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Effect of Gas Permeability of Porous LSM Cathode on Low Frequency Impedance Plots

Tomoo MOTOKI, Tatsuru NAMIKAWA and Yohtaro YAMAZAKI*

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1 INTRODUCTION

Solid oxide fuel cells (SOFCs) directly convert the free energy of fuel gas to electric energy. Many efforts have been made on SOFCs to reduce operating temperature because it widens the choice of alloy cell stack materials. The cost of production of SOFC stacks will be reduced considerably by the use of conventional heat resistant alloys. Preparation of high quality electrolyte thin films on porous support electrodes is the present objective to achieve the advancement of low temperature operating cells. A thick porous electrode is indispensable to a thin film cell, because the electrode supports a thin fragile electrolyte film. The concentration polarization in such thick electrodes must be considered in the operation of the thin film cells at high current densities. The gas permeability, porosity and bending strength of porous $\text{La}(\text{Sr})\text{MnO}_3$ (LSM) cathode prepared by the extrusion-sintering method, were measured at Fujikura Ltd.¹⁾ And the investigation about gas diffusion behavior in LSM substrate using AC impedance method was reported by Osaka Gas Co.Ltd.²⁾ However, details in electrochemical properties of thick porous LSM cathodes have not been investigated.

In this study, we prepare porous thick LSM electrodes by sintering, and the electrochemical properties of the electrode on YSZ electrolyte plate are investigated by AC impedance method. The concentration polarization of O_2 in the electrode is studied in connection with the porosity and gas permeability of the electrode.

2 EXPERIMENTAL

Two LSM powders were used for the preparation of thick porous LSM cathode which have various porosities.³⁾ One was as purchased powder of $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ (ATD Co.), and the other powder was prepared by thermally treating the purchased powder at 1550 °C in air

for 3h to increase the grain size. The two powders were mixed with various weight ratios of 1/1, 1/5 and 0/1. One ml of 1 wt% aqueous solution of polyvinylalcohol ($n=1500-1800$) was added to 10 g of each mixed LSM powder. The powder was pressed with a pressure of 8.62×10^7 Pa to form a disk (2.6 mm thick, 18 mm in diameter). The pressed disks were fired at 1400 °C for 3h in air. The diameter of thick porous LSM cathodes was about 18 mm and the thickness was 2.60 mm. The porosities were 9.5, 28, 53 and 56 % for the various mixing ratios of the two LSM powders. The gas permeability coefficient of the LSM cathodes was determined by measuring the flow rate of permeated air through the samples. The measurement was made at room temperature with a pressure difference of 1.0×10^4 Pa. The gas permeability coefficients of these LSM cathodes were $<1.0 \times 10^{-6}$, 3.0×10^{-4} , 7.0×10^{-3} and $2.0 \times 10^{-2} \text{ cm}^4 \text{ g}^{-1} \text{ sec}^{-1}$, respectively.

Each LSM cathode was stuck on a 0.25 mm thick 8YSZ plate (8mol% $\text{Y}_2\text{O}_3\text{-ZrO}_2$, TOSOH Co., TZ-8Y) with Pt paste, and heated at 900 °C for 2h in air. A Pt electrode was prepared on the opposite side of the YSZ plate by screen printing. The Pt electrode was used as anode.

The correlation between the impedance of the cathode reaction and the gas permeability coefficient of each porous cathode was investigated by using the AC

Fig.1 Cell configuration.

Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology (4259 Nagatsuta, Midori-ku, Yokohama 226, Japan)

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Fig.2 AC impedance plots for porous thick LSM cathode with 8YSZ electrolyte, porosity of electrode : (a) 53 %, (b) 9.5 %.

impedance method. The cell was mounted between two alumina tubes (Fig.1). Air flowed down to the cathode with a rate of 50 ml min⁻¹. Anode was only exposed to air. The measurement was made at 900 °C in air. The potential differences of 100 and 450 mV were applied between the cathode and anode. The impedance of the cells was measured with the AC voltage of ± 10 mV in the frequency range from 0.01 to 10⁵ Hz. An impedance response analyzer (NF Electronic Instruments 5080) was used for the measurement.

3 RESULTS AND DISCUSSION

Figures 2 (a) and (b) show the impedance plots for the cathodes with the porosities of 9.5 % and 53 %. Two semicircles are observed in high frequency region and low frequency region. Both semicircles enlarged when the overpotential increased from 100 mV to 450 mV.

Impedance measurement was also made, for comparison, with a Pt/YSZ/Pt cell without the LSM cathode. The result showed one semicircle in the high frequency region. This semicircle includes the impedance relating to the grain boundaries of the electrolyte and the finite length diffusions of oxide ion at anode and cathode interfaces. When measurement was made with porous thick LSM cathodes, the second semicircle appeared in low frequency region. Therefore, these second semicircles are expected to correspond to the finite length

Fig.3 Impedance for electrode reaction (R_E) as a function of the gas permeability coefficient of electrode material.

diffusion of O₂ gas in the porous thick LSM cathode. The intercept of the second semicircle is represented as R_E . The value of R_E was normalized with the electrode area. The relationship between R_E and gas permeability coefficient is shown in Fig.3. R_E decreased when the porosity and gas permeability coefficient increased.

Because the values of Fig.3 in the region of gas permeability coefficient from 10⁻⁴ to 10⁻¹ are relatively low, we can expect that the concentration polarization in the porous thick LSM cathodes does not severely confine the functions of thin film high temperature fuel cells.

4 CONCLUSIONS

An AC impedance analysis was made on LSM electrodes with various porosities and gas permeabilities, in order to study the polarization in porous thick LSM cathodes which are necessary for thin film SOFCs. It was found that the polarization in conjunction with the gas transport in the thick electrode could be detected as a semicircle in a low frequency region near 4.0 Hz in the AC impedance plot.

The impedance of electrode reaction which was estimated from the impedance plot in the low frequency region, was related linearly to the logarithm of gas permeability of electrode material.

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