FABRICATION AND CHARACTERISTICS OF ANODE-SUPPORTED TUBE FOR SOLID OXIDE FUEL CELL

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ABSTRACT

As a preliminary experiment for the development of anode-supported tubular cell with proper porosity, we have investigated the anode substrate and the electrolyte-coated anode tube. The anode substrate was manufactured as a function of carbon content in the range of 20 to 50 vol.%. As the carbon content increased, the porosity of the anode substrate increased slightly and the carbon content with proper porosity was obtained at 30 vol.%. The anode tube was fabricated by extrusion process and the electrolyte layer was coated on the anode tube by slurry dipping process. The anode-supported tube was cofired successfully. Their sintered property and microstructure were examined. The porosity of the anode tube was 35%. From the gas permeation test, the anode tube was found to be porous enough for gas supply. On the other hand, the anode-supported tube with electrolyte layer indicated a very low gas permeation rate. This means that the coated electrolyte was dense. Based upon these experimental results, we will fabricate and test the anode-supported tubular cell.

INTRODUCTION

Solid oxide fuel cells (SOFC) have been investigated for a highly efficient and clean power generation system. Several different designs of SOFC are presently under development. The tubular SOFC is the most advanced technology because of advantages of easy sealing between cells, and high resistance to thermal stress. The cathode-supported structure has been developed mainly in the tubular type (1). Recently, in the case of planar design, attention has been given to anode-supported type, which has the advantage of high mechanical strength and easy fabrication with low cost (2). A good performance was obtained from the anode-supported planar cell. The concept of anode supported planar design may be extended to the tubular design to improve the fabrication process and the cell performance.

In this work, we have studied the anode-supported tube to determine the feasibility of anode-supported tubular SOFC. In order to give proper porosity to anode substrate, the...
Carbon powder was added to anode material, and the sintering properties of the anode substrate were examined. Then the anode-supported tube was manufactured by using extrusion process and the electrolyte layer was coated on the tube by slurry dipping process. The gas permeability and microstructures of the anode-supported tube are reported.

**EXPERIMENTAL**

Anode powder was prepared from 8 mol% Y₂O₃-stabilized ZrO₂ (YSZ: Tosoh Co.) and NiO powders. The NiO and 8 mol.% YSZ(NY) powders were weighed in a selected proportion and mixed in ethanol by ball milling for 24 h. The mixture was dried over a hot plate and then heated at 550 °C. The sample was pulverized and heated in air at 1400 °C for 5 h for presintering treatment, which makes the powder stable electrochemically (3). The NY powder had 40 vol.% nickel metal after reduction.

In order to find optimum content of carbon as a pore former, the NiO-8YSZ pellets were prepared using die pressing process as a function of carbon content in the range of 20 to 50 vol.%. After mixing anode and carbon powders with 2 wt.% polyvinylalcohol by high energy milling machine for 12h, the mixture was axially pressed in a mold with 6000 psi. Then these pellets were heat-treated at 500 °C for 3h, 750 °C for 2h, and 950 °C for 2h step by step to remove carbon (4) and sintered at 1400 °C in air. Their density was obtained by measuring volume and weight of the sintered body.

The anode paste for extrusion process was prepared by mixing anode powder, carbon powder, binder, and distilled water. The anode and carbon powders were mixed by ball milling in ethanol solution for 14 days and then the mixture was dried over a hot plate. Since the extruded body must have sufficient strength, the binder for the paste should be prepared carefully. Thus we selected the mixed binders including various organic substances. The organic binder in 50 vol.% and the distilled water in 30wt.% were added to the dried powder, which was thoroughly mixed by shear mixer and aged for 24 h at room temperature to obtain the desired plastic characteristics. Then the paste was extruded in the form of tube. The extruded anode tube was dried at 200 °C for 24 hours, and was presintered in air at 1300 °C, and sintered in air at 1400 °C. The porosities of the presintered and sintered anode tubes were examined.

The electrolyte slurry for coating on the anode tube was prepared from 8 mol% YSZ and additives. This electrolyte slurry was coated on the outside of the presintered anode tube by slurry dipping process. After the electrolyte was applied, the anode tube with electrolyte layer was dewaxed at 350 °C and cofired at 1400 °C. After cofiring, the outside diameter and thickness of the tube was 25mm and 2mm, respectively. The gas permeation tests of the anode tubes were carried out and the microstructures of all specimens were observed by scanning electron microscope.
RESULTS AND DISCUSSION

To fabricate anode-supported tube with optimum porosity, the pore former and its content must be decided. The carbon was selected as a pore former because the carbon powder is known to give porosity to the sintered ceramic body (5). Fig.1 shows the effect of carbon contents on relative density of the sintered anode substrate manufactured by die pressing method. The relative density was defined as the percentage between sintering density and theoretical density. The relative density of the anode substrate decreased from 60 to 40 % with increasing carbon content. Although it is not clear whether the low relative density originated from open or closed pores, the sintered anode substrates are considered to have sufficient porosity. Fig.2 indicates the microstructures of the anode substrates with 20 and 50 vol.% carbon contents. It is confirmed that greater the carbon content, the more porous the anode body is. The carbon content has no effect on particle size in the anode substrate, which is consistent with the published result (5).

To make clear the pore content of the anode substrate, their porosities were measured by mercury porosimeter and the results are presented in Table 1. The porosity of the anode substrate manufactured by die pressing method increased slightly with carbon content but the porosity difference between 30 and 40 vol.% carbon is not large. Excessive carbon content may increase the residual carbon content in the sintered anode substrate due to incomplete combustion of carbon during heat treatment. Thus the 30 vol.% carbon content was selected for making the anode-supported tube by extrusion process.

Fig. 3 shows the photograph and the microstructures of the anode tube. The sintered tube indicated shrinkage of 22.7% and had high mechanical strength. The porosities of the anode tube were 43 and 35 % after presintering and sintering, respectively, as shown in Table 1. It is noted that the porosity of the anode tube made by the extrusion is higher than that of the anode substrate by die pressing, which is attributed to the difference in the binder content and the manufacturing process. As compared with the presintered tube, the pore size distribution curve of the sintered tube shifted to large pore and indicated bimodal behavior, which resulted from pore coarsening.

The cofired electrolyte layer from the presintered state was dense and adherent with anode tube. Thickness of the electrolyte layer was about 60 μm. When the anode tube was dipped one time, the electrolyte layer with about 20 μm thick was obtained and the anode-supported tube of Fig.3 was obtained from dipping three times. The thickness of the coated electrolyte layer was found to depend on viscosity of the electrolyte slurry and dipping time. Thick coating layer was obtained from high viscosity of the slurry and long dipping time, which created cracks across the coated anode tube due probably to the shrinkage difference between anode tube and electrolyte. Thus for the electrolyte coating, it is favorable to use the properly dilute slurry and to dip several times.

The gas permeation rate in the electrolyte is critical in SOFC because gas leak across electrolyte layer produces a direct chemical reaction of gases, but the gas
permeation across the anode tube should be high for sufficient gas supply. Fig.4 shows the gas permeation rates of the anode tubes with and without electrolyte layer as a function of differential pressure. The anode tube itself had high permeation rate. On the other hand, the anode tube with electrolyte layer indicated a low gas permeation rate at even 63 psi. Since the anode tube is porous, it is clear that the coated electrolyte layer plays a role of barrier to gas permeation. This means the coated electrolyte layer is dense.

CONCLUSIONS

The NiO-8YSZ substrates were investigated as a function of carbon content and the anode tube was manufactured by extrusion process and the electrolyte was coated on the tube by slurry dipping process. The following results are summarized:
(1)The porosity of the anode substrate increased slightly with carbon content and anode substrate with proper porosity was obtained at 30 vol. % carbon content.
(2)Anode-supported tube was manufactured effectively by using extrusion process and the electrolyte layer was coated successfully on the tube by slurry dipping process. The porosity of anode tube was 35 % at 30 vol.% carbon before reduction.
(3)The gas permeation rate of the anode tube itself was very high but the anode tube with electrolyte layer indicated a very low gas permeation rate at even 63 psi. This means that the coated electrolyte layer was very dense. Based upon these experimental results, the cathode coating and the single cell tests are in progress.

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REFERENCES

1. S.C. Singhal, in Solid Oxide Fuel Cells V, U. Stimming, S.C. Singhal, H. Tagawa and W. Lehnert, Editors, PV 97-40, p.37, The Electrochemical Society Preceedings Series, Pennington, NJ (1997).
2. H.P. Buchkremer, U. Diekmann, L.G.j. de Haart, H. Kabs, D. Stover and I.C. Vinke, in Third European Solid Oxide Fuel Cell Forum, Philippe Stevens, Editor, p.143, European Fuel Cell Forum, Nantes/France (1998).
3. T. Kawada, N. Sakai, H. Yokokawa, M. Dokiya, M. Mori, and T. Iwata, J. Electrochem. Soc., 137, 3042 (1990).
4. Korean Standard Testing Method for Ash in Graphite, KS L 3412:1977.
5. R. Okuyama and E. Nomura, Denki Kagaku, 62(4), 339 (1993).
Fig. 1 Effect of carbon content in the sintered anode substrate on the relative density.

Table 1. The porosity of anode support with various carbon contents manufactured by the die pressing and extrusion processes.

| Process               | Die Pressing Process | Extrusion Process |
|-----------------------|----------------------|-------------------|
| Carbon Content (vol %)| 20       | 30    | 40    | 30    |
| Porosity (%)          | 25       | 29    | 31    | 35(43*) |

*Presintered body

Fig. 2 The microstructures of NiO-8YSZ substrates with (a) 20 vol. % carbon and (b) 50 vol. % carbon.
Fig. 3 The microstructures of (a) presintered and (b) sintered anode-supported tubes, (c) the cross section of sintered anode tube with electrolyte layer, and (d) the photo of anode-supported tube manufactured by extrusion process.

Fig. 4 The gas permeation rate of sintered anode-supported tube with and without coated electrolyte.