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Fabrication of seven cells in single tubular solid oxide fuel cell using multi-pass extrusion process

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Abstract

A solid oxide fuel cell (SOFC) with high specific electrolyte surface area was fabricated using the multi-pass extrusion process. The cell configuration was NiO-YSZ/YSZ/LSM. In this design, one tube contained 7 individual fuel cells. The outer diameter of the tube was 5 mm and 4.1–4.2 mm after extrusion and sintering, respectively. The length of the cell was optimized to 3–5 cm with continuous channels of 400–450 μm in diameter. The porous microstructures of the anode and the cathode and the dense microstructure of the electrolyte were observed by scanning electron microscopy. The relative density of the electrolyte was >96% and the thickness was 15–20 μm. The XRD profiles indicated no undesirable phases after co-sintering at 1300 °C.

Keywords: A. Extrusion; SOFC; Volumetric power density; Tubular design

1. Introduction

With the development of micro-solid oxide fuel cells (SOFCs), a new term has been coined volumetric power density (VPD). It means the power density per unit volume of the SOFC module. In order to broaden the applications of SOFCs, it is necessary to improve the VPD. This can be done by utilizing high performance SOFC materials and/or increasing the surface areas of the electrodes for electrochemical reactions [1]. Since oxygen ions are transferred through the dense membrane of the electrolyte, the rate of transfer can be improved by thinning the membrane and by increasing the contact area between the electrodes and the electrolyte.

Several designs of SOFCs have been developed to improve the power output and reduce the manufacturing cost, including planar and tubular types [2]. Both designs have advantages and disadvantages. Planar type SOFCs have much higher power density. Nevertheless, the tubular design has been examined extensively because of certain desirable characteristics. For example, the small tubular type has a rapid start up time [3], excellent thermal shock resistance and very good power cycling. Hence, micro-tubular SOFCs have good potential to be used for transportation applications and small scale power generation systems. Moreover, the VPD of a SOFC can be increased considerably by decreasing the size of the SOFC to micron level [3,4].

Efforts have been made to fabricate SOFCs with a high electrolyte surface area in order to achieve high VPD [5]. Multi-tubular SOFCs with 61 cells in a single tube have been fabricated. In addition, Yamaguchi et al. reported a honeycomb-type of SOFC [5]. However, it turned out that both types of SOFCs have some drawbacks. It is difficult to obtain very thin, dense electrolytes for honeycomb-type SOFCs. For those two designs, achievement of good current collection was also difficult.

To overcome the above-mentioned problems, a new design has been proposed where the electrolyte surface area has been reduced to some extent by reducing the number of cells in a single tube and increasing the channel diameter. In this work, a multi-tubular SOFC that contained 7 unit cells in one tube has been fabricated using the multi-pass extrusion process [6]. The goal of this work was to fabricate a SOFC with a high specific surface area of the electrolyte. The diameter of this cell was 4.1–4.2 mm after sintering. The characterizations and properties of this cell have been reported.

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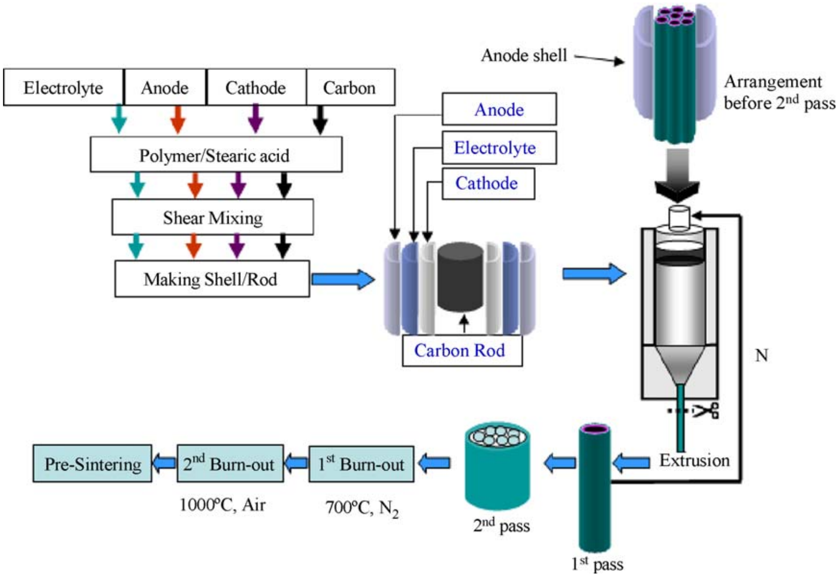

Fig. 1. Schematic diagram of experimental procedure.

2. Experimental procedure

Materials used in this experiment were 8 mol% yttria stabilized zirconia (8YSZ) as electrolyte, NiO-8YSZ as anode and $La_{0.8}Sr_{0.2}MnO_3$ (LSM) as cathode. NiO powders were purchased from Junsei Chemical Co. Ltd., Japan, 8YSZ (TZ-8Y) powders were purchased from Tosoh Corporation, Tokyo, Japan and LSM powders were synthesized by a solid state reaction method [7]. NiO-8YSZ anode powders were prepared by a mechanical mixing method. Activated carbon powders (SMC, Taejon, Korea) were incorporated in both electrodes as a pore forming agent. Ethylene vinyl acetate (EVA) (Elvax 210 and 250, Dupont, Wilmington, DE) and stearic acid ($CH_3(CH_2)_{16}COOH$, Dae-jung Chemicals and Metals Co., Gyonggi, Korea) were used as binder and lubricant, respectively. Using the above starting materials—8YSZ/EVA/lubricant (50:40:10), NiO–8YSZ/EVA/lubricant (50:40:10), LSM/EVA/lubricant (50:40:10), and carbon/EVA/lubricant (48/45/7)—homogenous mixtures were made using a shear mixer (Shina Platec. Co., Suwon, Korea) at 120 °C for 40 min. A schematic diagram of the fabrication process is shown in Fig. 1.

Anode, cathode and electrolyte half shells were prepared with a shear mixed mass using a homemade die. Using the shear mixed mass of carbon, a carbon rod was extruded. The shells of SOFC materials and carbon rod were arranged like a fuel cell structure, keeping the carbon rod inside. This arrangement was set in a die and extrusion was performed at 120 °C using a universal testing machine (R&B, Korea). In this way, the extruded body obtained was termed as the 1st pass extruded body. The 1st pass extruded body was used to prepare the 2nd pass extruded body. In another die, 7 1st pass extruded bodies were arranged in a thin anode tube of two shells (shown in Fig. 1) and extruded in the same way as before. During extrusion, the samples were cut to the desired length. Then, three different types of heat treatment were performed. The 1st burn-out was carried out at a maximum temperature of 700 °C under N_2 atmosphere. In this process, polymer binders were removed. The 2nd burn-out was conducted under an air atmosphere to remove the carbon. After this burn-out, continuous channels were obtained. Then the samples were sintered at 1300 °C for 3 h. The microstructure analysis and phase detection were carried out by scanning electron microscopy (SEM, JSM-635, JEOL, Tokyo, Japan) and X-ray diffraction (XRD, D/MAX-250, Rigaku, Tokyo, Japan), respectively. For measurement of the relative density of the electrolyte, the sample was prepared with only 8YSZ, using the same conditions and same extrusion method employed for the SOFCs. The relative density of the electrolyte was measured by the Archimedes method with an immersion medium of water.

3. Results and discussion

Fig. 2 shows the XRD profiles of multi-tubular SOFC (a) after 1st burn-out, (b) after 2nd burn-out and (c) after sintering at 1300 °C. In profile (a), carbon, cubic (c) ZrO_2, LSM and Ni peaks appeared as the main peaks. All peaks were expected except the peaks of Ni. Actually, NiO was used as a starting material. This is due to the carbo-thermal reaction between NiO and the pore forming agent carbon. Since the 1st burn-out was carried out at 700 °C under N_2 atmosphere, this type of reaction was feasible. In profile (b), the peaks of c-ZrO_2, LSM and NiO appeared as the main peaks but the peaks of carbon and Ni disappeared. The 2nd burn-out was carried out under air atmosphere. Hence, the carbon was burnt out and Ni was oxidized to NiO. The profile taken after sintering shows all the expected peaks without any undesirable peaks. This suggests that the co-sintering of SOFC materials did not show any phase change.

Fig. 3(a) and (b) shows the optical micrographs of 2nd pass extruded bodies in cross-section and longitudinal direction, respectively. The outer layer of the whole sample is the anode,

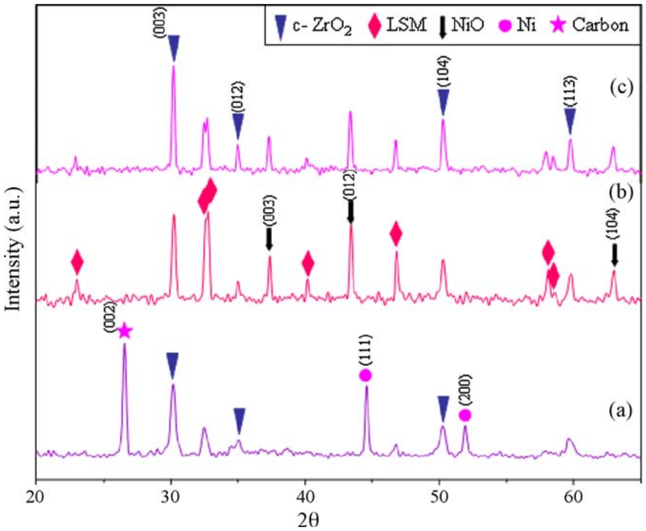

Fig. 2. XRD profiles of multi-tubular SOFC (a) after 1st burn-out, (b) after 2nd burn-out and (c) after sintering at 1300 °C.

which is connected to all 7 unit cells. The thin white layer corresponds to the electrolyte material. In the longitudinal sections, all layers are clearly visible. This suggests that the extrusion was perfect and sound. Fig. 3(c) shows the photographs of the SOFCs sintered at 1300 °C for 2 h. The lengths of the samples were 3–5 cm and the diameter was 5 and 4 mm after extrusion and sintering, respectively. During extrusion, the extruded body can be cut to the desired length. Because of the differences in thermal expansions of the SOFC materials, cracks and defects may appear during co-sintering. Thus, in this experiment, the sample length was limited to 5 cm to avoid damage or any other defects during co-sintering by keeping the thermal expansion in the tolerable range. The scanning electron microscopy images of the sintered SOFC in Fig. 3(d) shows 7 continuous channels, which were formed after burning out of the carbon. Each continuous channel was surrounded by a porous LSM layer and a dense electrolyte layer, respectively, as evident in the enlarge image of Fig. 3(e). The anode layer in between two adjacent continuous pores acts as an anode to both unit cells. If the fuel is supplied on the outer surface of the SOFC, it can travel through the whole anode area by diffusion. The interfaces between electrolyte and anode/cathode were free of any delaminations or cracks. The average diameter of the continuous channels was 400–450 μm and the thickness of the electrolyte layers was 15–20 μm.

Fig. 4 shows SEM images of (a) a longitudinal section and (b–d) its enlarged images sintered at 1300 °C. Continuous channels are shown with arrows in Fig. 4(a). These are the path of oxidant gas, which can flow without any hindrance through these channels. The microstructure of the electrolyte layer is quite dense. The relative density of the electrolyte layer was 96%, measured by Archimedes' principle. The microstructure of the anode and the cathode was porous. Activated carbon was used as a pore forming agent in both the anode and the cathode, and the amount added was 30 vol.%. The anode porosity is increased after the reduction of NiO to Ni.

Even though the activity of the cathode loses porosity to some extent due to the co-sintering, the SOFC increases the volumetric power density significantly. Total power output would come from 7 cells with a diameter of ~4 mm. The electrolyte area per unit volume of the cell would be very high. For this design of SOFC, a new current collection method and experimental set up need to be explored because both electrodes are exposed on the cross-sectional area, which would allow the fuel gas to enter in the cathode also. Fortunately, current collection from the electrode in the channel region can be achieved by inserting Pt/Ag wire or mesh into the channels [5] and from the outer surface, it can be achieved by winding Pt/Ag wire. Gas flowing only through the channels can be ensured by coating a dense layer of electrolyte on the cross-sectional area. This procedure for measuring the performance of multi-tubular cells will be reported in another work.

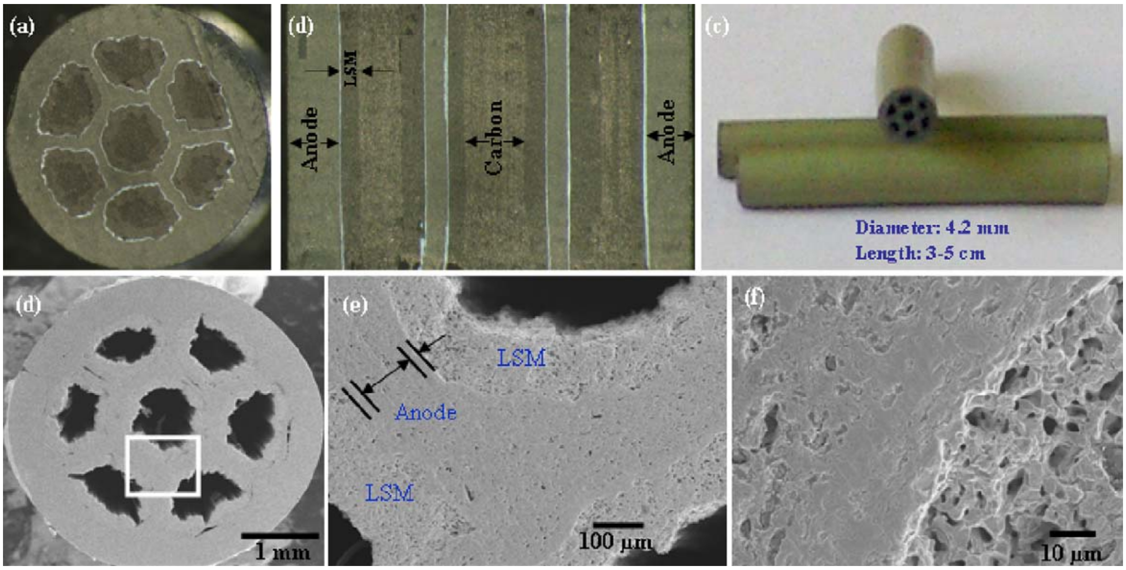

Fig. 3. Optical images in cross-section (a), longitudinal direction (b), photograph of sintered SOFC (c), scanning electron microscopic images of sintered SOFC in cross-section (d), and it is enlarge images (e, f).

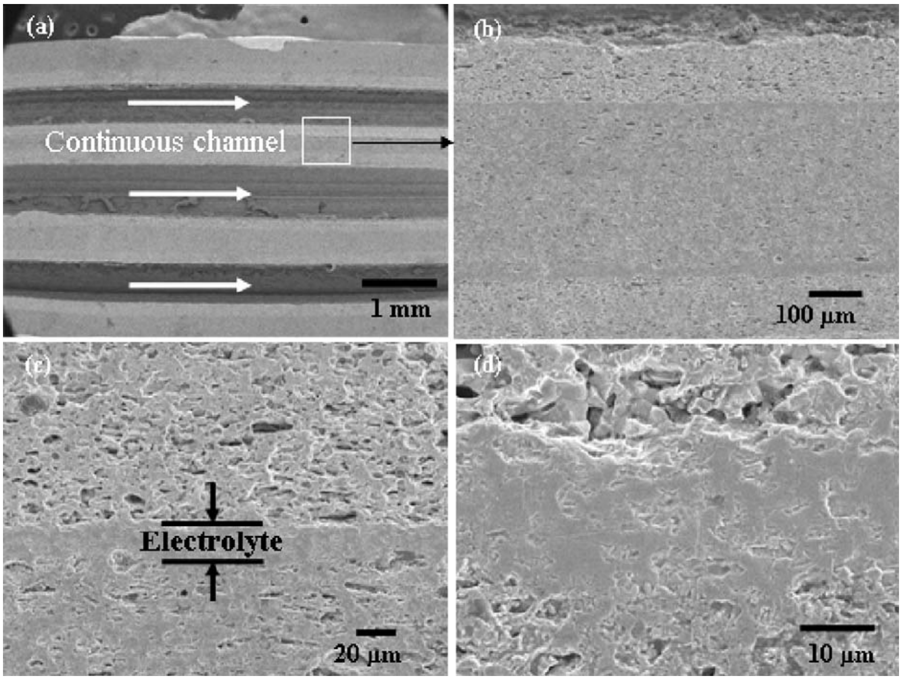

Fig. 4. Scan electron microscopic images of (a) longitudinal section and it's enlarge images (b, c, d) sintered at 1300 °C.

4. Conclusion

A multi-tubular SOFC with 7 cells in one tube has been fabricated without any appreciable imperfection. The diameter of the tube was 4.1–4.2 mm after sintering and the diameter of the continuous channels was around 450 μm. The length of the tube was limited to 3–4 cm to avoid failure due to the thermal expansion. The microstructure of the anode and the cathode was porous while that of the electrolyte was dense. This SOFC is compact; therefore, it would have high volumetric power density.

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