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Fabrication and characterization of micro tubular SOFCs for operation in the intermediate temperature

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Abstract

Tubular SOFC systems appear to be well-suited to accommodate repeated cycling under rapid changes in electrical load and in cell operating temperatures. Our goal is to develop innovative processing method to fabricate new micro tubular SOFCs with sub-millimeter diameter and its stack module which enable to generate high volumetric power density. In this study, micro tubular SOFCs under 1 mm diameter have been successfully fabricated and tested in the intermediate temperature region (550 °C or under). The cell consists of NiO–Gd doped ceria (GDC) as an anode (support tube), GDC as an electrolyte and (La, Sr)(Fe, Co)O_3 (LSCF)–GDC as a cathode. The single tubular cell with 0.8 mm diameter and 12 mm length generated over 70 mW at 550 °C with H_2 fuel, which indicates that the cell generated over 0.3 W cm^{-2} at 550 °C.

Keywords: Tubular SOFCs; Intermediate temperature; Stack; Micro SOFC

1. Introduction

SOFC technology has been much paid attention in recent years as a keystone of the future energy economy and nowadays, reduced temperature SOFCs have been extensively studied because operating SOFCs under 650 °C decreases material degradation and prolongs stack life time, reduces cost by utilizing metal materials [1,2]. Many kinds of SOFC systems have been designed and proposed for reduced temperature operation. Among them, anode-supported SOFCs with thin film electrolyte are suited for reduced temperature operation and some groups have already reported outstanding results with high power density of 0.8–2 W cm^{-2} at 600 °C or under using planer anode-supported SOFCs [3–5].

On the other hand, tubular solid oxide fuel cells (SOFCs) systems have shown many desirable characteristics over systems with planar SOFCs [6–8]. Tubular SOFCs systems appear to be well-suited to accommodate repeated cycling under rapid changes in electrical load and in cell operating temperatures. Siemens Westinghouse have successfully conducted long-term tubular SOFCs operation over 70,000 h. Small-scale tubular SOFCs, reported by Kendall and Palin, and Yashiro et al., could endure thermal stress caused by rapid heating up to operating temperature. Therefore, tubular SOFCs can be expected to be used for cogeneration and transportation application.

In addition, when the diameter of tubular SOFCs becomes in the range of millimeter to sub-millimeter, it is possible to design SOFC stacks with high volumetric power density, which are not possible with planer SOFC design. Our goal is to develop innovative processing method to fabricate such a new micro tubular SOFC stack with high volumetric power density. In this study, micro tubular SOFCs under 1 mm diameter have been fabricated using traditional extrusion and coating technique and tested in the intermediate temperature region under 600 °C.

2. Experimental details

Fig. 1 represents the single cell fabrication process. NiO–Gd doped ceria (GDC) tubes were extruded from a plastic mass through a die forming a 1 mm outside diameter. The mass was created by mixing commercially available NiO power (Wako Pure Chemical Industries, Ltd.), GDC powder (Anan Kasei, Inc.) and cellulose (Uken Kogo, Inc.) as binder. This was mixed with water for 1–2 h and left to age overnight. A vacuum was applied to the mixing chamber for 10–30 min to remove air from the

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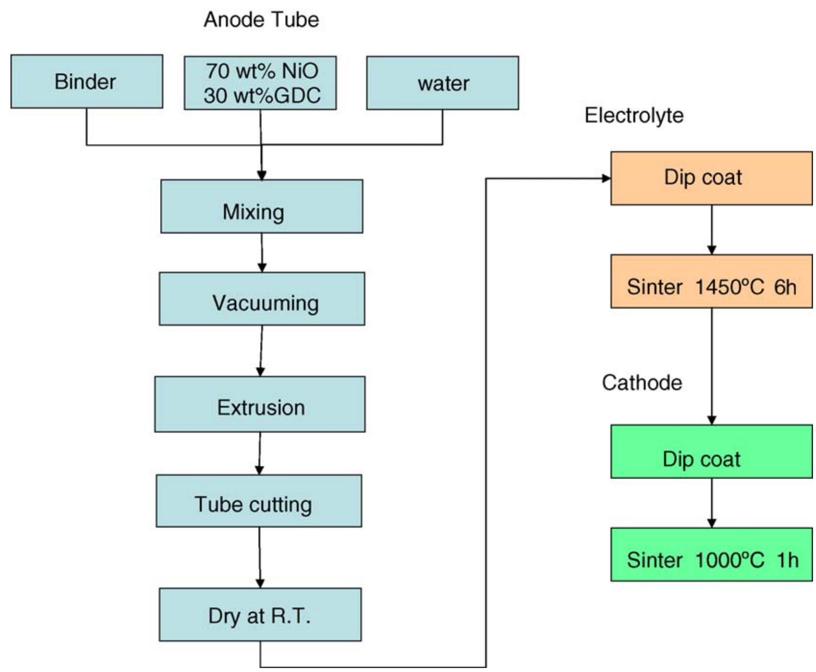

Fig. 1. Single cell fabrication process.

mass. The tube was extruded from the mass using a ram extruder (Miyazaki Tekko, Inc.) with an in-house designed die. After drying, the tubes were cut to length and then dip-coated in a GDC slurry for an electrolyte, which is composed of GDC power (same as described above) and organic ingredients such as binder (poly vinyl butyral), dispersant (fish oil) and solvents (toluene and ethanol). The coatings were left to dry in air, then sintered at 1450 °C for 6 h in air.

Next, the anode tubes with electrolyte were dip-coated in cathode slurry, which consists of $La_{0.8}Sr_{0.2}Co_{0.6}Fe_{0.4}O_3$ (LSCF) (Seimi Chemical, Inc.) and the GDC power, and organic ingredients. Organic ingredients were similar with those of the electrolyte slurry. After dip-coated the cathode slurry, the tubes were dried in air and sintered at 1000 °C for 1 h in air to complete a cell. SEM (JOEL, JSM6330F) was used to check the microstructure of the cell.

The performance of the cell was investigated using an experimental apparatus as shown in Fig. 2. The Ag wire was used for collecting current for anode and cathode sides, which were both fixed by Ag paste. As can be seen in Fig. 2, current collection from anode side was only made from an edge of the anode tube. Twenty percent H_2 (humidified by bubbling water at room temperature) in N_2 was used as a fuel in the flow rate of 25 $cm^3 min^{-1}$. Cathode side was open to the air without flowing gas. The size of the cell was 0.8 mm diameter and 12 mm length with active cathode length of 8 mm, whose active cell area is 0.2 cm^2. The *V–I* characterization and impedance analysis were made using a Solartron 1260 frequency response analyzer with a 1296 Interface.

3. Results and discussion

Fig. 3a and b show a picture of tubes after drying at room temperature and cross-sectional SEM images of the tube with an electrolyte after sintering at 1450 °C for 6 h in air, respectively. As can be seen in Fig. 3b, a crack-free dense electrolyte with a thickness of about 20 μm has successfully prepared on the anode tube by co-sintering method. The thickness of the anode tube was about 0.2 mm and the porosity of the anode determined to be around 30% (before reduction) using Archimedes' principle.

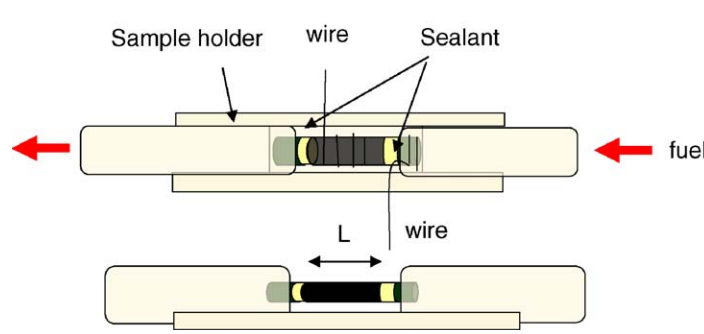

Fig. 2. Experimental apparatus of the single tubular cell measurement.

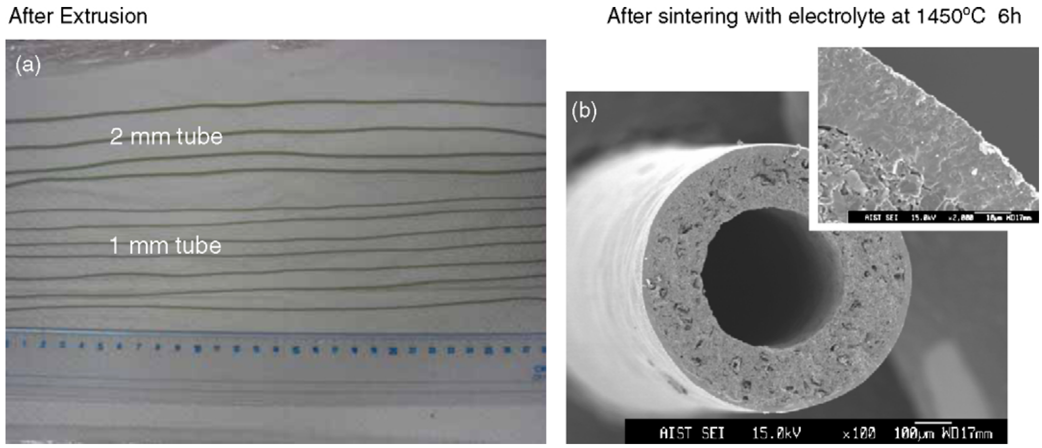

Fig. 3. (a) Picture of tubes after drying at room temperature and (b) cross-sectional SEM images of the 0.8 mm tube after sintering at 1450 °C for 6 h in air.

Note that such structure (thin support body with high porosity) can be mechanically stabilized by tubular shape.

The conductivity of the anode tube in the reducing atmosphere was determined and shown in Fig. 4a. The conductivity appeared to be between 1234 and 700 S cm^{-1} in the range of temperature between 400 and 600 °C. These values are relatively lower compared to those of typical Ni–GDC cermet due to high porosity of the anode tube. From these values, the area specific resistances of anode tube with 8 mm length and 0.8 mm diameter at various temperatures were estimated as a function of the tube thicknes in Fig. 4b. As a current collector, the area specific resistance of the anode tube in the reducing atmosphere expected to be lower than 0.1 Ω cm^2, which were achieved by using this anode with 0.2 mm thick under 600 °C. Tube thickness can be optimized by the cell operating temperature and the electrode area of the cell, which gives total resistance of the cell. Note that tube length of a few centimeters will be the limit of use of the anode tube as a current collector due to an increasing ohmic resistance. Therefore, stack design will be of importance for the practical application of the micro tubular SOFC.

The performance of the micro tube cell was then investigated and shown in Fig. 5. As can be seen, the peak power density of 22, 41 and 70 mW were obtained respectively at 450, 500 and 550 °C from the single tubular cell with the length of 12 mm (active length = 8 mm) and the diameter of 0.8 mm. The power density of the cell was estimated from the area of cathode (0.2 cm^2) as shown in Fig. 6. The peak power density of 110, 205 and 350 mW cm^{-2} was obtained at 450, 500 and 550 °C, respectively. The OCVs obtained here are not high enough to achieve efficient energy conversion for practical applications due to a use of ceria-based electrolyte, even though the peak power densities

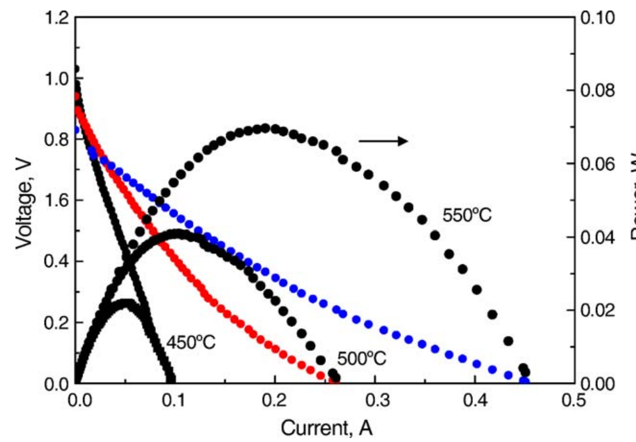

Fig. 5. The performance of the 0.8 mm tubular cell. Cell voltage and power as functions of current and temperature.

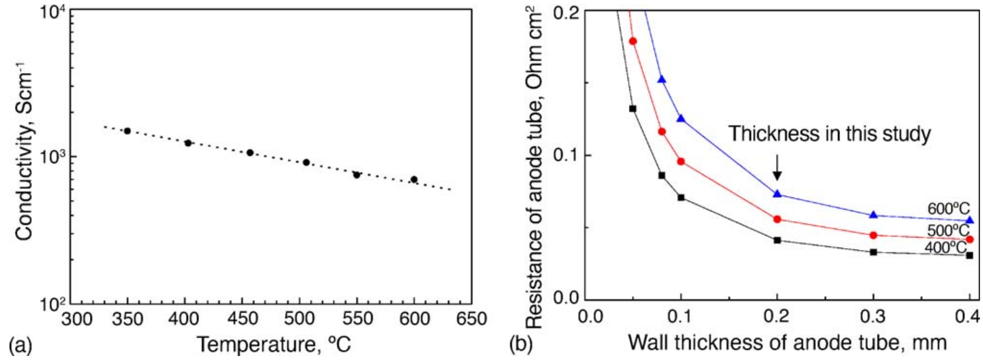

Fig. 4. (a) The electrical conductivity of the anode tube and (b) estimated area specific resistances of the anode tube (8 mm length and the area of 0.2 cm^2 were used for estimation) at various temperatures as a function of the tube thickness.

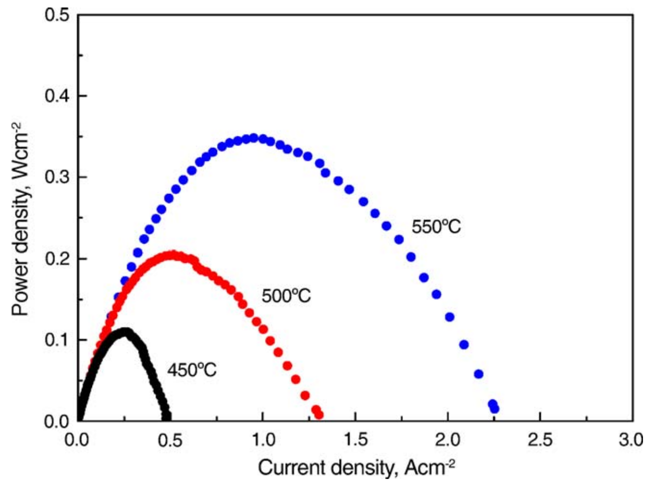

Fig. 6. The power density of the tubular cell estimated from the area of the cathode.

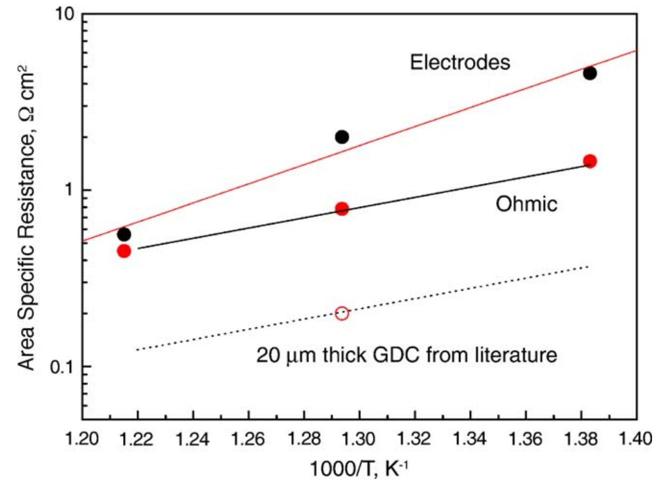

Fig. 8. Area specific resistance of electrodes and electrolyte for the micro tubular SOFC along with the GDC resistance from the literature [11].

are relatively high. The solution for this problem can be found in the literature and will be considered in the study as well [9,10].

The results of impedance analysis were shown in Fig. 7. The impedance spectra were obtained at 5 mA biased. Ohmic resistance at 500 °C obtained from impedance analysis turned to be about 4 Ω. The electrolyte resistance of 20 μm thick with the area of 0.2 cm^2 can be estimated about 1 Ω at 500 °C ($\sigma \sim 0.01$ S cm^{-1}) [11], therefore, this may be related to problems regarding to current collection, except due to the resistance of the anode tube, which was 0.35 Ω at 500 °C.

Fig. 8 shows the area specific resistances (ASR) of electrodes and electrolyte as a function of reciprocal temperature determined raw impedance plots as indicated in Fig. 7, with ASR of 20 μm thick GDC from the literature [11]. The ASRs of electrodes at various temperatures were 4.6, 2.0 and 0.56 Ω cm^2, respectively at 450, 500 and 550 °C. High values of total ASRs compared to the obtained power density shown in Fig. 6 were resulted from the sharp voltage drops at the range of <0.05 A in Fig. 5. The ASR of ohmic appeared to be about 0.3 Ω cm^2 higher

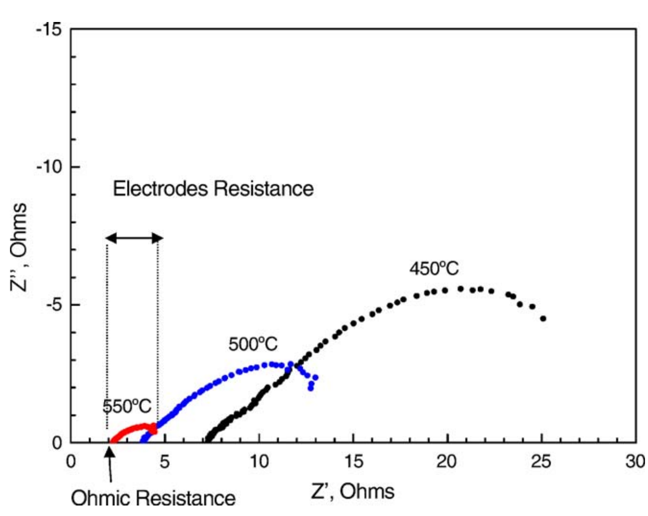

Fig. 7. Impedance spectra of the tubular cell obtained at various temperatures obtained at 5 mA bias.

than the value of GDC from literature. It is shown that further improvement of cell performance can be expected by solving this problem, which is currently undergoing.

According to the size and performance of the single tubular cell, a stack with 100 tube cells (10 × 10) in 1 cm^3 can possibly be fabricated, which can be expected to generate 4 and 7 W cm^{-3} at 500 and 550 °C, respectively. Therefore, developing of stack fabrication method will be a key for realizing high volumetric power SOFC system, which is currently under investigation.

4. Summary

Micro tubular SOFCs under 1 mm diameter have been successfully fabricated and tested in the intermediate temperature region under 600 °C. The cell consists of NiO–Gd doped ceria as an anode (support tube), GDC as an electrolyte and (La, Sr)(Fe, Co)O_3 (LSCF)–GDC as a cathode. The cell generated 0.35 W cm^{-2} at 550 °C operating temperature with H_2 fuel. The single tubular cell with 0.8 mm diameter and 12 mm length (cathode length 8 mm) generated over 70 mW at 550 °C, which indicated a possibility of building cell stack with volumetric power density of 7 W cm^{-3} by stacking 100 tubes in 1 cm^3. Fabrication of the new micro tubular SOFC stack is currently on-going to deliver SOFC system with high volumetric power density.

Acknowledgement

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References

[1] B.C.H. Steele, A. Heinzel, Nature 414 (2001) 345–352.
[2] S.M. Haile, Acta Mater. 51 (2003) 5982–6000.
[3] J. Yan, H. Matsumoto, M. Enoki, T. Ishihara, Electrochem. Solid-Sate Lett. 8 (8) (2005) A389–A391.
[4] Z. Shao, S.M. Haile, Nature 431 (2004) 170–173.

[5] T. Hibino, A. Hashimoto, K. Asano, M. Yano, M. Suzuki, M. Sano, Electrochem. Solid-Sate Lett. 5 (11) (2002) A242–A244.
[6] N.M. Sammes, Y. Du, R. Bove, J. Power Sources 145 (2005) 428–434.
[7] K. Kendall, M. Palin, J. Power Sources 71 (1998) 268–270.
[8] K. Yashiro, N. Yamada, T. Kawada, J. Hong, A. Kaimai, Y. Nigara, J. Mizusaki, Electrochemistry 70 (12) (2002) 958–960.
[9] K. Eguchi, T. Setoguchi, T. Inoue, H. Arai, Solid State Ionics 52 (1992) 165.
[10] D. Hirabayashi, A. Tomita, T. Hibino, M. Nagao, M. Sano, Electrochem. Solid-State Lett. 7 (10) (2004) A318–A320.
[11] B.C.H. Steele, J. Mater. Sci. 36 (2001) 1053–1068.