DEVELOPMENT OF ANODE-SUPPORTED TUBULAR SOFC STACK

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ABSTRACT

We developed induction furnace brazed anode supported tubular and flat tube SOFCs to improve power density and studied basic technology of key components for making stacks from them. Performance of the flat tube cell showed 210 mW/cm² (0.7V, 300 mA/cm²) at 750°C. Induction furnace brazing was applied to connect ceramic and metal parts and their gas permeability was tested. The results indicated that the induction furnace brazing method could be used effectively for making anode supported tubular and flat tube cell stack. Through these experiments, we obtained basic technology of such cells and established a proprietary concept of the anode-supported tubular and flat tube cell stack.

INTRODUCTION

Solid oxide fuel cells (SOFCs) have been developed as clean and efficient power source generating electricity from various fuels. The SOFC has several distinct advantages: simplicity, high power density, low production cost, excellent integration with simplified reformer, and so their commercialization should be realized within a few years (1,2). The market for SOFC systems ranges from residential micro-cogeneration systems to small-scale distributed power generators and cogeneration systems for commercial and office buildings. These applications require operation reliability for easy and frequent start-ups and shut-downs.

In order to increase lifetime and to allow cost reduction by using less expensive materials for interconnect, many researchers are currently concentrating on development of SOFCs to be operated at reduced temperatures below 800°C. Anode-supported SOFC may be one of the candidates for the intermediate temperature SOFCs (2-5,8,9). Most of researchers have worked only on the planar anode-supported cell but the anode-supported tubular design also has excellent potential according to our previous studies (4,5,8,9). In this work, we have developed an induction furnace brazed anode supported flat tube and tubular cell to improve power density and studied basic technology of their components.

EXPERIMENTAL

The extruded anode-supported tubular and flat tube serves as fuel electrode and other cell components were coated in the form of thin layers onto it. The 40 vol% Ni/YSZ (8 mol% Y₂O₃-stabilized ZrO₂) anode powder was prepared by mixing 8 mol% yttria stabilized zirconia (TZ-8Y, Tosoh Co.) and nickel oxide (NiO, Junsei Chemical Co.) powders.
Anode powder and activated carbon as pore former were weighed, mixed in ethanol and then dried. Organic binder and distilled water were added to the dried powder, and then the well-dispersed paste was extruded in the form of tubular and flat tube. The extruded flat and circular tubes were dried in a drying oven, followed by presintering at 1300°C. The YSZ electrolyte layer was coated on the presintered anode tube by slurry dip process to form a dense layer and cofired at 1400°C. Mixture of LSM ((La0.85Sr0.15)0.95MnO3) and YSZ, and LSM and LSCF (La0.6Sr0.4Co0.2Fe0.8O3) for multilayered cathode were coated subsequently onto the co-sintered flat tube substrate by slurry dip process and sintered at 1200°C. Performance characteristics of single cell were evaluated in humidified hydrogen with 3% H2O and air.

Ni-Cr filler alloy paste (Alpha Co. in Korea) was pasted into the gap between cell and metal brazing cap. By using induction heater, only the pasted part was heated slowly to 1150°C in Ar + 4% H2 atmosphere and cooled to room temperature. By using the flat tubular cells, we designed the 2x2 cell anode-supported flat tube SOFC stack.

RESULTS

Figure 1 shows the extruded anode supported flat tube cell structure. Electron current path in tubular type SOFC is geometrically determined by half circle of the cell, so the power per mass or per volume is much poorer than the planar type. With the flat tubular design, it is possible to enhance the power density by providing additional electron current path through the ribs as shown in Figure 1(b). Also, it has higher mechanical strength than conventional type at high temperatures. Figure 1(c) shows flat tubular cell coated with electrolyte and cathode layer on the porous flat tubular anode substrate. The thickness of co-fired anode tube was 1.9 mm, which has 20 μm thick electrolyte and 20 μm thick cathode layer as shown in Figure 4. In addition, the anode-supported tubular cell in which the electrolyte and the cathode layer were coated on the porous tube by slurry dip coating is shown in Figure 2. The tubular cell had an outside diameter and thickness of approximately 6 mm and 2mm, respectively. Both the electrolyte and the cathode layers had a thickness of 44 μm. Also, Figure 3 shows the structure of an induction brazed anode supported tubular and flat tube cell.

Figure 1. Photos of anode supported flat tubular cells. (a) as-extruded and presintered of flat tube, (b) transverse section of flat tube, (c) flat tubular cell coated with electrolyte and cathode layer.

Figure 2. Structure of anode supported tubular SOFC cell.
The microstructures of electrolyte and cathode multilayer, composed of LSM ((La$_{0.85}$Sr$_{0.15}$)$_{0.9}$Mn$_{0.1}$)/40 wt% YSZ composite, LSM, and LSCF (La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3}$) layers, are shown in Figure 4. As can be seen in Figure 4(a), microstructure of electrolyte was uniformly distributed and LSM/YSZ composite layer was adapted to lower polarization loss due to an increase in the triple phase (LSM/YSZ/pore) boundary length (7). LSCF as current collector layer was coated on LSM layer.

Figure 4. The microstructures of electrolyte (a) and transverse sectional view of anode, electrolyte, and cathode layers (b) in a flat tube cell.

Figure 5 shows the optical microstructure of brazing joint between anode supported cell (ceramic) and filler alloy and metal cap. As can be seen in Figure 5, the contact part between anode supported cell (ceramic) and filler alloy has dense joining part.

Figure 5. Microstructure of brazed joint between anode supported cell and brazing cap. (a): anode supported cell (ceramic), (b): filler alloy, (c): metal brazing cap.
Gas permeability tests are usually used to estimate characteristics of membranes (6). From the gas permeability result of anode supported tubular cell as a function of differential pressure, by He leak test, the value of He permeability through a brazed joint between anode supported cell and brazing cap was so trivial that it is acceptable to use it as a connector between ceramics and metal parts.

![Gas Permeability Test](image)

**Figure 5.** Gas permeability of anode supported tubular cell as a function of pressure difference by He leakage test.

Induction brazed anode supported flat tube cell, with an effective cell area of 33 cm$^2$ produces 210 mW/cm$^2$ (0.7 V, 300 mA/cm$^2$) power at 750°C as shown in Figure 6.

![Current-Voltage Characteristics](image)

**Figure 6.** Current-voltage characteristics of anode supported flat tube cell fabricated by induction brazing method.

By using the flat tube cells fabricated by induction brazing method, we designed a 2x2 cell anode-supported flat tube stack as shown in Figure 7. Its test is in progress.
CONCLUSIONS

Induction brazed anode-supported flat tube and tubular solid oxide fuel cells were developed and fabricated to improve power density. Electrolyte (20 μm) and multilayered cathode composed of LSM [(La0.85Sr0.15)0.9MnO3]/YSZ composite, LSM, and LSCF (La0.6Sr0.4Co0.2Fe0.8O3) were coated onto the anode substrate by slurry dip coating. It showed good performance of 210 mW/cm² (0.7 V, 300 mA/cm²) at 750°C. Induction brazing as a way of connecting ceramic and metal parts was used and their gas permeabilities were examined. The results confirm the suitability of the induction brazing method for anode supported flat tube and tubular SOFC stack.

REFERENCES

1. N. Q. Minh, H. Takahashi, *Science and Technology of Ceramic Fuel Cells*, Elsevier Science, (1995).
2. K. Huang, M. Feng, J. B. Goodenough, *J. Am. Ceram. Soc.*, 81, 357 (1998).
3. P. Charpentier, P. Fragnaud, D. M. Schleich, E. Gehain, *Solid State Ionics*, 135, 373 (2000).
4. R. H. Song, E. Y. Kim, D. R. Shin, H. Yokokawa, in *SOFC-VI*, U. Stimming, S. C. Singhal, H. Tagawa, Editors, PV99-19, 845 (1999).
5. R. H. Song, K. S. Song, Y. E. Ihm, H. Yokokawa, in *SOFC-VII*, H. Yokokawa, S. C. Singhal, Editors, PV2001-16, 1073, The Electrochemical Society, Pennington, (2001).
6. S. D. Kim, S. H. Hyun, J. H. Moon, J. H. Kim, R. H. Song, *J. Power. Sources*, 139, 67 (2005).
7. J. Q. Li, P. Xiao, *J. of European Ceramic Society*, 21, 659 (2001).
8. R. H. Song, J. H. Kim, H. J. Son, D. R. Shin, H. Yokokawa, in *SOFC-VIII*, S. C. Singhal, M. Dokiya, Editors, PV2003-07, 1029, The Electrochemical Society, (2003).
9. J. H. Kim, R. H. Song, K. S. Song, S. H. Hyun, D. R. Shin, H. Yokokawa, *J. Power Sources*, 122, 148 (2003).
10. R. Wilkenhoener, H. P. Buchkremer, D. Stoever, D. Stolten, *J. Mat. Sci.*, 36, 1783 (2001).