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Short communication

Fabrication of micro-tubular solid oxide fuel cells with a single-grain-thick yttria stabilized zirconia electrolyte

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ABSTRACT

This study discusses the fabrication and electrochemical performance of micro-tubular solid oxide fuel cells (SOFCs) with an electrolyte consisting a single-grain-thick yttria stabilized zirconia (YSZ) layer. It is found that a uniform coating of an electrolyte slurry and controlled shrinkage of the supported tube leads to a dense, crack-free, single-grain-thick (less than 1 μm) electrolyte on a porous anode tube. The SOFC has a power density of 0.39 W cm^{-2} at an operating temperature as low as 600 °C, with YSZ and nickel/YSZ for the electrolyte and anode, respectively. An examination is made of the effect of hydrogen fuel flow rate and shown that a higher flow rate leads to better cell performance. Hence a YSZ cell can be used for low-temperature SOFC systems below 600 °C, simply by optimizing the cell structure and operating conditions.

1. Introduction

Recently, solid oxide fuel cells (SOFCs) have become closer to commercialization for local and emergency power generation, and much effort has been undertaken to widen their use of application [1–5]. Lowering the operating temperature is a very effective way to help accelerate their commercial viability, as it can improve the life time of the cells, as well as their modules, and may offer the potential for rapid start-up, which would allow for their use in applications such as portable power sources. Hence, many studies on SOFCs aim at lowering their operating temperature by utilizing new materials for cell components [6–12]. The use of a micro-tubular design has been shown to be effective for this purpose, since it has been shown to have high thermal stability under rapid heating, as well as a high electrode area per unit volume [13–16]. As a matter of fact, using micro-tubular SOFC fabrication technology, an ideal cell structure was established by realizing dense, thin electrolytes on a porous electrode support. As a result, over 1 W cm^{-2} of power density was obtained using gadolinia-doped ceria (GDC) and scandia stabilized zirconia (ScSZ) with nickel cermet anode at/below 600 °C [16,17].

On the other hand, a conventional yttria stabilized zirconia (YSZ) electrolyte is still attractive because of its long-term reliability, as well as cost factors. In fact, SOFCs utilizing a YSZ electrolyte have been shown to be operable down to 700 °C by reducing the electrolyte thickness [18]. Further lowering of the cell operating temperature with a YSZ electrolyte relies on thin electrolyte fabrication technology. An example in the literature of one such technology was reported by Huang et al. [19], who realized a 100-nm thick YSZ electrolyte and platinum electrodes by means of sputtering, lithography and etching technology, and demonstrated a power density of 0.4 W cm^{-2} at 400 °C.

In this study, a conventional fabrication method (slurry dip-coating) and materials (YSZ) are utilized for preparing a thin electrolyte on a micro-anode-supported tube to seek the possibility of using such conventional materials for low-temperature operation at or below 600 °C.

2. Experimental

The micro-tubular SOFCs consisted of nickel–yttria stabilized zirconia (Ni/YSZ) for the anode, YSZ for the electrolyte, and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-y}$–gadolinia-doped ceria (LSCF/GDC) for the cathode, with an inter-layer of gadolinia-doped ceria (GDC) placed between the cathode and the electrolyte. Note that all materials used for the SOFC fabrication are commercially available.

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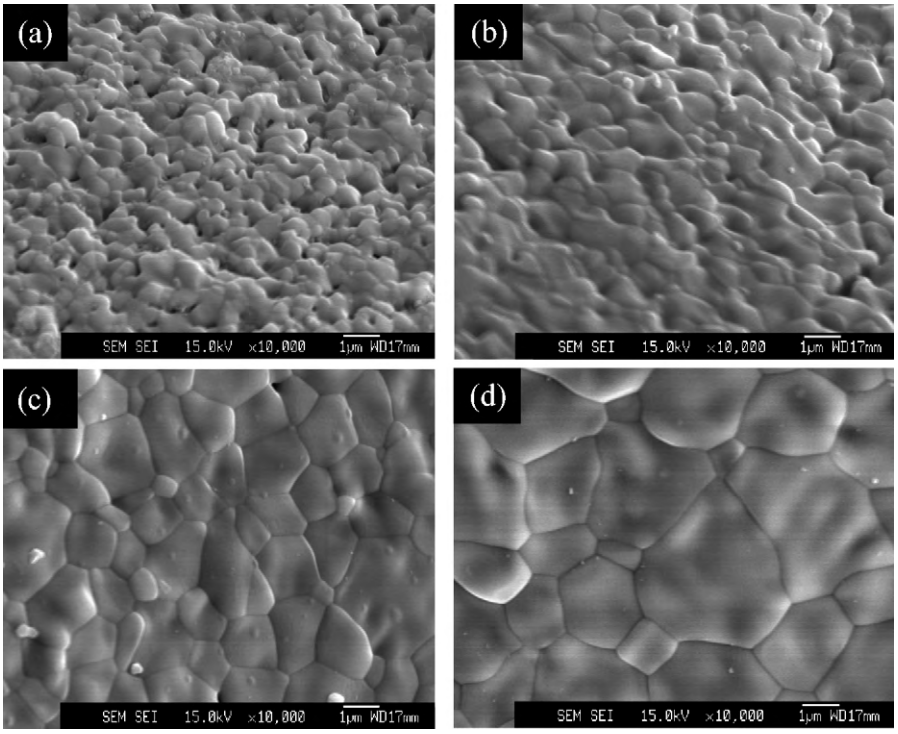

Fig. 1. Scanning electron microcopy images of electrolyte surface prepared on a porous anode substrate co-sintered at (a) 1250 °C (b) 1300 °C (c) 1350 °C and (d) 1400 °C.

2.1. Fabrication

Anode tubes were made from nickel oxide (NiO) powder (Sumitomo Mining Co., Ltd.), yttrium stabilized zirconia (YSZ) (8YSZ, Tosoh Co., Ltd.), poly methyl methacrylate beads (PMMA) (Sekisui Plastics Co., Ltd.), and cellulose (Yuken Kogyo Co., Ltd.). The powders were mixed for 1 h in a 5DMV-rr unit (Dalton Co., Ltd.), and after adding the correct amount of water, were stirred for 30 min in a vacuum chamber. The resulting mixture was left to age for over 15 h. The tubes were extruded, using the aforementioned extrudate, from a metal mould by using a piston-cylinder type extruder (Ishikawa-Toki Tekko-sho Co., Ltd.). A slurry for dip-coating the electrolyte was prepared by mixing YSZ powder, solvents (toluene and ethanol), binder (poly vinyl butyral), dispersant (polymer of an amine system) and plasticizer (dioctyl phthalate) for 24 h. The anode tubes were dipped in the slurry and coated at a pulling rate of 1.5 mm s^{-1}. The coated films were dried in air, and then co-sintered at 1250, 1300, 1350 or 1400 °C for 1 h in air. An inter-layer slurry of GDC (Seimi Chemical, Co., Ltd.) was dip-coated on the electrolyte layer of the tube and sintered at 1100 °C. A cathode slurry of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-y}$ (LSCF) (Seimi Chemical, Co., Ltd.) and the GDC powder (LSCF/GDC) was dip-coated on the inter-layer. The SOFCs were completed by sintering at 1000 °C.

2.2. Characterization

The microstructure of the thin-film electrolyte of the tubular cell was observed by means of scanning electron microscopy (SEM) (JEOL, JSM6330F). The electrochemical cell performance was investigated by using a potentiostat (Solartron 1296). The tested cell was co-sintered at 1350 °C, and the size was 1.7 mm in diameter and 20 mm in length with cathode length of 8.4 mm, and an effective electrode area of 0.45 cm^2. Silver wire served as a current-collector for both the anode and the cathode sides, which were both fixed with Ag paste. Current collection at the anode side was made from the edge of the anode tube, whereas collection from the cathode side was made from the whole cathode area. Hydrogen (humidified by bubbling through water at room temperature) was fed into the tubular cell at a flow rate of 10–40 mL min^{-1}. The cathode side was open to the air without flowing gas.

3. Results and discussion

Scanning electron microscopy (SEM) images of the surface of the electrolyte are shown in Fig. 1. They surfaces were co-sintered at different temperatures: (a) 1250 °C, (b) 1300 °C, (c) 1350 °C and (d) 1400 °C, respectively. It is observed that grain growth and densification take place without creating any cracks on the electrolyte surface. Below 1300 °C, some pores are observed at the grain boundaries, which disappear at above 1350 °C.

A cross-sectional SEM image of the cell co-sintered at 1350 °C is presented in Fig. 2. A dense electrolyte with a thickness of

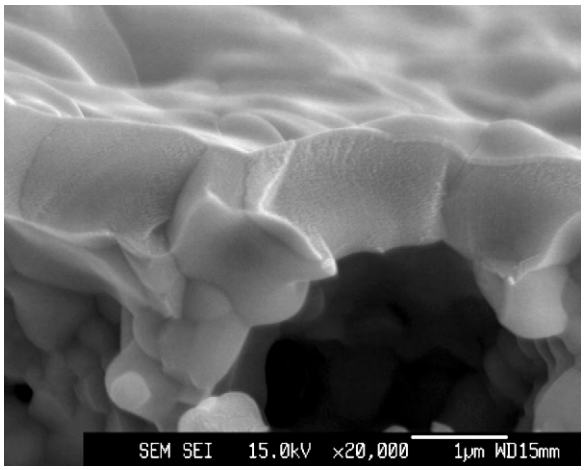

Fig. 2. Cross-sectional SEM image of electrolyte on porous anode co-sintered at 1350 °C.

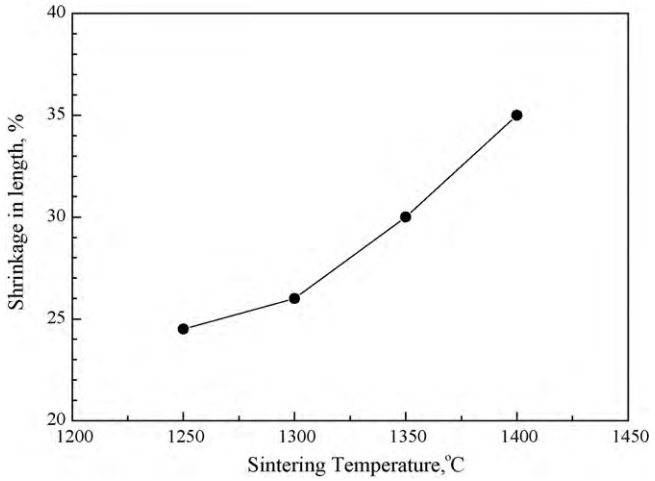

Fig. 3. Shrinkage ratio in length of tube as a function of sintering temperature.

about 1 μm has been successfully prepared on the porous anode-supported tube by using the co-sintering technique. Since the electrolyte consists of single grains and the individual grain boundaries traverse the entire thickness of the electrolyte, the effect of grain boundaries on the electrolyte resistance can be minimized.

During co-sintering of the anode tube and the electrolyte, the tube shrinks by up to 35% in length when the sintering temperature reaches 1400 °C, as shown in Fig. 3. The initial (green) tube diameter is 2.4 mm, and the diameters of the tubes range from 1.56 to 1.8 mm after sintering. Compared with a previous study [20] using GDC for the electrolyte and anode, the present results indicate that the shrinkage of the tube using YSZ is greater.

Fig. 4 shows the performance of the cell co-sintered at 1350 °C at (a) 550 °C and (b) 600 °C for various gas flow rates using humidified hydrogen. Maximum power densities of 0.2 and 0.39 W cm^{-2} at 550 and 600 °C are obtained at a fuel gas flow rate of 40 cm^3 min^{-1}. Note that the fuel utilization at maximum power densities varies from 4 to 14 vol.%, with higher utilization for lower flow rates and higher temperature. The results also indicate that the fuel flow rate influences the cell performance; the performance becomes lower as the fuel flow rate decreases. The open-circuit voltage (OCV) of the cell is slightly lower, i.e., about 1.0 V at 600 °C. This is possibly due to fuel/air leakage through pin holes in the electrolyte, which are not observed but may exist.

The impedance spectra in Fig. 5 demonstrate the effect of the fuel gas flow rate on SOFC performance, i.e., as the fuel gas flow rate decreases, the low frequency semi-circle increases. The gas diffusion in the anode microstructure is apparently improved by an increase in the fuel gas flow rate, which is the same as that observed for a tubular cell with an ScSZ electrolyte [17] and also reported elsewhere [21]. Note that all impedance spectra were obtained under OCV conditions. The present results show that the high-frequency intercepts of the cell in Fig. 5, corresponding to the ohmic resistances, are similar (about 0.3 Ω cm^2) for an operating temperature of 550 or 600 °C. According to the literature [1], the resistance of a 1-μm thick YSZ electrolyte ($\sigma \sim 0.0035$ S cm^{-1} at 600 °C) can be estimated to be about 0.03 Ω cm^2. Thus, it is concluded that the ohmic resistance corresponds to the sum of the electrolyte resistances and the anode resistances that arise during current collection.

The above findings are promising for the use of YSZ for low-temperature operation below 600 °C using conventional fabrication technology. The results also indicate that further improvement in cell performance could be made by optimization of gas flow rate, method of anode current collection, and anode microstructure, for example.

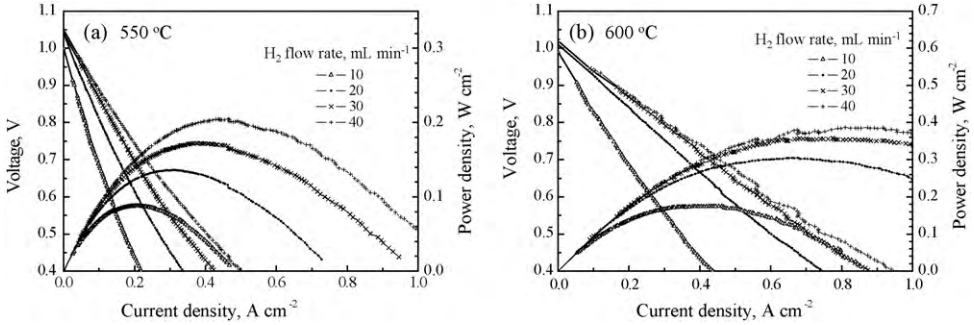

Fig. 4. Performance of cell (co-sintering temperature 1350 °C) obtained at (a) 550 and (b) 600 °C, for various flow rates of fuel gas.

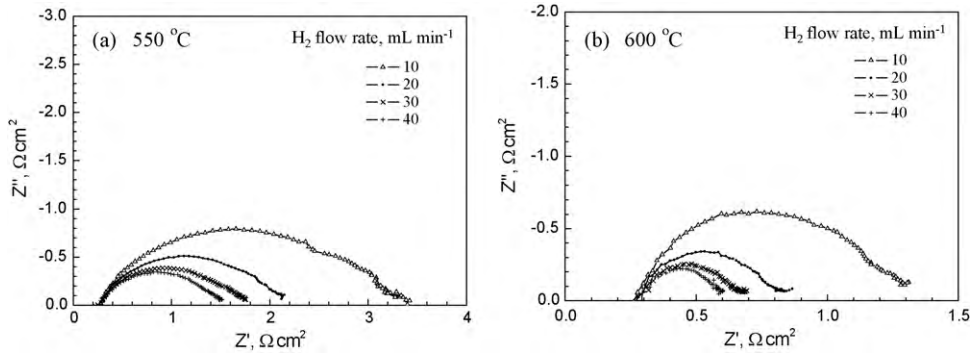

Fig. 5. Impedance spectra of cell (co-sintering temperature 1350 °C) obtained at (a) 550 °C and (b) 600 °C, for various flow rates of fuel gas.

4. Summary

A study has been made of the fabrication process and electrochemical cell performance of micro-tubular SOFCs with an electrolyte of single-grain-thick YSZ layer and an anode (tube support) of Ni/YSZ. It is found that a uniform coating of the electrolyte slurry and controlled shrinkage of the supported tube, by changing the sintering temperature, leads to the realization of a dense, crack-free, single-grain-thick electrolyte on a porous anode tube. The SOFC gives a power density of 0.2 and 0.39 W cm^{-2} at an operating temperature of 550 and 600 °C, respectively. The effect of the fuel (hydrogen) flow rate has been examined and the results show that a higher flow rate gives rise to better cell performance due to a decrease in overpotential related to gas transport. Hence a YSZ cell could be used for low-temperature operation, under 600 °C, by optimizing the cell structure and operating conditions.

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