ELECTROCHEMICAL PROPERTIES OF DENSE Sr-DOPED LANTHANUM MANGANITE ELECTRODES PREPARED BY A LASER ABLATION METHOD

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ABSTRACT
In order to clarify the reaction mechanism on SOFC cathode, it is necessary to evaluate the contribution of oxygen bulk diffusion of electrode materials. In this work, we prepared dense Sr-doped lanthanum manganites (LSM) films on yttria stabilized zirconia (YSZ) substrates by a laser ablation method using KrF eximer laser. Scanning electron microscopy measurements indicated that dense LSM films (6-32 μm) were formed. Using these samples, electrochemical properties (oxide-ionic conductivity and ac impedance) were measured in Ar-O2 atmospheres.

INTRODUCTION
Sr-doped lanthanum manganite (LSM) is considered as the most suitable cathode material for solid oxide fuel cell (SOFC) because of its high electrical conductivity, high catalytic activity of oxygen reduction, chemical stability and good thermal expansion matching with yttria stabilized zirconia (YSZ). At a cathode using perovskite-type oxide such as Sr or Ca-doped LaMO3 (M=Mn,Co) for SOFC, two reaction paths are expected as shown in Fig. 1. Usually, the cathodic reaction is considered to take place only at the three phase boundary (TPB) of gas / electrode (LSM) / electrolyte (YSZ)[1], because the oxygen ionic conductivity of LSM is very low. Several papers on dense cathodes have been reported[2-4]. However, it is not yet clear how much the contribution of oxide ionic conduction to the cathodic reaction is.

In this work, the authors aimed to evaluate the contribution of oxide ionic
conduction in the cathodic reaction of the LSM electrode. Usually, the cathodic reaction through the TPB is very fast compared with the reaction through the bulk oxide-ion diffusion. So, it is necessary to prepare the dense electrode (which does not have the TPB) to evaluate the contribution of the bulk ionic conduction to the cathodic reaction. We used the laser ablation method to prepare a dense LSM electrode and carried out some electrochemical measurements.

EXPERIMENTAL

2.1 Sample preparation

To make a dense LSM electrode, we used a laser ablation method. Fig.2 shows the sketch of apparatus of laser ablation. Table I shows the typical experimental conditions. We prepared two types of samples to use for the following measurements.

(a) samples for electron blocking electrode method

Fig.3 shows the cell configuration used for electron blocking electrode. At first, dense LSM films (0.8cm²) were deposited on the substrate (YSZ) by the laser ablation method, then dense YSZ films (0.48cm²) were deposited on the LSM films.

(b) samples for complex impedance measurement

After the deposition of dense LSM electrode, counter and reference electrode were made by painting and fired Pt paste.

The cross sectional scanning electron microscopy (SEM) image of a LSM film is shown in Fig.4.

2.2 Measurements of ionic conductivity using the electron blocking electrode

The oxide-ionic conductivity was measured by the electron blocking electrode method. Applied voltage was less than 100mV and less than 100μA dc-current was passed to the sample (type(a) in 2.1). The oxide-ionic conductivity was calculated from the terminal voltage and the film thickness.

2.3 Electrochemical Measurements of dense LSM electrode

The electrode impedance (10mHz-20kHz) was measured at the equilibrium electrode potential by three terminal method using a frequency analyzer (NF Circuit Design Block Co., Ltd., type 5020) and a potentiostat (Toho Tech. Co., type 2000). The oxygen partial pressure in the system was controlled by a thermal mass flow meter (flow rate was 5cm/sec) and checked by a zirconia oxygen sensor. The impedance measurements were carried out under different oxygen partial pressures (10⁻⁴-1 atm).

In this measurements, we used two types of substrates. One is the sintered...
RESULTS AND DISCUSSION

3.1 Oxide ionic conductivity($\sigma_{\text{ion}}$) of LSM

Temperature, oxygen partial pressure and film thickness dependence of $\sigma_{\text{ion}}$ were measured by the electron blocking electrode method. Fig. 5 shows the temperature dependence (700-1000 °C) of $\sigma_{\text{ion}}$ in air. The activation energy calculated from the result is 170kJ/mol.

Fig. 6 shows the oxygen partial pressure dependence of $\sigma_{\text{ion}}$ at 1000°C. $\sigma_{\text{ion}}$ increased with increasing the oxygen partial pressure. As shown in Fig. 7, $\sigma_{\text{ion}}$ was approximately independent of the film thickness. This results suggest that the film does not contain cracks nor pores and electrons are blocked.

3.2 Electrode impedance

The electrode impedance was measured at given temperatures under different oxygen partial pressures(1-10^{-4}atm) for two type of samples(type I and II in 2.3). Fig.7 and Fig.8 show typical electrode impedance plots as a function of oxygen partial pressure for sample type I and type II, respectively. For the sample type I, the electrode resistance, $R_e$, increased with decreasing oxygen partial pressure and this tendency was same as the results on electron blocking electrode. While $R_e$ of the sample type II showed reverse dependence. This means the deferent reaction mechanism exist for type I and type II samples. For type I, the dependence of $R_e$ on the oxygen partial pressure may be explained by the existence of pores or cracks in the electrode. However, this interpretation is not compatible with the result obtained for the electron blocking electrode. Further investigation is needed for the clarification of the reaction mechanism in details.

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Table I  Experimental conditions of laser ablation

| Laser                        | KrF eximer laser (wavelength: 248 nm) |
|------------------------------|---------------------------------------|
| Repetition rate              | 20 ~ 100 Hz                           |
| Energy density               | ~10 J/cm²                             |
| Oxygen partial pressure      | ~10⁻⁴ Torr                            |
| Target                       | (La₀.₉Sr₀.₁)₀.₉MnO₃ (sintered plate)   |
| Substrate                    | YSZ (sintered disk and single crystal) |
| Substrate Temperature        | 800°C                                 |

Fig. 1 Two possible paths for oxygen reduction at LSM/YSZ interface.

Fig. 2 Sketch of apparatus of laser ablation.
Fig. 3 Cell configuration used for electron blocking electrode.

Fig. 4 Cross sectional SEM image of dense LSM electrode.

Fig. 5 Temperature dependence (700-1000°C) of $\sigma_{\text{ion}}$ in the air.

Fig. 6 Oxygen partial pressure dependence of $\sigma_{\text{ion}}$ at 1000°C.
Fig. 7  Film thickness dependence of $\sigma_{\text{ioni}}$.

Fig. 8  Typical electrode impedance plot as a function of oxygen partial pressure for sample type I.

Fig. 9  Typical electrode impedance plot as a function of oxygen partial pressure for sample type II.