PERFORMANCE OF YSZ-SUPPORTED ANODE FOR SOFC SUBSTRATES

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ABSTRACT

Anode-supported SOFCs have better power output and long-term stability under high electric current flow. YSZ-supported anodes with a novel microstructure, consisting of nickel, coarse YSZ and fine YSZ powders, have been found to have good long-term stability. To use such materials for the substrate of anode-supported SOFCs, changes in the dimensional stability of the substrates were investigated under cell operation atmosphere, and three kinds of single cells using three different anodes were prepared and examined. Anode-supported SOFC using a substrate with high porosity showed better performance than that with low porosity.

INTRODUCTION

Solid oxide fuel cells (SOFCs) have been attracting interest because of their high efficiency, low emissions, large selectivity of electric generation capacity, and so on. To use SOFCs for practical applications, it is necessary to both reduce fabrication costs (1) and to achieve higher and more stable levels of generating performance. Recently, anode-supported SOFCs have attracted attention in expectation of achieving higher electric power, even at lower operating temperatures, and because of their high mechanical strength, and are being proposed and developed by many research and development institutes and/or companies (2, 3). Authors are also developing anode...
supported SOFCs using single cells with an interconnect layer (4), as shown in Figure 1, for operation at a higher temperature. It has been confirmed that such single cells show a high electric power generation property and excellent stability under high current density during long term operation (5), with the cell reaching approximately 2.25 A/cm² of current density at 0.60 V.

Anode-supported SOFCs generally use porous substrates made of a cermet of nickel (Ni) and yttria stabilized zirconia (YSZ). The authors have proposed a new concept concerning the microstructure of anodes, referred to as “YSZ-supported anodes”, to solve anode problems (6-8). Features of this concept are that YSZ powders are divided into two kinds, coarse and fine particles, and the YSZ framework is formed from both the coarse and the fine YSZ particles. Single cells with such YSZ-supported anodes exhibit improved long-term stability. To determine the optimal mixture and particle size ratios for the three powders in the anodes (Ni, coarse YSZ and fine YSZ), the changes and differences in dimensional stability, electrical conductivity and electrode characteristics were investigated under both cell fabrication and cell operation atmospheres. These results suggest a suitable range for the mixture and particle size ratios of the three powders for SOFCs (9, 10).

Consequently, it is believed that the anode-supported SOFCs would achieve higher performance if these two concepts for the construction of SOFC and anode materials were combined. Therefore, to evaluate the dimensional properties of the substrates and performance of the cells, three kinds of anodes were selected to prepare the substrate for single cell fabrication. In this paper, experimental results are discussed concerning the changes in the dimensional stability for the anode substrates under cell operation atmospheres. Furthermore, to compare and clarify performance of the anodes, three single cells using three different YSZ-supported anodes were fabricated, and their current density-cell voltage characteristics and anodic properties were measured.

EXPERIMENTAL

Sample Preparation

Three anodes were examined in this study, 4-6-1, 4-6-2 and 5-5-1, expressed by weight ratios in the form x-y-z for the coarse YSZ, the NiO, and the fine YSZ, respectively. Details of the preparation procedure for sample anode powders have been described elsewhere (6,7). For the reduction tests and measurement of substrate performance for single cells, the anode powders were molded into a pellet at about 10 MPa and sintered at 1673 K for 10 h in air. The preparation procedure for the anode-supported cells is shown in Figure 2. The porous anode substrates were adapted to the anode-supported cells without the interconnecting layer. The YSZ (TZ-8Y, Tosoh) electrolyte layer was fabricated by slurry coating onto the anode substrate and fired at 1673 K several times. The lanthanum manganite cathode powder, (La0.8Sm0.2)0.97MnO3, with added terpineol, was also slurry coated and baked at 1423 K for 4 h on the YSZ layer with an electrode area of 3.1 cm².

Measurement of Anode Characteristics

For reduction tests, the anode samples were placed in an alumina tube and held at 1273 K for 1 to 375 h in an H2 flow, humidified by water at around 293 K at about 100 cm³/min. The sizes and...
weights of the samples were then measured to derive their linear shrinkages and porosities. In the 
electrochemical measurements, gaseous H₂ humidified by water at 275 to 319 K (300 cm³/min) as 
fuel and air (1200 cm³/min) as oxidant were supplied to the anode and the cathode, respectively. 
The anode and current density-cell voltage characteristics of the cells were measured using an 
impedance/gain phase analyzer (SI 1620, Solartron) and bipolar power supply/amp (BWS 18-15, 
Takasago Ltd.). Data concerning current flow through the cell and steady-state impedance 
spectroscopy were measured simultaneously within conditions of almost open circuit voltage and 
polarization. At least 30 minutes were allowed for stabilization before each impedance run. After 
these measurements, the polished cross sections of the cells were observed with an electron-probe 
micro-analyzer (EPMA, JEOL Ltd., JXA-8900R).

RESULTS AND DISCUSSION

Reduction Test

Configuration stability and compatibility with other components in terms of thermal expansion 
behavior are important factors for SOFC anodes. The thermal expansion behaviors of anodes have 
al ready been investigated (11,12). Shrinkage of an electrode leads to a decrease in the gas 
permeability of the substrate, the occurrence of shear stresses at both the electrolyte/ and 
interconnector/substrate interfaces, and increases in contact resistance between the single cells 
when assembled as a stack. Figure 3 shows the changes in linear shrinkage for three substrates in 
humidified H₂ flow. The shrinkages of all samples, though 4-6-1 shrank the most of all, were 
little less than 0.5% after 375 hours. Therefore, it seems that the shrinkage of substrate under 
operation atmosphere has negligible effect on the cell performance.

Porosity of electrode is also an important factor, because of its effect on gas permeation, since low 
permeability can give rise to increases in overpotential related to gaseous diffusion. Figure 4
Figure 3. Change in linear shrinkage for anode substrates under experimental conditions.

shows the changes in porosity for sample substrates as a function of retention time in the reduction atmosphere at 1273 K. The porosities of all samples increased during the initial 50 h by approximately 15%. This phenomenon is accompanied by reduction of NiO to Ni with a simultaneous decrease in the volume and a strong agglomeration of Ni particles. However, all three samples did not show any change after the initial increase due to stabilization of the anode framework by both the coarse and fine YSZ. It was found that the porosity for the 4-6-2 anodes was about 30%, that is the smallest, because of the highest fine YSZ content of all the anodes in this study.

Figure 4. Change in porosity for anode substrates under experimental conditions.

Cell Performance

The polished cross section of the cell using the 4-6-1 anode substrate after the performance test is shown in Figure 5. It was confirmed that the YSZ layer with some closed pores was about 10 µm thick and that the microstructure of the anode substrate was similar to our previous studies (5).
Figure 5. Polished cross-section of single cell with 4-6-1 anode substrate after performance test.

Figure 6 shows current density-cell voltage characteristics for the respective cells in operation condition for about 50 h. Their open circuit voltages attained theoretical value (about 1.04 V); therefore, it seems that the YSZ electrolyte was gas-tight. Note that the performances of cells with the 4-6-1 and 5-5-1 anode substrates are similar, approximately 1.60 A/cm² current density at 0.60 V, and higher than that of the cell with the 4-6-2 substrate. It would appear that the electric power generation property of the anode-supported SOFC was affected by the porosity of the anode substrate, with a threshold at around 35% in porosity.

The AC impedance measurements were also conducted simultaneously in these experiments on each cell. The complex impedance plots of the cell using the 4-6-1 anode substrate at two fuel conditions are shown in Figure 7; one with humidified 100% H₂ as fuel, another with humidified 10% H₂ + 90% N₂. It can be seen that each plot consists of at least two semicircles. The length...
between the imaginary axis and the intersection of the semicircle on the highest frequency side means an ohmic resistance, which is related to that of the electrolyte. It can be seen also that the lengths to the intersections and the size of the first semicircle did not show any remarkable difference when the gaseous fuel was changed. On the contrary, the intersection of the secondary semicircle increased when H₂ content in the fuel was decreased. Therefore, it could be inferred that the secondary semicircle was basically related to anode reaction because its size was influenced by the atmosphere on anode side. Other cells using 4-6-2 and 5-5-1 substrates showed similar behavior.

Figure 8 shows overpotential plots with respect to the current density that were related to the first and second semicircle, respectively. These plots were obtained from the AC impedance measurements for all sample cells. Overpotentials related to the first semicircle for all cells were found to increase gradually with increased current density, and the tendency of all sample cells was to become similar. Concerning the second semicircles, it could be seen that the overpotentials for all sample cells became higher with increased current density. However, it was obvious that the overpotential for 4-6-2 was different than for 4-6-1 and 5-5-1; the value of 4-6-2 was higher than the others at the same current density, while it was hard to distinguish 4-6-1 from 5-5-1.

![Figure 7. Complex impedance plots for single cell using 4-6-1 anode at two fuel conditions.](image)

![Figure 8. Change in polarization behavior of the single cells.](image)
Because the shrinkage of all the substrates was slightly below 0.5%, it would appear that the anode performance had no dependency on the shrinkage. However, the substrates had different porosities; porosities of 4-6-1, 5-5-1 and 4-6-2 were about 43, 35 and 31%, respectively. From our results, it would be surmised that porosity of the anode substrate is important to achieve higher cell performance, especially if the porosity of the substrate is above about 35%.

SUMMARY

The present study has revealed that the microstructure of YSZ-supported anodes and their electrode characteristics correlate to each other, especially when the anodes are used as substrates for anode-supported SOFCs. Three kinds of YSZ-supported anodes were investigated concerning changes in dimensional stability, which are shrinkage and porosity, in the reduction tests. Furthermore, three kinds of single cells using these materials for SOFC substrates were fabricated and were simultaneously tested for their electric power characteristics and anodic properties under the generating test.

From results of the reduction test, porosity for the YSZ-supported anodes became greater without linear shrinkage during the initial 50 h and then became constant. Since the difference in anode substrates was basically porosity, it would appear that the difference was related to fine YSZ content in the YSZ-supported anodes, because the substrate with the highest fine YSZ content showed lowest porosity. Slight change in linear shrinkage could be attributed to the framework made of both the coarse and the fine YSZ powders in the substrate preparation. Concerning the generating test, all single cells showed similar performance in the region of low current density, but the cells using substrates with high porosity, above 35.0%, showed better electric generation performance, even when the current density was increased. It would appear that the anode polarization phenomena are strongly affected by the content of the fine YSZ, which affects the microstructure.

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