Oxygen potential distribution profile was measured around (La,Sr)MnO₃ electrode/YSZ electrolyte interface. The local oxygen potential was measured by a newly developed microprobe that detects oxygen potential on conductive solids. A model electrode/electrolyte interface was fabricated by embedding a small piece of La₀.₈Sr₀.₂MnO₃ in YSZ. When the electrode was polarized, the oxygen potential on the electrode surface shifted out of equilibrium. The potential shift was larger and faster around the electrode/electrolyte boundary and gradually faded with distance. The critical length was larger than 60 µm. A numerical calculation was made to simulate the relaxation behavior of the surface oxygen potential after an abrupt change in polarization voltage. The surface diffusion coefficient was roughly estimated to be about 5 x 10⁻⁶ cm² s⁻¹.

INTRODUCTION

Strontium substituted lanthanum manganite, (La,Sr)MnO₃₄, (LSM) is widely recognized as a standard cathode material for high-temperature solid oxide fuel cells (SOFCs). In a porous gas electrode, the electrochemical reaction takes place most preferably at triple-phase boundaries (TPB) of gas, electrode, and electrolyte. Under cathodic current flow, oxygen is depleted at TPB, which causes the overvoltage. Because the oxygen self-diffusion coefficient in LSM is small, oxygen transport through the electrode bulk is not significant except for a very small area (<0.1 µm) around TPB (1-3). The reaction proceeds mostly via surface diffusion. The oxygen potential profile on the electrode layer is determined according to the rates of surface diffusion and surface reaction. If surface diffusion is much faster than the surface reaction, the oxygen potential on the electrode surface will deviate from the equilibrium in order to widen the reaction area. In this case, electrode particles should have catalytic activity even in upper layer of the electrode. On the contrary, if surface diffusion is much slower, the electrochemical reaction is hardly affected by the material far from TPB. Optimum design of the electrode is thus dependent on the kinetics.

Knowledge of oxygen potential distribution in the electrode is important also to predict the long-term stability of LSM cathode. Due to the tendency of forming cation vacancies, LSM has rather large cation diffusivity (4). When it is placed under oxygen potential gradient, it causes kinetic demixing or kinetic decomposition. The steeper oxygen potential gradient would give faster degradation of the electrode composition and morphology around TPB.
Steele estimated the length of the active reaction site on LSM to be 50 to 170 μm at 1000°C from the isotope exchange coefficient (3). This means that the surface diffusion is fast enough, and the electrochemical reaction rate is controlled by the surface chemical reaction. On the contrary, Yasumoto et al. successfully explained the electrochemical behavior assuming surface diffusion control (5). It should be made clear by measuring the oxygen potential profile directly on the working electrode surface. In this study, a method of local oxygen potential measurement is developed, and distribution of oxygen potential is measured around a model interface of LSM and YSZ.

CONCEPT OF LOCAL OXYGEN POTENTIAL MEASUREMENT

In our earlier work, we proposed using a porous oxygen sensor (POS) to determine the oxygen potential on the working electrode surface (6). Figure 1 shows schematically the concept of the measurement. A porous pellet of oxide ion conductor (YSZ or doped ceria) is put on the working electrode. It has a reference electrode (PRE, POS-reference electrode) on the opposite side of the sample. The oxygen potential at the POS/sample contact is measured as emf between the working and the POS-reference electrodes. Under an open circuit condition, the surface of the working electrode is equilibrated with the gaseous oxygen and POS emf is zero. When the surface oxygen potential shifts from the equilibrium under current flow, the deviation is detected as the emf. The technique was applied to metal electrodes on YSZ and more recently to a dense (La,Sr)CoO$_3$ electrode on a ceria-based electrolyte (7,8). Because POS measures averaged information over the whole sample area, it is not applicable to quantitative analysis of an inhomogeneous surface such as a porous sample. Micro-POS developed in this study is intended to measure the local oxygen potential and its distribution on an inhomogeneous surface. Figure 2 shows a schematic drawing of μ-POS probe. By coating a noble metal wire with YSZ particles, a topologically equivalent structure such as POS is realized on its tip. Mounting the probe on a piezo scanner of AFM (atomic force microscope), the local oxygen potential is measured at a selected position on the sample surface.

EXPERIMENTAL

As the base structure of a micro-POS probe, we employed a “thermal probe” (TA-Instruments Co.) that is designed to be used with an AFM scanner (ThermoMicroscope Co., Explorer). It consists of a reflection mirror for laser position sensor, and the thermal
sensor probe made of a thin wire (5 mm φ) of platinum-rhodium alloy. The tip of the probe was dipped into water in which YSZ powder (TOSOH, TZ8Y) was dispersed. It was dried and heated up to 1200°C by applying electrical current to the wire. Figure 3 shows the resulting µ-POS probe. Small YSZ particles are observed covering the surface of the platinum-rhodium wire (Figure 4). Several clacks can be seen in the YSZ layer that may act as an oxygen path to the inner contact of the YSZ and the wire. The AFM image (topography) obtained with µ-POS probe had the same quality as those with the original probe. The lateral resolution was higher than 1 µm.

Figure 3. Optical microscope image of µ-POS probe. Figure 4. Surface SEM image of µ-POS.

A sample heating stage was newly designed to heat the sample up to 800°C under an AFM scanner mechanism. The sample was set in a small electric furnace with a platinum wire as a heating element. A DC power supply was used for heating. The probe was set to approach the sample surface through holes of alumina heat shielding plates. The surrounding parts of the sample stage were cooled by flowing water. The probe scanner was placed below the sample stage to avoid possible damage of the piezo elements by heat. Because the probe was originally designed as a temperature sensor, it was used to monitor the sample temperature.

Figure 5. Sample heating stage on AFM scanner.
A model electrode / solid electrolyte interface was fabricated. Lanthanum manganite (La$_{0.8}$Sr$_{0.2}$MnO$_3$; LSM) was used as the electrode material and YSZ (TOSOH TZ8Y) as the electrolyte. The powder of LSM supplied by Tokyo Gas Co., Japan (made by Praxair Inc., USA) was pressed into a pellet and heated to 1400°C. The sintered pellet was cut into small pieces and their surfaces polished. Platinum wire (0.1 mm Ø) was attached on one end of the LSM chip using a platinum paste. It was then embedded in YSZ powder, pressed, and heated at 1350°C for 2 hours. The sintered body was cut and polished as shown in Figure 6 to disclose the LSM/YSZ boundary line on the cross-sectional surface. The counter and reference electrodes were made with platinum paste. Electrochemical DC and AC measurements were done with a potentiostat (Toho Giken, Co., Model 2020) and an impedance analyzer (NF Circuit Block Co., 5080). The emf over µ-POS was monitored with another potentiostat operated in the electrometer mode (input impedance $10^{12}$ Ω). All the measurements were performed in air.

![Figure 6. Schematic view of the sample and optical microscope image of the surface.](image)

**RESULTS AND DISCUSSION**

Figure 7 shows typical topography of the sample surface around the electrode/electrolyte interface measured with the µ-POS probe at ca.700°C. Although the signal/noise ratio was not high enough at the present system, the interface position was clearly distinguished in this scale.

The AC impedance response of the working electrode is displayed with the solid line in Figure 8. At least two depressed semicircles are observed in a complex impedance plane. The impedance response in the high-frequency range is probably due to the current constriction effect of this particular electrode. Because it is embedded in the YSZ electrolyte, it has a large two-phase boundary area where AC current can flow, whereas DC current path is restricted to the single TPB line on the surface. The dotted and dashed lines in Figure 8 show the responses of µ-POS when it was put on the points A and B marked in Figure 7. In the vicinity of TPB, the µ-POS response showed a single pseudo-impedance arc. When µ-POS is put far from TPB, the characteristic frequency shifted lower and the signal became smaller.
Figure 7. Topography of around the LSM/YSZ interface.

Figure 8. AC impedance of the LSM electrode and POS response at the points A and B in Figure 7.
The DC polarization curve and μ-POS response are shown in Figure 9. Contrary to initial expectation, μ-POS showed a non-zero emf value even when no current was applied to the cell. The open circuit response was about 0.6 to 0.8 V in this experiment, randomly dependent on the probe position. A possible reason for the unexpected response could be instability of the reference potential of μ-POS. The internal contact of μ-POS, i.e., the contact between the YSZ coating and the Pt-Rh wire, was expected to behave as a reference electrode (PRE). The potential of PRE should be determined by the equilibrium with the gaseous oxygen. However, if the YSZ coating is not porous enough and some redox impurities exist around the internal contact, it would cause an unpredicted emf on μ-POS. Except for the non-zero bias problem, the POS response was reproducible and showed a clear tendency in the current and the position dependence. When the LSM working electrode was polarized to the anodic direction, the POS voltage shifted to the positive side, indicating that the oxygen potential increased on the working electrode surface. On the other hand, under cathodic polarization, POS signal shifted to negative, which means that oxygen was depleted on the electrode surface. The responses were quicker and more obvious when the probe was closer to the electrode/electrolyte boundary. When the probe was farther from the boundary, a large hysteresis was observed. These results are consistent with the AC response shown in Figure 8.

![Figure 9. Typical polarization curve of LSM electrode and POS response at A and B in Figure 7.](image)

To determine the position dependence of the relaxation time precisely, POS responses at various locations were recorded after an abrupt change in the working electrode potential. Figure 10 shows a typical result when the working electrode was polarized to -0.3 V versus the reference electrode. At P1, a relatively quick response was observed. The relaxation time was about 10 sec, which corresponded to the characteristic frequency observed for point A in Figure 8. When the probe was set farther from the three-phase boundary, the relaxation time became longer and the signal smaller. After the first relaxation, the POS potential continued to decrease gradually. There may be another relaxation mechanism such as bulk oxygen transport, but the reason for this is not clear.

To simulate the position and time dependency of the POS response, a numerical calculation was made for a model interface, as shown in Figure 11. For simplicity, the following assumptions were made in the calculation:
- The concentration of surface oxygen is proportional to the surface oxygen activity.
- The surface reaction rate depends linearly on the concentration of adsorbed oxygen.
- Diffusion is one-dimensional.
- The geometry of the sample is symmetrical.

Figure 12 shows the calculated relaxation curve when the diffusion coefficient is assumed to be $5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and the surface reaction rate constant $3 \times 10^{-5} \text{ s}^{-1}$. The model appears to explain the experimental data relatively well.

**Figure 10.** Position dependence of POS response after abrupt change of working electrode potential from 0 to -0.3 V versus air.

**Figure 11.** Model interface for simulation.

**Figure 12.** Simulated POS response (WE $0\Rightarrow -0.3$ V).
EFFECTIVE THICKNESS OF LSM CATHODE

The above results suggest that oxygen potential shift on LSM cathode extends to a significant area above the three-phase boundary during operation. The characteristic length of the active site on the model electrode was longer than 60 μm at 700°C. In a practical porous electrode, the active site area must be shorter because the surface of the porous electrode is not as smooth as that of the model electrode and includes many particle-to-particle contacts via narrow contact area. Actual effective area depends on morphology. Although further calculations are necessary to predict the oxygen potential gradient, it is clear that not only the three-phase boundary line but also the particles in the electrode layer should be designed at the reaction site to make a high performance electrode.

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