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Porous electrolyte-supported tubular micro-SOFC design

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ABSTRACT

Due to the poor redox cycling resistance of the second generation of μ-SOFCs, a new generation of SOFC has been recently developed using a porous electrolyte-supported structure to overcome this problem. In this research, the porous structure was successfully fabricated with slip casting using calcined YSZ (ZrO_2 + 8 mol% Y_2O_3) with or without graphite as a pore former. Calcination of YSZ powder at 1300–1500 °C prior to making the slip leads to growth of YSZ crystals and particle size which results in a decrease in surface area and powder sinterability. This was found to be an important criterion in developing the porous structure as, due to the high sinterability of non-calcined YSZ, even the addition of graphite is inadequate to generate sufficient open porosity. A dense YSZ electrolyte layer was immediately coated on the porous structure using YSZ calcined at 1300 °C with a sequential slip casting method. Sample thickness was found to be a function of both graphite content as well as YSZ calcination temperature. Physical properties of the porous YSZ supports and SEM analysis of the support and coated electrolyte are presented.

1. Introduction

Development of the 1st generation novel tubular μ-SOFC design based on ~2 mm diameter thin (~200 μm) dense YSZ electrolyte-supported cells was pioneered by Kevin Kendall in the 1990s [1,2]. Two major benefits of a small diameter thin walled μ-SOFC are high volumetric electrolyte surface area and extremely high thermal shock resistance. These benefits open up the possibility of using μ-SOFCs in portable applications with rapid on/off capabilities. However, due to the thickness (~200 μm) of the electrolyte, the cell has a relatively low power density and in order to achieve sufficient power, the cell should be operated at high temperatures leading to more rapid cell degradation [3]. Therefore, practical SOFC devices cannot be developed based on this tubular μ-SOFC single cell.

Accordingly, an anode-supported thin (~10 μm) electrolyte layer 2nd generation tubular μ-SOFC was developed [4–9]. The thin electrolyte layer enhances the power density resulting in operating temperatures even below 800 °C. A major drawback, however, of the anode-supported cell is the anode oxidation–reduction related microcracking of the cell. Any accidental oxidation of the anode can terminally damage the anode-supported SOFC device [10,11]. To overcome the redox cycling related problems and in order to improve the thermal shock resistance of the tubular fuel cells, Sarkar et al. [12] developed a 3rd generation 'porous electrolyte-supported' (PES) tubular μ-SOFC. The present paper describes the fabrication of such a 'tubular micro-SOFC' type single cell using the ceramic slip casting technique.

2. Experimental methods

In order to make a YSZ suspension for slip casting of the porous substrate, YSZ (Tosoh, TZ-8Y, 8 mol% Y_2O_3) calcined at 1300–1500 °C was mixed with water in a ratio of 52:48 wt.% and milled using 5 mm YSZ balls in a jar mill rotating at 80 rpm for 72 h after which the pH of the slip was set at 4.0 using HCl. Graphite was added in different volume percentages and the suspension was mixed shortly before casting. Different samples were slip cast as tubes for 1 min and as pellets in plaster molds with gypsum/water of 1.5/1 (~40% porous mold). Samples were removed from the molds, dried for 2 h at 100 °C, heat treated at 700 °C for 1 h to burn off the graphite and sintered at 1350 °C for 3 h. Due to the difficulties associated with measuring the physical properties of tubes leading to large experimental errors, pellets of 20 mm (diameter) × 5 mm (height) were slip cast and used for this purpose. Bulk density and open porosity of the pellets were determined by Archimedes principle considering the dry weight, saturation weight after boiling in distilled water for 2 h and also immersion weight in water. Closed porosity content was found using the theoretical density of YSZ (6.1 g/cm^3). Shrinkage and weight loss were calculated from the length and weight of the dry pellets before and after sintering. SEM was carried out on gold coated tubes using an FEI company XL30 SEM running at 20 kV.

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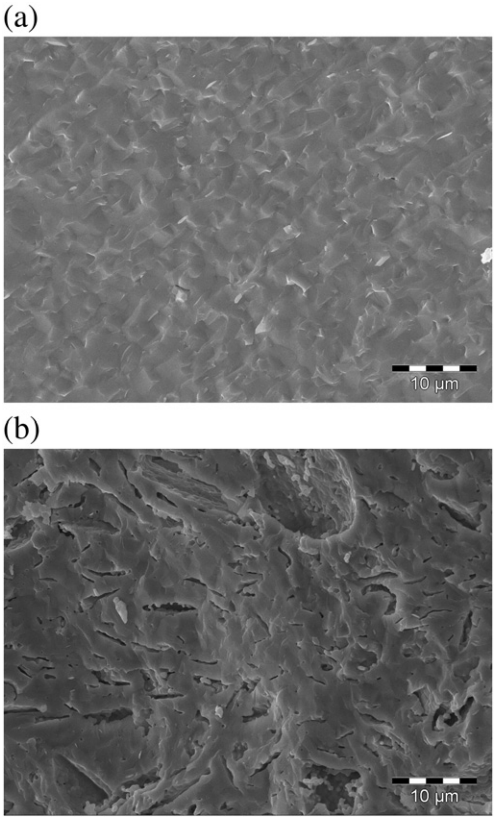

Fig. 1. SEM micrographs of the microstructure of tubes made of (a) non-calcined YSZ and (b) non-calcined YSZ + 20 vol.% graphite, both sintered at 1350 °C.

3. Results

Fig. 1(a) and (b) shows the microstructure of the tubes made of non-calcined YSZ and non-calcined YSZ + 20 vol.% graphite, respectively. It can be seen that the YSZ powder becomes dense after sintering at 1350 °C and minor amounts of closed pores remain in the microstructure which is inevitable. The addition of graphite does not generate significant open porosity inside the material as evidenced by the microstructure. The elongated closed pores are formed by graphite flakes which are burnt leaving void space. This clearly shows that non-calcined YSZ is not suitable for fabrication of a porous structure. The microstructure of the tube made of YSZ calcined at 1300 °C is shown in Fig. 2(a). It appears that the microstructure becomes dense after sintering at 1350 °C but some spherical closed pores are left. The addition of 10 vol.% graphite to the YSZ calcined at 1300 °C enhances the formation of a porous structure as shown in Fig. 2(b). A point worth noting is that when YSZ calcined at 1400 °C and 1500 °C is used for fabricating the tubes, even without the addition of graphite, samples contain considerable amounts of open pores (Fig. 2(c) and (d)). However, it is obvious that when graphite is added to the composition, structures will become even more porous.

Fig. 3 shows the porous support structures made of YSZ calcined at 1300 °C with 30 vol.% graphite, YSZ calcined at 1400 °C with 15 vol.% graphite and YSZ calcined at 1500 °C with 10 vol.% graphite coated with YSZ electrolyte still calcined at 1300 °C. The support and electrolyte were co-fired at 1350 °C. It can be seen that a thin layer of dense YSZ which can act as the electrolyte has been coated successfully on the porous supports.

4. Discussion

Table 1 shows the physical properties of the tubes made using different calcining temperatures and graphite contents. It appears that

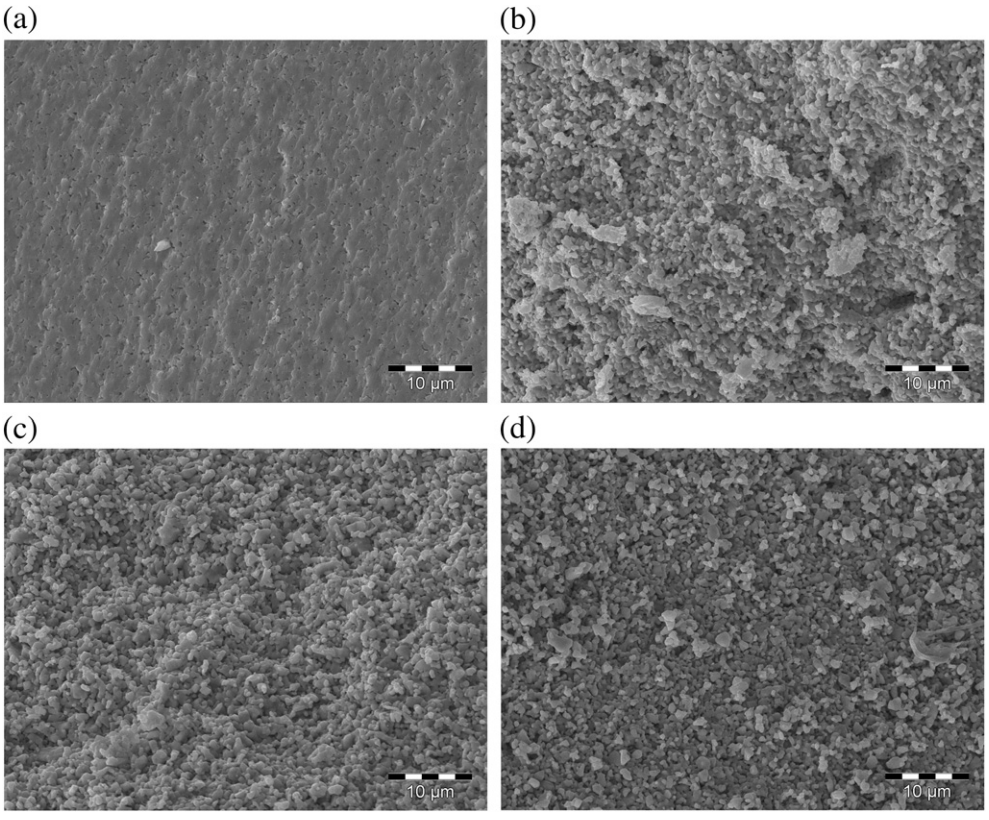

Fig. 2. SEM micrographs of the microstructure of tubes made of (a) calcined YSZ at 1300 °C, (b) calcined YSZ at 1300 °C + 10 vol.% graphite, (c) calcined YSZ at 1400 °C and (d) calcined YSZ at 1500 °C, sintered at 1350 °C.