DIRECT-WRITE FABRICATION OF SOLID OXIDE FUEL CELLS

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ABSTRACT

Line-shaped solid oxide fuel cells (SOFCs) with a multilayered structure have been fabricated using the direct-writing process. Partially stabilized zirconia (PSZ) substrate with sufficient mechanical strength and gas permeability was used as a support for SOFC. The cell comprises the single line-shaped electrode and electrolyte of Ni-YSZ cermet anode, YSZ electrolyte, and LSM cathode. A syringe filled with electrolyte paste and each electrode was loaded into the computer-controlled robo-dispensing machine and the paste dispensed onto a moving plate through a 0.21 mm diameter cylindrical nozzle under a pressure of 0.1 torr. The effective reaction area of fabricated SOFC was 0.03 cm², and the thicknesses of anode, electrolyte, and cathode were 20 μm, 15 μm and 10 μm, respectively. The single line-shaped SOFC fabricated by the direct-writing process exhibited OCV of 0.95 V and maximum power density of 0.35 W/cm² at 810°C.

INTRODUCTION

SOFC is expected to be a strong candidate for the next-generation power system due to its high efficiency, waste-heat utilization, and low emission of pollutants to the environment (1,2). Most research and development activities on SOFC are focused on the commercially viable SOFC manufacturing technology with high electrochemical performance, transformation of stack designs, and cost-effective process.

In general, four common stack designs have been proposed and developed for SOFCs: segmented-cell-in-series design, tubular design, monolithic design, and planar design (1-3). Each stack design has a unique manufacturing process. For example, in the general manufacturing process, each electrode device is commonly fabricated via a multilayer build sequence that uses thick film process technologies such as screen printing (4-6) and tape-casting or a tape calendaring process (7,8). As device complexity increases, so does the need for alternative fabrication methods that offer simple and rapid means of integrating multiple materials in multilayers. The direct-write method can allow us the flexibility to design and fabricate the device rapidly in complex multilayer shapes without expensive tooling, dies, or molds (9-11).

Although the drying process is hard to satisfy, the direct-write approach yields significant
advantages over the conventional method for producing multilayer devices, such as those based on lamination of tape-cast layers with screen-printed elements, including the ability to modify patterned designs on-line during production and to incorporate multiple materials in individual layers. Therefore, this method not only increases reproducibility but also makes it possible to produce a micropatterned structure of several materials (11).

In this study, we extended the application of the direct-writing process to the fabrication of SOFCs. As a feasibility study, single line-shaped SOFCs with multilayered structures were produced. This SOFC design type can be easily integrated in series on a plane. The paste materials for each SOFC component that give rise to the desired microstructure were developed and the processing parameters were optimized.

**EXPERIMENTAL PROCEDURE**

Commercial partially stabilized zirconia (PSZ) (TZ3YS, Tosoh Corp.) powder was used to prepare porous support substrate for SOFCs. To obtain a porous microstructure, we used two different methods: resin-containing granular powders and pore-former. PSZ powder was calcined at 1000°C for 2 hours and processed into granules via the liquid concentration process (LCP). The detailed procedure of LCP has been explained elsewhere (12). The granules of PSZ were then uni-axially pressed at 7 MPa and sintered at 1100°C for 1 hour. Starch powders of ~35 μm average particle size were used as the pore former. The calcined PSZ powders were mixed with the starch at 15 wt%. The PSZ pellet was also similarly fabricated.

Commercial NiO (Sumitomo Chemical Co.), yttria stabilized zirconia (YSZ) (TZ3YS, Tosoh Corp.), and (Laₐ₀.₇Sro.₃)o.₉sM₇O₃ (LSM, Seimi Corp.) powders were used as received for each component of SOFCs. They were processed into pastes for the direct writing process. The NiO-YSZ cermet anode paste with a solids loading of 15 vol% was prepared by dispersing a mixture of NiO and YSZ in a weight ratio of 6:4 in α-terpineol, which contains ethyl cellulose and an appropriate dispersing agent, followed by planetary milling at 250 rpm for 12 hours with zirconia balls in a Teflon® mill container. The YSZ electrolyte and LSM cathode pastes were prepared in the same manner as anode paste with the same solids loading.

A syringe was filled with electrode and electrolyte paste and loaded into the computer-controlled robo-dispensing machine. Each paste was dispensed through the cylindrical nozzle 0.21 mm in diameter under air pressure of 0.1 torr onto a moving plate with 1.22 mm/s. First of all, the anode paste was dispensed on the PSZ porous substrate with the length of 10 mm and the width of 0.5 mm. After drying of the anode paste at 90°C for 50 min, the electrolyte paste was dispensed with the length of 12 mm and the width of 1.5 mm. The anode/electrolyte and the PSZ substrate were co-fired at 1350°C in an air atmosphere for 3 hours. The cathode layer was similarly dispensed and sintered at 1200°C for 1 hour. All the electrode/electrolyte lines were visually aligned during the direct writing process.

The porosity and gas permeability of PSZ substrate were measured with a mercury porosimeter (Micrometrics, USA) and perm porometer (PMI, USA), respectively. The
rheological characteristics of each paste were measured with a cone and plate-type viscometer (CV100, Haake). The resulting SOFC was observed using optical microscopy (DMLM, Leica) and environmental scanning electron microscopy (ESEM) (FEIXL-30 FEG, Philips). The cell was placed in the hot zone of a vertical furnace and gold wires used as a current collector for anode and cathode lines at both ends. The current-voltage and power characteristics were measured with an SOFC test station (Toyo, SAT890-100 W) in the temperature range of 700°~800°C. Air was used as an oxidant, and 3% moisturized hydrogen gas (H₂ + 3% H₂O) was used as a fuel with flow rate of 700 and 500 sccm, respectively.

RESULTS AND DISCUSSION

The substrate that supports SOFC structure requires good mechanical strength and porosity for fuel transport to the anode. To achieve this, two approaches were tested. Figure 1 (a) represents the microstructure of PSZ formed after completely burning out the starch used as a pore former. Relatively large pores with a nonuniform size distribution of 25–50 μm were observed. In contrast, the PSZ substrate made with the LCP method showed a uniform microstructure composed of very fine pores with a narrow distribution of around 1.5 μm. The surface microstructure of the substrate plays an important role in multilayer structure fabrication by the direct-writing process. Successive deposition of pastes and drying on top of a substrate with a rough surface finish leads to either pinhole formation or crack generation in the electrode/electrolyte lines during drying. The PSZ substrate made with starch as a pore former had large pores whose size was close to one-tenth of the dispensed line width, resulting in defect generation during drying. Therefore, we used the substrate prepared from the LCP granulation method.

The PSZ substrate processed by the LCP method showed a relatively high porosity of 40 percent and a permeability constant of 3.69 x 10^12 m², indicating that gas permeated through the substrate at 600 cc/min when the pressure difference was about 30 psi. The substrate also maintained enough mechanical strength to be used as a support.

The line width and height of the resulting pattern of selective paste dispensing depend on the rheological behavior of the paste and on processing parameters such as the speed of the nozzle head, the gap between the substrate and the nozzle, the size of the nozzle

Figure 1. Cross-sectional SEM image of porous PSZ substrate manufactured by (a) pore former (starch) and (b) LCP granulation process.
orifice, the substrate roughness, and the applied pressure level. The rheological behavior of the paste determines the spreading and wetting characteristics of the paste extruded from the nozzle tip and the microstructural features of the formed line patterns.

Thus the amounts of binder and dispersant for each paste were optimized to produce an SOFC component with desirable microstructure and line dimensions. The apparent viscosities ($\eta_{app}$) of anode and electrolyte pastes were measured with a shear rate range of $0 \sim 200 \text{ s}^{-1}$, as shown in Figure 2. The viscosities depend on the binder content and the type of powder in the paste.

![Figure 2. Rheological behavior of each constituent paste with varying binder concentration.](image)

The line pattern of the high-viscosity paste was thicker than that of the low-viscosity paste under the same processing conditions. The electrolyte layer formed from the paste with 10 wt% ethyl cellulose was $\sim 40 \mu\text{m}$ thick; with the paste of lower binder content it was $\sim 25 \mu\text{m}$ thick. The thicker layer cracked during drying; the thinner layer survived. Each layer of an SOFC component must have good electrochemical performance; the electrolyte should be thin with no pinhole defects to minimize ohmic resistance, and the thickness and porosity of the electrodes must be controlled. Thus, the composition of the paste and the processing conditions were optimized. Figure 3 shows the resulting single line-shaped SOFC with multilayer aligned cell design.

![Figure 3. Cross-sectional SEM image of direct-write fabricated cell after sintering.](image)
Figure 3 shows the cross-sectional microstructure of direct-write SOFC manufactured by the dispensing process. The PSZ substrate was observed to have a uniform porous structure, whereas the anode layer was about ~20 μm thick and slightly dense due to the relatively high firing temperature of 1350°C. The YSZ electrolyte was almost fully densified with a thickness of ~15 μm. The cathode layer also showed homogeneous porous structure with a thickness of ~15 μm. All the layers exhibited good adhesion to each other without delamination. In addition, each layer has the microstructure that is necessary to enhance unit cell performance.

The area of the porous substrate unoccupied by the line-shaped SOFC cell was sealed using Mn-added PSZ paste and ceramic/glass composite sealant, and the electrical contact leading to the each electrode at its ends was made with Au paste.

Figure 4 shows the cell performance curves of the direct-written cell under the operating condition of 3% H2O added hydrogen as a fuel and air as an oxidant at 755°C and 810°C. Open circuit voltage (OCV) was 0.95 V at 810°C, which was slightly lower than the theoretical value. This low OCV may result from the existence of a little gas leakage across imperfect sealing of the porous support. The maximum power density is 0.35 W/cm² at 810°C.

CONCLUSIONS

We have developed a novel manufacturing technique called the direct writing by dispensing method. The paste compositions for each component and the processing parameters must be well-controlled to produce SOFCs with the desired microstructure and cell configuration. Our preliminary study demonstrated that the resulting cell shows a maximum power density of 0.35 W/cm² at 810°C. The present method is suited for fabricating integrated SOFCs and for adaptation to large-scale manufacturing process.
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