STUDY ON THE EXTENSION OF REACTION ZONE FROM Ni/YSZ INTERFACE BY USING FIXED FILM ELECTRODES

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ABSTRACT

Effect of Ni film thickness and the porous ceramic layer thickness on polarization at the anode of SOFC was measured by using the fixed film electrode at around 1273 K. The electrode impedance was dependent on the thickness of the porous layer but not on that of Ni film. On the other hand, dc polarization was affected by neither thickness at high partial pressure of hydrogen. Effective reaction zone for the rate determining process was evaluated as less than 1 μm along the Ni thickness from the electrode/electrolyte. Not a diffusion process, but an activation process should be important for the rate determining step. \( P_{H_2} \) and \( P_{H_2O} \) dependencies of the interface resistance were similar to that which have been obtained from a Ni pattern electrode and a Ni-YSZ cermet electrode by other researchers.

INTRODUCTION

High temperature solid oxide fuel cells (SOFC) are expected to be the next power generation process because of not only their high energy conversion efficiency but also very small effect to the environment. One of the most important technology in their development is the design of a low polarization electrode.

Ni is generally used as the anode material from catalytic activity and economic view points. Many of past researches have been concerned with the Ni anode on ytttria stabilized zirconia (YSZ) electrode (1-6). Ni has been commonly used as Ni-YSZ cermet (1-4) because the cermet provides many Ni/YSZ contacts by the dispersed Ni particles and prevents the Ni particles from sintering at high temperature operation. Without such electrode structure, poor reproducibility and performance degradation over time appears on the polarization behavior, since electrode morphology strongly affects the
polarization. The electrode reaction is believed to occur at a line on the three phase interface, gas/electrode/electrolyte. Therefore an electrode structure that has a long three phase line and a preparation method for such a structure are important.

An extension of effective reaction zone around the line is also important knowledge for the determination of electrode thickness. However, the number of studies concerned with the extension has been very few. Kleitz et al. (7) recently discussed the extension of the reaction zone over solid electrolyte surface and Pt/YSZ and Ag/YSZ interface at the oxygen electrode. They analyzed that some experimental results indicated an extension of the order of 100 μm and others smaller than 1 μm. The extension seems to depend on the oxygen pressure. To evaluate the extension along the electrode surface, it is useful to investigate the effect of the electrode thickness on the polarization. Mizusaki et al. (8) studied the effect of electrode thickness on the cathodic polarization for O₂, La₀.₆Ca₀.₄MO₃ (M=Mn, Co) (smearred and sintered layer)/YSZ. The extension along the thickness increased with increasing the overvoltage, and the evaluated extension reached 160 μm at the voltage of 150 mV. To evaluate the length of the three phase line at Ni anode, Ni film patterned by micro lithography (5,6) were used. For the study on anode reaction, Ni-YSZ cermet is not suitable for this subject, because it is difficult to make uniform thin layer like 1 or 2 μm due to agglomeration and sintering. Also interpretation of the polarization into an activation term and a concentration one may be difficult since the three phase line of the cermet may grow into the electrode layer. A proper electrode of suitable structure should be used for this subject.

We have used a fixed film electrode (9,10) that is a thin film covered by a porous ceramic layer. It has been confirmed that the fixation is effective to reduce the sintering effect for a cathode Pt film (10) even when the film was as thin as 0.5 μm. Since the thickness of the film electrode and that of the porous ceramic layer on it can be changed independently, this fixed film electrode was expected to be useful in the experiment.

In this paper, effects of the thickness of Ni film and that of the porous ceramic layer on the anode polarization were measured by using the fixed film electrode and the extension of the reaction zone around the three phase interface are discussed. Polarization characteristics at different partial pressure of H₂ and H₂O were also investigated.
EXPERIMENTAL

Fixed film electrode and the fuel cells

Figure 1 shows the configuration of the fixed film electrode used in this experiment. A 3 mol %-yttria partially stabilized-zirconia (PSZ) disk of 25 mm diam. and 200 μm thick (Nippon Syokubai Co., Ltd.) was used as the solid electrode. On a surface of the disk, Ni film was deposited in a rectangle (5 mm x 10 mm) by using sputtering technique, and almost 90 % of the film was covered with a porous ceramics layer plasma-sprayed as shown in the figure. The material plasma-sprayed was 8 mol %-yttria stabilized-zirconia powder. A narrowly cut Pt-mesh was put on the uncovered surface of the Ni film (see Fig. 1), which was fixed with a ceramic bond. This Pt-mesh was used as a current collector. A small amount of Pt paste was fastened on the mesh to achieve good electrical contact. On another surface, a fixed electrode of Pt film was also made in the similar manner. A small Pt electrode was set at the periphery and used as a reference.

The thickness of Ni prepared was from 0.8 μm to 12.9 μm and that of the ceramic layer was from nil to 207 μm. On the other hand, all Pt films and their ceramic layers were 1 μm and 50 μm in thickness, respectively.

The cell was set between the mullite tubes that was horizontally arranged in an electric furnace. At the start up, it was heated up to 1273 K in air and kept for 2h. After that, H2-H2O-N2 gas mixtures were let flow to the chamber of the Ni electrode and air to another chamber of Pt electrode. The anode chamber was sealed with a glass ring. The Ni film was considered to be partially oxidized to NiO so that the fuel cell is described as follows.

H2-H2O-N2, (Porous layer), Ni (NiO) / PSZ / Pt, (Porous layer), Air

The partial pressure of H2, PH2, was controlled in the range from 3 kPa to 100 kPa by changing the flow rate of H2 to that of N2 and measured by a FID gas chromatography. Whereas the partial pressure of water, PH2O, was set between 1 kPa and 30 kPa by controlling the temperature of the bath for water vapor saturation. The reference electrode was measured at almost 3 mm above the Ni electrode by using a thermocouple.

Electrochemical measurements

Electrochemical measurements of the electrode impedance and the dc-polarization were conducted using a three-terminal method. The impedance measurement was made with a frequency response analyzer (Model-5020, NF Circuit Co., Ltd.) and a
potentiostat (HA-301, Hokutodenko Co., Ltd.) applying sinusoidal waves with 10 mV peak in the frequency range from 10 mHz to 20 kHz. A current interruption method was used for the dc polarization measurement with a system of a current pulse generator (HC-111, Hokutodenko Co., Ltd.) and transient converter (TCC-DG-8000E, Riken Denshi Co., Ltd.) which was on line with a computer. Voltage drop at 1 or 2 μs later from the current interruption was calculated as the polarization. Most of the measurements were carried out around 1273 K.

The area of Ni film deposited (5 mm x 10 mm) was regarded as the effective electrode area in the calculation of impedance and polarization shown below.

RESULTS AND DISCUSSION

Effect of porous ceramic layer

As shown below, maximum current densities of over 800 mA/cm² were obtained from the fuel cells. This assured that the area of Ni film that was covered by the porous ceramic layer played a role as the electrode. If the maximum current had been brought from the uncovered area (1 mm x 5 mm) of Ni film, the solid electrolyte should have had a smaller ohmic resistance than theoretical.

Figure 2 shows the impedance plots obtained for Ni 2 μm anode with various porous ceramic-layers of different thicknesses. One depressed semicircle was obtained from the Ni film which did not have a porous ceramic on it. Second semicircle appeared at the low frequency side of the plots for the Ni film which had the porous layer. The magnitude of the second semicircle increased with increasing thickness of the porous layer, while that of the first semicircle was almost the same. An interface resistance $R_1$ was obtained from the figure as the length of the real axis cut by the semicircle. Figure 3 shows relation between $R_1$ and the thickness of the ceramic layer. $R_1$ increased linearly with increasing thickness of the porous layer. Here we can divide $R_1$ into two: $R_1$ that was not affected by the thickness of the ceramic layer and $R_2$ that is proportional to the thickness. $R_1$ and $R_2$ correspond to the resistance of the first and the second semicircle in Fig. 2, respectively. $R_2$ was attributed to diffusion resistance of $P_{\text{H}_2\text{O}}$ through the porous layer on the basis of its $P_{\text{H}_2\text{O}}$ dependence that is mentioned later in this paper. Therefore, $R_1$ is the resistance that can be attributed to a process around electrode/electrolyte interface and/or through the Ni film. On the basis of the relation of Fig. 2, the following equations were derived

\[
R_1 = R_1 + R_2 \\
R_2 = k \delta_c
\]
where \( k \) is a constant determined by the porosity of the porous ceramic-layer and \( \delta_c \) is the thickness. \( k \) was determined as 0.016 \( \Omega \text{ cm}^2/\mu\text{m} \) from the figure. \( R_1 \) and \( R_2 \) were calculated from \( R_i \) by using these equations when \( P_{\text{H}_2\text{O}} \) was the same as that of Fig. 2. On the other hand, \( R_1 \) and \( R_2 \) were evaluated by dividing \( R_i \) into two from the shape of overlapping semicircles when \( P_{\text{H}_2\text{O}} \) was not the same as that of Fig. 2.

Figure 4 shows current-voltage curves for Ni 2 \( \mu\text{m} \) anodes covered with a layer of different thicknesses. IR drop was removed from the voltage. We can not find clear dependence of the ceramic layer thickness in the curves. This suggests that concentration polarization by the ceramic layer was negligibly small in the dc polarization in this experiment. If the \( \text{H}_2\text{O} \) diffusion through the ceramic layer that was detected in the impedance plots of Fig. 2 reflected the diffusion of produced \( \text{H}_2\text{O} \) at the three phase line to outside the porous layer, effect of the ceramic layer thickness on the polarization ought to be expected. However we can not see the effect in Fig. 4.

**Effect of Ni film thickness**

Figure 5 shows relation between \( R_1 \) and the Ni film thickness for all electrodes used in this experiment, where \( R_1 \) was calculated by using eqs. [1] and [2]. The trend has been that with an increase in the Ni thickness, \( R_1 \) was almost constant between 1 and 2 \( \Omega\text{ cm}^2 \) and independent of the Ni thickness. Unevenness in the data may be caused by difference in the coefficient of eq. [2] for the ceramic layers prepared by different lots of the plasma spray. From this figure, we can say that the extension that is less than 1 \( \mu\text{m} \) from the electrode/electrolyte interface is important for the electrode impedance at the anode. Figure 6 shows the IR free i-V curves obtained for the fuel cells of different Ni thickness. All i-V curves agreed with each other irrespective of the Ni thickness. This suggests that the extension of the reaction zone was independent also of current density in the range of this experiment. We can conclude that the extension of the effective reaction zone is very small that is less than 1 \( \mu\text{m} \), and that is independent of the current density.

**Effect of partial pressure of \( \text{H}_2 \) and \( \text{H}_2\text{O} \)**

Figure 7 shows effect of partial pressure of hydrogen, \( P_{\text{H}_2} \), on \( R_1 \) at 1270 K. The interface resistance \( R_1 \) was hardly affected by \( P_{\text{H}_2} \) in the range from 3 kPa to 100 kPa at 1270 K. Since also the shape of the impedance plot was not affected by \( P_{\text{H}_2} \), we can say \( R_1 \) was not affected by \( P_{\text{H}_2} \) in the range.
Figure 8 shows effect of partial pressure of H2O, $P_{H2O}$, on the interface resistance. Since the ceramic layer of the electrode was relatively thick, 94 μm, separation of $R_1$ and $R_2$ from $R_i$ was easy. The interface resistance decreased with increasing $P_{H2O}$. The order of $P_{H2O}$ dependence on the resistance was -1/2 for $R_1$ and -1 for $R_2$. -1 dependence on $P_{H2O}$ in addition to the linear dependence on the ceramic layer thickness as shown in Fig. 3 suggests that $R_2$ can be attributed to diffusion of H2O through the ceramic layer. The direction of the diffusion is considered to be that from the outside to inside of the porous ceramics as pointed out above. Therefore the process for $R_1$ is considered to be an activation process but not a diffusion process.

$P_{H2O}$ and $P_{H2}$ dependencies on $R_1$ shown in Figs. 7 and 8 agreed with that obtained as an electrode interface conductivity by a Ni pattern electrode at 973 K (5). Therefore the rate determining process caused around the electrode/electrolyte interface of the fixed film electrode was considered to be the same as that caused by the Ni pattern electrode.

Figure 9 shows $P_{H2}$ dependence on the IR free i-V curves at 1274 K. Larger open circuit voltage was obtained at higher $P_{H2}$ as expected from the Nernst equation. Although the open circuit voltage were different at each $P_{H2}$, the shape of the curves were similar except for the range of high current-density at $P_{H2} = 12$ kPa. Limiting currents were observed at the range when $P_{H2}$ was as low as 12 kPa. Figure 10 shows $P_{H2O}$ dependence on the IR free i-V curves at 1271 K. The larger the $P_{H2O}$, the more sharp drop of potential near i=0 was obtained, while the slope of the curve at high current density was almost the same. Similar results have been obtained by using Ni-YSZ cermet (4) and the Ni pattern electrode (5). This indicates that the rate determining process for the different type of Ni electrode was the same. As to the reaction kinetics around the three phase line, Mizusaki et al. (5) explained the results by the reaction of H2 gas and the adsorbed oxygen on the Ni surface as the rate determining process. Such a rate determining process should occur at a very narrow zone of less than 1 μm on the Ni surface around the three phase line on the bases of our results.

CONCLUSIONS

Effect of the porous ceramic layer appeared on the electrode impedance but not on the dc polarization. On the other hand, effect of the Ni film thickness did not appear to both of them. An activation process is important for the anodic polarization but not the diffusion one. Effective reaction zone for the rate determining process is determined less than 1 μm along the Ni thickness from the electrode/electrolyte interface. The second semicircle appeared at low frequency side of the impedance plot was attributed to the diffusion of H2O to the reaction zone through the porous ceramic layer.
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Figure 1. Configuration of the cell with the fixed film electrodes.

Figure 2. Effect of the porous ceramic-layer thickness on the electrode impedance at H₂-H₂O atmosphere of 1273 K.

Figure 3. Relation between the interface resistance $R_i$ and the thickness of the porous ceramic layer.

Figure 4. Current-voltage curves (IR free) at 1273 K for the anodes of Ni 2 µm that covered by the porous ceramic layer of different thickness.
Figure 5  Relation between the interface resistance $R_j$ and the Ni film thickness at H$_2$-H$_2$O atmosphere of 1273 K.

Figure 6  Current-voltage curves (IR free) of the fuel cells that Ni film thickness was different.

Figure 7  Relation between the partial pressure of H$_2$ and the interface resistance $R_j$ obtained by the fixed Ni electrodes.

Figure 8  Effect of partial pressure of H$_2$O on the interface resistances $R_1$ and $R_2$ obtained by the fixed Ni electrodes.
Figure 9: Current-voltage curves (IR free) for the fixed Ni electrodes obtained at different partial pressure of H₂.

Figure 10: Current-voltage curves (IR free) for the fixed Ni electrodes obtained at different partial pressure of H₂O.