

## In-situ Measurement of Oxygen Potential around (La,Sr)MnO<sub>3</sub> / YSZ Interface

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### INTRODUCTION

In a porous gas electrode of a Solid Oxide Fuel Cell (SOFC), the electrochemical reaction takes place most actively at a triple phase boundary (TPB) of gas, electrode and electrolyte. Under current flow, oxygen is accumulated or depleted, respectively, at TPB, which causes the overvoltage. The oxygen potential profile inside the electrode layer is determined according to the kinetic parameters such as surface diffusion coefficient and the surface reaction rate. Thus, information on the oxygen potential profile, if available, would be useful to understand the electrode reaction kinetics and to design a better electrode. In LaMnO<sub>3</sub> based cathodes, it is important also to predict the long-term stability since the oxygen potential gradient may lead to kinetic demixing of the electrode material.

The authors already developed a method to measure oxygen potential on an electrode surface by using a "porous oxygen sensor (POS)" [1]. It consists of a porous YSZ pellet with a platinum reference electrode on one side. The other side of the pellet was put on the sample surface, and the surface oxygen potential was determined from emf across the porous YSZ. The POS measurement gives an averaged information on the whole electrode surface. In this study, topologically equivalent structure with POS is made into a micro-probe as shown in Fig.1, and the two-dimensional distribution of the surface oxygen potential is measured on a model interface.

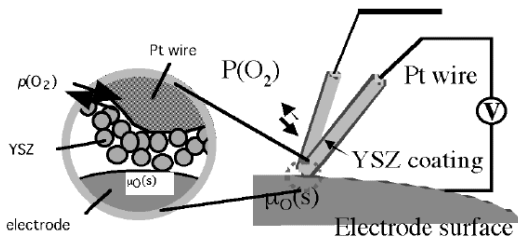


Fig.1 Schematic drawings of micro-POS measurements.

### EXPERIMENTAL

Micro-POS was fabricated by coating a Pt-Rh wire (5 $\mu$ m thick, TA instruments Co., "thermal probe") with porous YSZ as schematically shown in Fig.1. The wire was first soaked into a YSZ-dispersed water, and then, dried and heated up to 1200 °C. Several cracks can be observed in the YSZ layer. They are expected to act as an oxygen path to give a reference potential at the Pt-Rh wire/YSZ contacts. The probe was mounted on an AFM scanner and put on a selected position of a sample surface.

A model electrode / solid electrolyte interface was fabricated with La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> (LSM) and YSZ. A small piece of sintered LSM (ca. 0.5 mm x 1mm x 5 mm) was embedded in YSZ powder, pressed and heated at 1350 °C for 2 h. It was cut and polished as shown in Fig.2 so as to disclose the LSM/YSZ boundary line on the surface. The counter and the reference electrodes were made with platinum paste. 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 to the sample surface through holes of two alumina heat shields. The probe scanner was placed below the sample to avoid possible damage by heat.

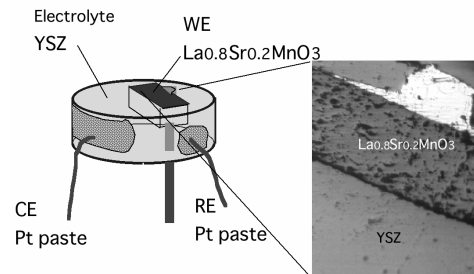


Fig.2 Schematic drawing and optical photograph of the sample LSM/YSZ interface.

### RESULTS AND DISCUSSION

Electrical current through WE and CE was measured as a function of the working electrode potential. Contrary to the initial expectation, micro-POS showed non-zero emf value (around 0.6 to 0.8 V) when no current was applied to the cell. It is probably because the YSZ coating was not porous enough and some red-ox impurities might exist around the Pt-Rh/YSZ contact. Apart from the non-zero bias problem, however, the POS response was reproducible, and showed clear tendency in the current and the position dependence. When the LSM working electrode was polarized to the anodic direction, POS voltage shifted to the positive side indicating that the oxygen potential increased around TPB, and vice versa. The responses faded and the time constant became larger when the probe was put farther from TPB. The critical distance is determined by the ratio of the diffusion and reaction rates. In order to investigate the relaxation behavior precisely, the POS responses at various locations were recorded after an abrupt change of the working electrode potential from 0 V to -0.3 V vs. air. Figure 3 shows a typical result. A larger and quicker response was observed when the probe was put closer to TPB.

The response was compared with a numerical calculation under simple assumptions, and it was found that the relaxation curve was explained well when the surface diffusion coefficient was assumed to be  $5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

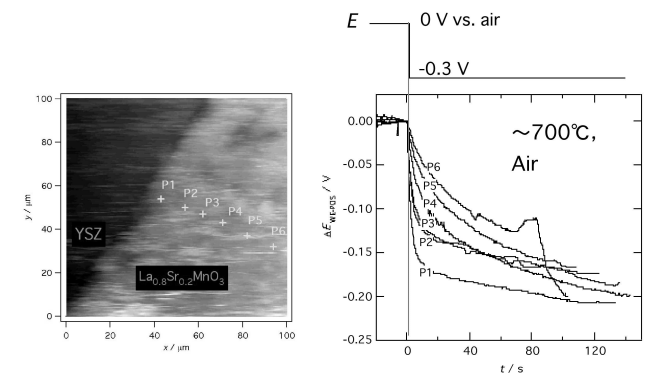


Fig.3 Topological image of the sample around TPB and the relaxation of  $\mu$ -POS response after an abrupt change of the working electrode potential.

### REFERENCES

- (1) T. Kawada, B. A. van Hassel, T. Horita, N. Sakai, H. Yokokawa, M. Dokiya, *Solid State Ionics*, **70**,65 (1994)