode surface.

The contribution of the oxygen incorporation reaction (process 3) to the overall impedance still remained in a certain amount. The resistance of the process 3, R_3, was calculated by subtracting R_2 from the total electrochemical resistance. The oxygen partial pressure dependence of R_2 and R_3 are plotted in Fig.6. The resistance of the surface adsorption process, R_2, is almost proportional to $p(O_2)^{-1/2}$. On the other hand, the ionization process is less dependent on $p(O_2)$ especially at 873 K. The reaction kinetics are still to be studied in detail.

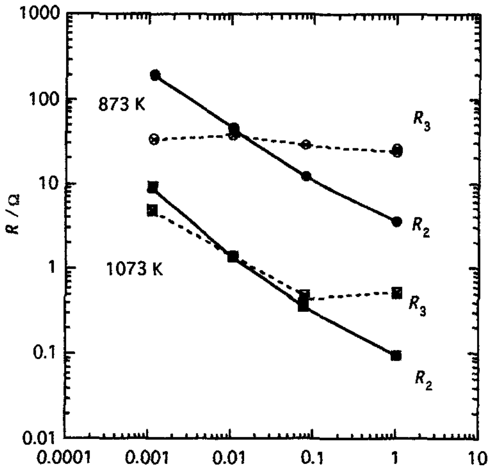

Fig.6 Oxygen partial pressure dependence of R_2 and R_3 at 1073 K and 873 K.

The highest frequency response around 300 kHz appeared only in the pseudo-impedance. Since the response time of the potentio-stat is about 2μs, this is possibly due to artifact from the equipments. The highest frequency intercept of the POS pseudo-impedance should fall on to zero in the ideal case. However, it showed around 10 ohm in all the measurements. It is probably due to the ohmic resistance of the lead wire for the working electrode, the contact resistance of the current collector, and/or the in-plane resistance of the electrode film.

3.2. DC Polarization

Typical dc polarization curves are shown in Fig.7. The electrode potential was calculated by subtracting the ohmic drop, and plotted against the equilibrium potential in 1 bar oxygen. The surface oxygen potential was calculated from the POS signal by equation [1]. The contribution of the high frequency resistance observed in POS pseudo-impedance was subtracted before the calculation.

When the electrode polarization increased, the surface oxygen potential shifted from the equilibrium. The amount of the surface potential shift was close to the electrode polarization voltage especially in the cathodic direction and in the low oxygen partial pressures. In such conditions, gas phase transport impedance should be taken into consideration. Especially, the POS itself might be the obstacle for the gas phase transport, which can be another reason of the POS response. In the present experiment, however, this effect was negligible. The temperature dependence of

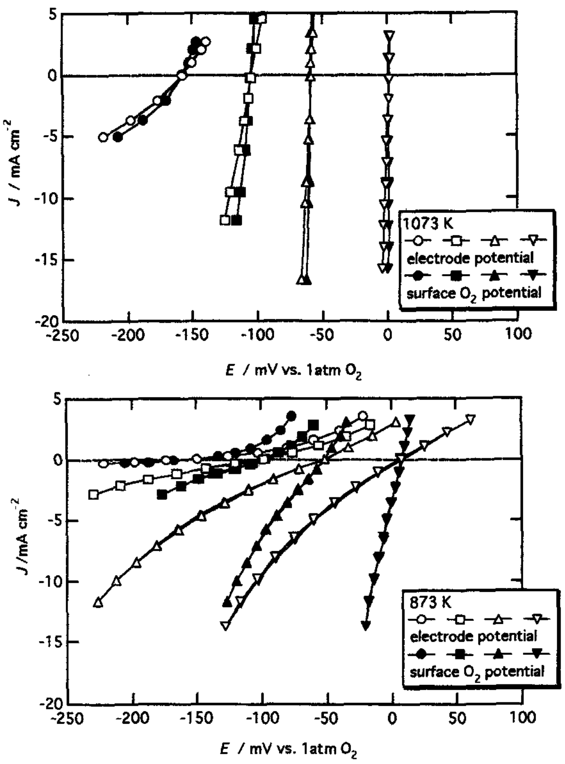

Fig.7 DC Polarization and surface oxygen potential.

the polarization and the POS response are too large to be explained by the gas phase transport.

From above discussions on ac and dc responses, it is concluded that highly non-equilibrium oxygen was induced on the electrode surface at high current densities. It should be noted that the surface oxygen potential became even higher than 1 bar when the electrode was polarized to the anodic direction.

3.3 Possibility of Space Resolved Measurement

The micro-POS was tested to measure the distribution of the oxygen potential on the electrode surface. The test cell of a smaller size (3mm in diameter) was prepared for easier handling of the micro-POS in the space resolved measurements. In this case, platinum paste was used on the periphery of the electrode for current collection.

As the first approach, the oxygen potential on the (La,Sr)CoO_3 electrode surface was compared with that on the platinum paste current collector by putting the micro-POS on each spot. Figure 8 shows a typical example of the results. On the oxide electrode, the response was similar to that for the larger sample as shown in Fig.7. When the micro-POS was put on the platinum paste, however, it gave only small voltage shift. Although the signal was not as stable as that obtained with the larger POS, the clear difference was detected between the oxide electrode and the platinum layer. If this method is applied to an electrode with more complicated morphology, the distribution of the surface oxygen potential will be imaged.

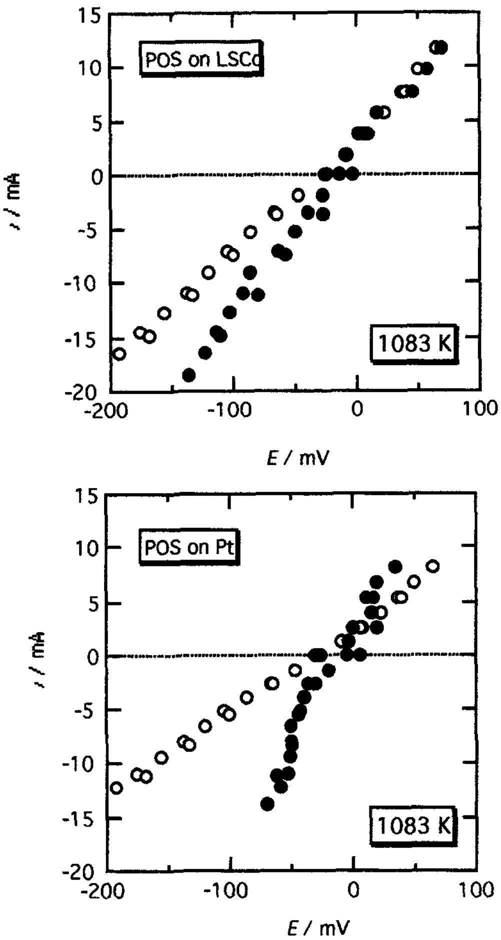

Fig.8 DC Polarization and surface oxygen potential on the oxide electrode and on the Pt current collector. measured by micro-POS.

ACKNOWLEDGEMENT

This study was performed through Special Condition Funds of the Science and Technology Agency of the Japanese Government.

REFERENCES

1. K. Masuda, A. Kaimai, K. Kawamura, Y. Nigara, T. Kawada, J. Mizusaki, H. Yugami, H. Arashi, Proc. 5th Intern. Symp. SOFC, edt. by U. Stimming et al., the Electrochem. Proc. Vol. 97-18, 473 (1997)
2. T. Kawada, K. Masuda, J. Suzuki, A. Kaimai, K. Kawamura, Y. Nigara, J. Mizusaki, H.Yugami, H. Arashi, N. Sakai and H. Yokokawa, *Solid State Ionics*, **121**, 271(1999)
3. T. Kawada, S. Haga, K. Kawamura, Y. Nigara, A. Kaimai , J. Mizusaki , Proc. 6th Symp. SOFC, edt. by S.C.Singhal et al.the Electrochem. Proc. Vol. 99-x, xxx (1999)
4. V C. G. Vayenas, S. Bebelis, S. Neophytides, and I. V. Yentekakis, *Appl. Phys.* **A49** (1989) 95
5. T. Kawada, B.A. van Hassel, T. Horita, N. Sakai, H. Yokokawa and M. Dokiya, *Solid State Ionics*, **70/71**, 65-71 (1994)

(Received December 17,1999 ; Accepted February 15,2000)