PERFORMANCE OF SOLID OXIDE FUEL CELLS WITH
CONTROLLED MICROSTRUCTURE OF ANODE SUBSTRATE

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ABSTRACT

Solid oxide fuel cells (SOFCs) have been developed while pursuing low production cost and high performance with anode-supported planar type single cells at Korea Electric Power Research Institute. Anode-supported single cells have been manufactured by press molding, screen printing, and co-firing. They have been formed in the size 5 x 5 cm² and about 1.8 mm thick. The structure of anode-supported planar cells was used to investigate internal resistance and anode polarization resistance for improved performance. In our study, an important factor for determining cell performance was found to be the anode raw material quality assurance. The manufactured cells were evaluated on the basis of their microstructure and electrochemical performance. We have significantly improved cell performance during the past few years.

INTRODUCTION

Solid oxide fuel cells (SOFCs) are considered to be one of the most important alternative sources for generating electric power in the future because of their high conversion efficiency and environmental compatibility. There are two basic design variations in planar-type SOFCs. The electrolyte-supported SOFC is composed of an electrolyte made of 8YSZ with a thickness of about 150 μm and electrodes deposited via a screen printing method with an average thickness of about 50 μm on each side. The anode-supported SOFC has an electrolyte (5~20 μm) deposited on top of the anode substrate by various coating methods. The cathode is deposited by the same technique as the electrolyte. The advanced technology in the anode-supported planar SOFC is the processing method of the anode substrate.

In general, the principal components of a SOFC cell are the electrolyte, anode, and cathode. Each component serves several functions in the cell and must meet certain requirements. The main function of the electrolyte is to conduct ions between anode and cathode, and the cathode's function is to provide reaction sites for the electrochemical reduction of an oxidant. It is particularly important to understand in detail the electrode reaction on the anode side. The SOFC anode providing reaction sites for electrochemical oxidation of the fuel must have sufficient electronic conductivity for electron flow at the operating temperature in the reducing environment (1). In general, the maximum possible anode conductivity is desirable to minimize ohmic losses. At the same time, the anode must be porous enough to allow gas transport to the reaction sites.
The characteristics and stability of the anode microstructure are known to significantly affect electrode electrochemical performance. The anode must maintain its dimensions and desired microstructure in a hydrogen atmosphere over long-term operation because significant structural changes can cause degradation in cell performance and mechanical integrity (2,3).

Nickel (Ni) and yttria stabilized zirconia (YSZ) cermet has been used as the anode material for SOFCs because Ni offers electronic conductivity and YSZ ionic conductivity (1,4). The anode reaction mechanism strongly depends on the contact of metallic Ni, YSZ ceramic, and pores at the three-phase boundary (TPB). Therefore, the microstructure and composition of the anode substrate could influence electrochemical activity.

In this study, we investigated the performance of SOFCs and the effect of NiO/YSZ composition ratio, the volume, and the average particle size of graphite that is added as a pore former to obtain a large amount of TPB and sufficient gas transport. We were able to optimize the performance of the anode substrate.

**EXPERIMENTS**

**Fabrication of Samples**

Commercial powders of nickel oxide and 8 mol% Y_2O_3 stabilized ZrO_2 (8 YSZ, Tosoh TZ-8YS) were used as raw materials to produce the anode substrate. The materials were mixed by a milling process with a weight ratio of NiO/YSZ=6:4, 5.5:4.5, 5:5 and 4.5:5.5. Subsequently, graphite powders, which provide additional porosity, organic binders, and ethyl alcohol, were added to the powder mixture and the mixture dried in an oven. We considered several average particle sizes (44, 75, 150 μm) and volume fractions (18, 24, 30 vol%) of graphite. The anode substrate was made by pressing the powder mixture using a rectangular mold and firing it at 1400°C in air for 1 hr. YSZ was coated on the substrate surface by a slurry coating process and cofired with the anode substrate at 1550°C for 2 hr for densification of YSZ with a thickness of about 20 μm. Through the production step, the cell was designed to form a 5 x 5 cm² cell about 1.8 mm thick. Then they were ground 1.4 mm thick to measure by the cell tester. The (La_0.6Sr_0.4)(Co_0.2Fe_0.8)O_3 mixed with Sm-doped ceria for the intermediate temperature range was deposited on the top of sintered YSZ by screen printing technology. Finally, an active cathode dimension of 0.636 cm² (dia.= 0.9 cm) was accomplished.

**Measurements of Cell Performance**

The performance of anode-supported single cells was evaluated using a cell testing furnace with hydrogen as fuel at 650°C, 700°C, and 750°C, respectively. The output voltage of cells was measured by a digital multimeter. Electrochemical impedance spectroscopy was recorded across the cell.

After the cell test, the microstructure of the anode substrate was investigated with a polished cross-section view observed by optical microscope. Various measurements such as area fraction and average mean diameter were investigated using an image analysis program. To compare with image analysis, the porosity of the samples also was measured using a mercury porosimeter.
RESULTS AND DISCUSSION

Figure 1 shows a cross section view of anode-supported single cell made at our laboratory. The total thickness of this cell was about 1.8 mm and YSZ thickness was about 20 μm. The porosity was estimated to be about 28% by mercury porosimeter. Figure 2 shows a complete single cell with a cathode area of 4.7 x 4.7 cm² and a thickness of about 1.8 mm.

![Figure 1. Micrograph of cross section.](image1)

![Figure 2. Anode-supported single cell.](image2)

**Image Analysis and Porosity**

We used optical microscopy to analyze each phase of images in the Ni-YSZ cermet from an unclear phase boundary. Microstructures like the diameter of the particle and area fraction were investigated. The microstructures shown in Figure 3 suggest that the Ni connectivity increased and Ni distribution was improved with an increase in Ni content. Ni content was important because the connectivity of the Ni phase is an important factor in electron transfer, which directly affects cell performance. A sample of the composition ratio (4.5:5.5) showed a significant reduction in Ni connectivity as well.

![Figure 3. Optical microstructures of Ni/YSZ anode substrates.](image3)

(a) NiO/YSZ=6:4  
(b) NiO/YSZ=5.5:4.5  
(c) NiO/YSZ=5:5  
(d) NiO/YSZ=4.5:5.5
Table 1 shows the average area fraction and mean diameter of pore, Ni, YSZ, and Ni/YSZ ratio by image analysis of various specimens. As NiO content increased, area fraction and average particle size of Ni also increased, but the porosity value stayed the same. The particle size of graphite also affects final porosity. Samples of 44 and 75 μm graphite showed similar porosity but one of 150 μm had slightly higher porosity and possible lower TPB density.

Table 1. Area fraction and diameter of Ni, YSZ and porosity by image analysis and porosity of mercury porosimeter.

| NiO/YSZ ratio | Graphite Volume (%) | Graphite Size (μm) | Ni/YSZ | fra./dia.(Ni) | fra./dia.(YSZ) | fra./dia.(porosity) | porosity of Hg |
|---------------|---------------------|--------------------|--------|---------------|----------------|---------------------|----------------|
| 6:4           | 24                  | 75                 | 1.127  | 39.7/5.1      | 35.2/4.2       | 23.7/4.1            | 28.7           |
| 5.5:4.5       | 24                  | 75                 | 0.938  | 37.2/4.7      | 39.6/4.8       | 23.2/3.9            | 29.2           |
| 4.5:5.5       | 24                  | 75                 | 0.722  | 31.8/4.5      | 44.0/4.8       | 25.8/4.1            | 28.4           |

Graphite Size

| Graphite Volume (%) | Graphite Size (μm) | Ni/YSZ | fra./dia.(Ni) | fra./dia.(YSZ) | fra./dia.(porosity) | porosity of Hg |
|---------------------|--------------------|--------|---------------|----------------|---------------------|----------------|
| 5.5                 | 24                 | 75     | 0.652         | 27.3/4.3       | 41.8/5.1            | 25.7/4.4       | 29.8           |
| 5.5                 | 24                 | 150    | 0.722         | 27.9/4.5       | 38.4/4.3            | 36.1/5.2       | 31.9           |
| 5.5                 | 18                 | 75     | 0.889         | 36.8/5.1       | 41.4/4.8            | 22.4/3.7       | 27.5           |
| 5.5                 | 24                 | 75     | 0.722         | 31.8/4.5       | 44.0/4.8            | 25.8/4.1       | 28.4           |
| 5.5                 | 30                 | 75     | 0.789         | 25.7/5.2       | 32.5/5.3            | 40.7/6.2       | 39.8           |

Figure 4 shows optical microstructures for various graphite contents: 18, 24, and 30 vol%. From the results, the anode substrate with 24 vol% graphite had the desired porosity. We detected the appropriate gas transport and Ni/YSZ connectivity for TPB. In this case, the average mean pore diameter was about 4 μm on the anode substrate. We found that the proper porosity was about 28% for optimized performance with 24 vol% and 44 μm graphite. These data tend to have good agreement with the porosity value given by the mercury porosimeter except for the graphite size (150 μm) and volume (30%) added that revealed larger porosity by separating particles from the sample through polishing.

Figure 4. Optical microstructures of anode substrate with various graphite contents (dia. = 75 μm).
Performance of Single Cell

The NiO/YSZ ratio was varied to optimize anode polarization resistance and internal resistance (IR). Figure 5 shows the electrochemical performance of a single cell with hydrogen gas as fuel at 650°C and 700°C operating temperature. Flow rates of hydrogen and air were 100 and 250 scm, respectively, and humidity was 3%. The electrical performance of Ni/YSZ cermet depends strongly on nickel content. Power density increased with increased Ni content. Though an increase in Ni content led to increased anode polarization resistance, it seemed to reduce IR. We considered that Ni connectivity for the electron path directly affects cell performance. Nevertheless, it is known that the ratio (5:5) was optimized, so we concluded that the 6:4 ratio of NiO/YSZ was best for a high-performance cell. We could not find any damage or failure during sintering and cell testing of the anode due to the 6:4 composite ratio. From the results, we see that sufficient porosity and optimized TPB were obtained with average graphite particle size of 44 μm and 24 vol% graphite in the anode substrate. When 18 vol% graphite was added, the lower power density achieved contributed more to TPB density than to IR. Table 2 shows that the average particle size of graphite also was important to obtaining high performance. At 650°C, we obtained maximum power density with a 6:4 ratio of NiO/YSZ, 24 vol% graphite, and 44 μm average particle size.

Figure 5. I-V and I-P performance of a single cell.

![Graphs](a) 650°C (b) 700°C

Table 2. Performance of manufactured cell at 650°C.

| NiO/YSZ ratio | Graphite Volume(%) | Graphite Size(μm) | Pmax | IR  |
|---------------|--------------------|-------------------|------|-----|
| 6:4           | 24                 | 75                | 507  | 0.34|
| NiO/YSZ ratio |                    |                   |      |     |
| 5:5           | 4.5:5.5            | 24                | 396  | 0.44|
| 5:5           | 24                 | 75                | 421  | 0.49|
| 5:5           | 24                 | 150               | 387  | 0.44|
| 5:5           | 18                 | 75                | 377  | 0.45|
| 5:5           | 24                 | 75                | 421  | 0.49|
| 5:5           | 30                 | 75                | 257  | 0.5 |
AC impedance spectroscopy was performed to investigate the influence of the substrate material on the electrochemical reaction for the frequency range $10^{-2}$ to $10^5$ Hz. Figure 6 shows the impedance spectrum of single cells with functions of weight ratio of NiO/YSZ and average particle size of graphite, measured at 650°C with H2 and air at open circuit voltage. Impedance plots showed the existence of two semicircles. In general, the intercept of the left semicircle (high frequency) is attributed to IR, and diameters of the semicircles depend on the polarization resistance of the electrode (5).

Through recorded spectrum, Figure 6 (a) showed a shift to lower IR from the intercept by an increase in Ni content except at composite ratio 5:5. In this result, we suppose that IR and polarization resistance were affected by the NiO/YSZ ratio. Increased Ni content decreased the IR of the cell and increased the polarization resistance of the anode. Table 2 shows the effect of the relation of IR with average particle size of graphite on cell performance. Anode with 44 μm of graphite size has much lower IR than samples with other sizes. Although the anode with 24% graphite volume has higher IR than the 18% sample. Therefore, we concluded that cell performance was more affected by mass transfer and TPB density according to proper graphite volume than IR.

![Figure 6](image.jpg)

**Figure 6.** Impedance characteristics of single cells at 650°C according to (a) weight ratio of NiO/YSZ and (b) added average graphite particle size.

**CONCLUSIONS**

The microstructure of anodes was investigated to optimize TPB for high cell performance because the electrochemical activity of the SOFC depends strongly on microstructure and cell material. Microstructures of anodes were obtained and characterized by image analysis and we confirmed the influence of microstructure on cell performance. Our results showed that an increase in Ni content directly affected cell performance by Ni connectivity for the electron path and reduced IR due to good contact with the electrolyte. Average particle size (44 μm) and volume of graphite (24 vol%) also were important to achieving high performance. We found that the open porosity of the anode substrate was about 28 vol% with average mean pore diameter of 4 μm for improved performance.

Consequently, the cell showed a maximum power density of 507 mW/cm² at 650°C with a 6:4 ratio of Ni/YSZ and 24 vol% and 75 μm average particle diameter of graphite. By controlling the Ni/YSZ composite ratio and graphite volume and average particle size, we were able to significantly improve cell performance.
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