EFFECT OF IONIC-CONDUCTIVITY OF ZIRCONIA IN Ni-ZIRCONIA CERMET ANODE ON ITS PERFORMANCE

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ABSTRACT

The polarization behavior of the Ni-zirconia cermet on 3 mol% yttria-doped zirconia electrolyte (3Y-electrolyte) is affected by the ionic conductivity of zirconia in the cermet. To study the cause of this effect, an experiment was carried out using the same cermets but another electrolyte: 8 mol% yttria-doped zirconia (8Y-electrolyte). The experimental results showed that there was no big difference in the polarization behavior among the cermets on 8Y-electrolyte contrary to the previous results with 3Y-electrolyte. The inconsistency between these experiments with different electrolytes suggests that the extension of the active three-phase zone into the cermet was negligible.

INTRODUCTION

In the development of solid oxide fuel cells (SOFCs), design of electrode microstructure for low overpotential is one of the important technologies. A quantitative analysis of the reaction zone in an electrode may provide effective strategies for improvement in its design. Ni-zirconia cermet has been widely used as anode material of SOFCs. The cermet is usually used to stabilize the Ni particle dispersion and to moderate the mismatch of the thermal expansion coefficients between Ni and zirconia. Also an extension of the active three phase zone into the cermet layer has been mentioned, since an additional three-phase zone forms in a porous cermet with ion-conductive zirconia like yttria stabilized zirconia (YSZ). However, the extension of the three-phase zone in the cermet has not yet been quantified.

To quantify the extension of the active three phase zone into a Ni-zirconia cermet from the electrode/electrolyte interface, we have investigated the effect of ionic conductivity of zirconia in the cermet on the polarization behavior using 3 mol% Y2O3 doped zirconia as electrolyte (1). It was found that the electrode impedance and the dc polarization decreased with increasing ionic conductivity of zirconia in the cermet. From the results, a calculation was attempted to estimate the amount of active three-phase zone additionally formed assuming that the increase was due to the enlargement of the active three-phase zone into the cermet layer. This effect may be due to following two reasons. One is the enlargement of the active three-phase zone into the cermet layer resulting from an increase of the ionic path length. Another is due to catalytic effect of the zirconia on
the electrode reaction. However, the experiment was carried out using only one electrolyte and we have no idea about the case with different electrolytes. We have now carried out similar experiment with another solid electrolyte, 8 mol% yttria stabilized zirconia electrolyte (8Y-electrolyte). In this paper, we describe the experimental results and discuss the cause of the effect of the ionic conductivity of zirconia on the polarization behavior by comparing the results with that from 3 mol% yttria stabilized zirconia electrolyte (3Y-electrolyte).

EXPERIMENTAL

The experimental procedure was similar to that of the previous one (1) except that 8 mol% Y2O3 doped zirconia electrolyte was used.

The Ni-zirconia cermets were prepared from NiO powder (Wako Pure Chemical Industries, Limited) and yttria-doped zirconia powders with 0, 3, 6 and 8 mol% yttria contents (Tosoh TZ0, TZ3Y, TZ6Y and TZ8Y, respectively). Hereafter, we designate these zirconia powders as 0Y, 3Y, 6Y and 8Y, respectively, and the Ni-zirconia cermets with each zirconia powder as 0Y-cermet, 3Y-cermet, and so on.

The properties of the zirconia powders, i.e., impurities, specific surface area and particle density, were almost the same except for the yttria content. As is well known, the ionic conductivity increases with increasing yttria content in this range. The zirconia powder with 0 mol% yttria undergoes a volumetric change at around 1300 K due to a change of crystal phase between monoclinic and tetragonal and this may give rise to a difference in the microstructure of the cermet compared to other cermets. However, 0Y-cermet was used as the reference.

The NiO and the zirconia powder were weighed in a volumetric ratio of Ni : zirconia equal to 50 : 50 and were mixed with a high-speed vibrating mill. The mixed powder was preheated at 1673 K for 4 h in air and then ground to obtain the raw cermet powders with similar particle size distribution. The raw cermet powders were the same as that used in the previous experiment. Similar dispersion of NiO and similar particle size distribution with average size of 1μm in every powder were observed as shown in the previous report (1).

The raw cermet powder was coated on the surface of a solid electrolyte disk with 25 mm diam and 200 μm thickness. The solid electrolyte was 8 mol% yttria stabilized zirconia, 8Y-electrolyte. The coated disk was then baked at 1673 K for 4 h in air so that the coated layer could be used as the Ni-zirconia cermet anode. On another surface and at the periphery, Pt paste was coated and baked at 1273 K for 1 h and used as the cathode and the reference, respectively.

The cell was set in a high-temperature fuel cell setup and the electrode impedance and the anodic dc polarization were measured in an H2-H2O gas mixture at 1073 – 1273 K.
RESULTS AND DISCUSSION

Microstructure of the Cermet Electrode

In this study, a similar microstructure for all cerments was important because the microstructure affects the polarization behavior. Figure 1 shows SEM photographs of the typical cross sectional view of the cerments used. The structure of the porous layer and the interface between the cermet and the electrolyte looks similar in the microscopic view. The porosity and other properties for the cermet obtained from the SEM observation are listed in Table 1. The porosity of each cermet was between 0.42 and 0.45.

Effect of Zirconia in the Cermet on the Electrode Performance

Figures 2 and 3 show the electrode impedance plots obtained for the cermet electrodes with different zirconias at 1073 K and 1273 K, respectively. A single depressed semicircle was obtained for each cermet. The semicircle for 0Y-cermet was far larger than that for the others. An interfacial conductivity, 1/Ri, between the cermet layer and the 8Y-electrolyte was calculated as the length of the real axis intersected by the semicircle. Figure 4 shows the relationship between the interfacial conductivity and the ionic conductivity of zirconia in the cermet. The value of the ionic conductivity was measured for a sintered pellet (3). The interfacial conductivity for 0Y-cermet was far smaller than that of the others. This may result from the volumetric change in zirconia due to the crystal phase change. Therefore, the results of 0Y-cermet are ignored in the following discussion. A trend seen in this figure is that the interfacial conductivity was almost the same among the cerments and not affected by the ionic conductivity of zirconia.

Figure 5 shows the Tafel plot of the anodic currents for the cermet electrodes at 1273 K. The curves of the anodic currents for the 3Y-, 6Y-, and 8Y-cermets on 8Y-electrolyte were almost similar to each other. To compare the overpotential characteristics quantitatively, the kinetic parameters for the Tafel equation, following Kawada’s equation (2) which was proposed for Ni-zirconia cermet anode empirically, were calculated from a curve fitting and are listed in Table 2.

\[ i_a = k \exp\left(\frac{2F\eta_a}{RT}\right) - \exp\left(-\frac{F\eta_a}{RT}\right) \]

where \( k \) is a constant, \( \eta_a \) is the anodic overpotential, and \( F, R \) and \( T \) represent the usual meanings, respectively. In the table, the parameters obtained from the cerments on 3Y-electrolyte from the previous experiment (1) are also included for comparison.

In the fitting of Tafel equation, the slope of the straight line was weakly affected by the current range. For the 3Y-, 6Y-, and 8Y-cermets on 8Y-electrolyte, however, it was found that the value of parameter was nearly the same among these cerments. The exchange current density, \( i_0 \), was within 30 to 50 and \( n\alpha \), the product of number of electron, \( n \), and the transfer coefficient, \( \alpha \), was between 3 and 4. This suggests that the
ionic conductivity of zirconia in the cermet did not influence the dc overpotential in the electrode system. However, this did not agree with the result, obtained from the 3Y-electrolyte system, that $i_0$ increased with increasing ionic conductivity from 30 to 90 keeping $n\alpha$ at 2.2. The difference in the value of $n\alpha$ between the cermet on 3Y-electrolyte and that on 8Y-electrolyte may suggest a difference in the reaction mechanism. By replotting a straight line for the 8Y-cermet/3Y-electrolyte, the overpotential curve could be characterized by $n\alpha = 3.5$ and $i_0 = 37 \text{mA/cm}^2$ that are almost similar to that obtained from 8Y-electrolyte.

On the other hand, Kawada’s equation could be fitted to the curves well in the range below 500mA/cm$^2$ for every cermet except 0Y-cermet in the table. The constant $k$ for the cermet on 8Y-electrolyte was around 90 and it was similar to that for 8Y-cermet/3Y-electrolyte. From Table 2, we may say that the rate constant for the anodic current was almost the same among the cermets on 8Y-electrolyte and the value was similar to that for 8Y-cermet on 3Y-electrolyte previously obtained.

Figure 6 shows a comparison of the trend shown in Figure 4 with that of the cermet electrodes on 3Y-electrolyte obtained previously (1). In the case of the cermet on 3Y-electrolyte, the interfacial conductivity increased with increasing ionic conductivity of zirconia in the cermet. In contrast, it was almost constant for the cermets on 8Y-electrolyte. The trend in the interfacial conductivity for the cermets on 3Y-electrolyte and 8Y-electrolyte agreed with that in the kinetic parameter $i_0$ and $k$ shown in Table 2. If the ionic path length into the cermet layer is substantially increased with increasing ionic conductivity of zirconia, the interfacial conductivity and the kinetic parameters should increase not only in the case of 3Y-electrolyte but also for 8Y-electrolyte. However the experimental results were not so. This fact suggests that the increase in the interfacial conductivity in the 3Y-electrolyte system was not due to the conductive effect. The results in those experiments may be interpreted by a catalytic effect of zirconia on the electrode reaction. It has been reported that the overpotential at the Pt- and ceria-based anodes decreases with increasing ionic conductivity of the zirconia electrolyte (3, 4). This suggests that zirconia influences the activity of the electrochemical reaction and it becomes higher with the ionic conductivity. In our experiments, zirconia in both the cermet and the electrolyte at the electrode/electrolyte interface may have a chance to act as a catalyst for the electrode reaction. If zirconia with higher ionic conductivity dominates the catalytic activity, the results shown in Fig. 6 and Table 2 may be explained by the catalytic effect. Namely, the zirconia powders with higher conductivity than that of 3Y-electrolyte dominate the activity at the 3Y-electrolyte system; on the other hand 8Y-electrolyte with largest conductivity dominate the activity at the 8Y-electrolyte system.

**SUMMARY**

Effect of ionic conductivity of zirconia in a Ni-zirconia cermet anode on the polarization behavior was investigated with 0Y-, 3Y-, 6Y- and 8Y-cermets and 8Y-zirconia as electrolyte. The interfacial conductivity and the dc polarization for the 3Y-, 6Y- and 8Y-cermets were similar to each other. This result did not agree with that of the

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cermets on 3Y-zirconia electrolyte. The inconsistency of the trends between 3Y- and 8Y-zirconia electrolyte systems suggests that the extension of the active three-phase zone into the cermet by the zirconia powder was negligible.

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Figure 1 SEM photographs of the cross sections of each cermet electrode on 8Y-electrolyte: (a) 0Y-cermet, (b) 3Y-cermet, (c) 6Y-cermet, and (d) 8Y-cermet.
Table 1 Properties of the cermet electrodes prepared on the 8Y-electrolyte

| Type     | Thickness [μm] | Weight [mg] | Bulk density [g/cm³] | Porosity [-] |
|----------|----------------|-------------|----------------------|--------------|
| 0Y-cermet| $1.6 \times 10^2$ | 34.0        | 4.3                  | 0.42         |
| 3Y-cermet| $1.6 \times 10^2$ | 32.2        | 4.1                  | 0.44         |
| 6Y-cermet| $1.4 \times 10^2$ | 27.9        | 4.0                  | 0.45         |
| 8Y-cermet| $1.7 \times 10^2$ | 35.5        | 4.2                  | 0.42         |

Figure 2 Electrode impedance plots obtained for the cermet electrodes with different zirconias at 1075K.

Figure 2 Electrode impedance plots obtained for the cermet electrodes with different zirconias at 1273 K.
Figure 4 Relationships between the ionic conductivity of zirconia in the Ni-zirconia cermet and the interfacial conductivity.

Figure 5 Tafel plot of the anodic currents obtained from the cermet on 8Y-electrolyte at 1273K
Table 2 Kinetic parameters obtained for the anodic current at 1273 K

| Electrode         | Tafel equation | Kawada's equation |
|-------------------|----------------|-------------------|
|                   | nα  | i₀ (mA/cm²) | K (mA/cm²) |
| 0Y-cermet/8Y-electrolyte | -   | -              | -          |
| 3Y-cermet/        | 3  ~ 4 | 30.0 ~ 36.6 | 85         |
| 6Y-cermet/        | 3  ~ 4 | 33.1 ~ 49.4 | 98         |
| 8Y-cermet/        | 3  ~ 4 | 30.0 ~ 35.2 | 85         |
| 0Y-cermet/3Y-electrolyte | 2.2 | 28.5         | 43         |
| 3Y-cermet/        | 2.2 | 35.2         | 53         |
| 6Y-cermet/        | 2.2 | 48.9         | 73         |
| 8Y-cermet/        | 2.2(3.5) | 90.0(36.6) | 92         |

Figure 6 Comparison of the interfacial conductivity of Ni-zirconia cermet on 8Y-electrolyte with that on 3Y-electrolyte (1).