

Temperature-Controlled Microextrusion Printing for Mesoscale Interfacial Designing in Solid Oxide Fuel Cells

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Abstract

A temperature-controlled microextrusion printing technique is proposed to realize the increased aspect ratio of mesoscale convex structures at the anode–electrolyte interface in solid oxide fuel cells (SOFCs). The rheological properties of the anode ink for microextrusion printing are experimentally measured at various temperatures, and it is found that the viscosity of the ink and the wettability of the ink to the anode substrate decrease at lower temperatures, which is desirable for the ink to retain its shape on the substrate. The anode-supported SOFC button cells are fabricated by microextrusion printing with and without temperature control and compared in terms of their interfacial structures and electrochemical performance. The aspect ratio of the interfacial structure is increased from 0.16 to 0.28 by lowering the ink temperature, resulting in a higher interface enlargement of 25%. Owing to the enlarged interfacial area, enhanced cell performance is also achieved.

Keywords: Electrode–Electrolyte Interface, Microextrusion Printing, Powder Suspension, Rheology, Shape Retention, Solid Oxide Fuel Cell, Temperature

1. Introduction

Solid oxide fuel cells (SOFCs) are a type of fuel cells that are operated at relatively high temperatures, typically around 700 °C, and they offer various advantages over other types of fuel cells, including enhanced reaction kinetics, fuel flexibility, and the capability of direct internal reforming of hydrocarbons [1, 2]. Therefore, SOFCs are expected to be the devices that realize clean and high-power generation in the following decades. However, to become economically competitive with well-established energy conversion technologies, it is always necessary to pursue the development of cells with the high power density and low operating temperature [3, 4].

An electrode–electrolyte interfacial area modification is one of the approaches to enhancing the electrochemical performance of SOFCs. The electrochemical reactions in SOFC electrodes mainly occur near the electrode–electrolyte interface [5-8]. Therefore, enlarging the reaction region near the interface is considered effective in decreasing the activation overpotential associated with the electrochemical reaction [9]. Since the thickness of the reaction region, also called the active thickness, is around 10–20 μm , structures on a similar geometrical scale are desirable. In addition, the ohmic loss in the electrolyte is also decreased by the interfacial enlargement, as reported by Seo et al. [10] because the local ionic current density is reduced compared with a conventional cell at the same cell current density.

Thus far, various fabrication technologies, such as laser-assisted machining and micro powder imprinting [11-13], have been proposed for electrode–electrolyte interface enlargement, and enhanced electrochemical performance has been achieved. A more

detailed literature review on interfacial modification techniques can be found in our previous reports [10, 14]. However, it was reported that the grooved structures fabricated by the subtractive techniques are difficult to control precisely. Also, the cell components are prone to damage during mechanical processing [12, 15, 16]. As an alternative, a microextrusion-printing-based additive manufacturing technique is appreciated because of less material waste, free contact with printed objects, and the capability to fabricate precise structures [17]. We have applied this technique to the fabrication of anode-supported SOFCs to obtain enhanced cell performance [10, 14]. However, the interface enlargement achieved in that study was no more than ca. 11% because the anode ink was prone to spread on the anode support disc after deposition, indicating that the shape retention after the deposition of the anode ink was poor. In addition, numerical simulation results have shown that there remains far more potential for cell performance enhancement if we can achieve a greater electrode–electrolyte interface enlargement on the mesoscale (10–100 μm) [9, 18–20]. This might be achieved by improving the capability of the anode ink for shape retention during the microextrusion printing process.

The rheological properties of the ink can be a determining factor of the quality of the printed structures [17, 21]. During the microextrusion printing process, the ink must flow smoothly through a micronozzle but, on the other hand, maintain the shape after deposition. The ink used for microextrusion printing is usually a non-Newtonian and shear-thinning fluid whose viscosity depends on the shear rate. A typical method of improving the shape retention of the ink is to increase the solid load in the ink mixture to reduce the fluidity of the ink [10, 22, 23]. However, a highly viscous ink might clog a micronozzle with an extremely small inner diameter. Alternatively, the temperature is also

a well-known factor that affects the rheological behavior of non-Newtonian fluids [17]. However, temperature has not been the main focus of the studies of microextrusion printing in the literature and its effects on fabricated structures have not been investigated or understood.

In this work, therefore, a temperature-controlled microextrusion printing method is proposed to improve the shape retention capability of the printed ink and applied to the fabrication of SOFCs to enhance their electrochemical performance by increasing the electrode–electrolyte interfacial area. Specifically, the temperature of the anode substrate is lowered during the printing process to prevent the deposited anode ink filament from deforming on the surface, while the temperature of the micronozzle is kept at room temperature to avoid clogging. First, the rheological properties of a homemade anode ink are experimentally measured at several temperatures. Second, an anode support layer with a mesoscale convex surface is fabricated by temperature-controlled microextrusion printing. The aspect ratio of the fabricated convex structures is analyzed by cross-sectional microscope imaging. Subsequently, the electrochemical performance of the cell fabricated by temperature-controlled microextrusion printing is evaluated and compared with those of the flat cell and the cell fabricated by conventional microextrusion printing without temperature control.

2. Experimental

2.1. Anode ink and anode support disc

A terpeneol-based anode ink was used in this study for microextrusion printing. Fine-grade NiO powder (Sumitomo Metal Mining Co., Ltd., Japan) and $\text{Y}_{0.08}\text{Zr}_{0.92}\text{O}_{1.96}$ (YSZ)

powder (TZ-8Y, Tosoh Corp., Japan, crystallite size = 22 nm) were mixed with a homemade ink binder (96 wt% terpineol and 4 wt% ethylcellulose) for 12 h at 500 rpm using a planetary ball miller to obtain a homogeneous anode ink. The weight ratio of the NiO–YSZ mixed powder (NiO: YSZ = 65.8:34.2 wt%) in the anode ink was 60 wt%. This yields the volumetric ratio of powder: binder = 18.6: 81.4. The air was removed from the anode ink through the degassing process of stirring at 0.15 atm for 10 min.

A tape-casting technique was used to fabricate the porous anode substrate. First, the mixed powder consisting of 54 wt% NiO powder (FUJIFILM Wako Pure Chemical Corp., Japan, average particle size of *ca.* 1–2 μm), 36 wt% YSZ powder, and 10 wt% pore former (crosslinked polymethyl methacrylate, Techpolymer SSX-series, Sekisui Kasei Co., Ltd., Japan, average particle size of *ca.* 8 μm) as a pore former was prepared by planetary ball milling. The obtained mixed powder was mixed with ethanol as a solvent and Triton X-100 (MP Biomedicals, LLC) as a dispersant for 24 h. Subsequently, polyvinyl butyral (PVB, Mowital B60H, Kuraray Co., Ltd., Japan) as a binder and polyethylene glycol (PEG400, FUJIFILM Wako Pure Chemical Corp., Japan) and glycerine (Nacalai Tesque Inc., Japan) as plasticizers were added to the mixture and mixed for 24 h to form a homogeneous anode slurry. The detailed composition of the anode slurry is summarized in Table 1. The obtained slurry was stirred at 0.15 atm for 10 min to remove the dissolved gas before tape casting. Subsequently, the slurry was tape-cast on a glass plate at a speed of 10 mm s⁻¹ with a doctor blade gap of 2.0 mm using a commercial tape caster (Imoto Machinery Co., Ltd., Japan). Afterward, the tape was thoroughly dried and cut into a disc shape with a diameter of 30 mm. The obtained green disc was pre-sintered at 1150 °C for 2 h to ensure robustness for the subsequent fabrication processes.

2.2. Rheological and wetting properties of the anode ink

The rheological properties of the prepared anode ink at various temperatures were experimentally studied. A rotational double coaxial cylinder viscometer (Viscolead ADV, Fungilab, S.A., Spain) was used to measure the shear stress and apparent viscosity of the anode ink. The measurement was conducted with a shear rate ranging from 0.08 to 25 s⁻¹. The temperature of the anode ink was maintained at 10, 25, or 50°C by immersing the cylinder in a thermostatic water bath.

The wettability of the anode ink to the porous anode support disc described in section 2.1 was investigated by measuring the contact angle formed between an anode ink droplet and the disc using an optical microscope (VHX-900 Series, KEYENCE Corp., Japan). The measurement was also carried out on an alumina substrate with a dense surface. The temperature of the disc/substrate was controlled using a Peltier element to investigate the effect of the disc/substrate temperature on the wettability of the anode ink to the disc/substrate.

2.3. Temperature-controlled microextrusion printing

Microextrusion printing technique was used to fabricate anode ridge structures on the surface of the flat anode support disc. To increase the shape retention capability of the printed anode ink, the temperature of the anode substrate was controlled. The experimental setup is schematically shown in Fig. 1. A gas-tight syringe filled with the prepared anode ink described in section 2.1 was vertically fixed on a syringe pump (Pump 11 Elite Nanomite, Harvard Bioscience, Inc., USA) above the anode support disc whose

temperature was controlled using a Peltier device. The printing was conducted on an anode support disc at 5 and 24 °C. The temperature of the anode ink in the syringe was kept at room temperature (around 24 °C). The position of the anode support disc was precisely controlled by manipulating motorized *x-y*-axis stages. In this study, we designate the patterned cell fabricated at room temperature as PTN_RT, the patterned cell fabricated at a low temperature (5 °C) as PTN_LT, and a flat cell without patterns as FLT. Table 2 shows the parameters used for fabricating PTN_RT and PTN_LT. The printing area was 16 mm × 16 mm for both patterned cells. The outer shape of the convex structures after printing was measured using a 3D surface profiler (VR-3100 Series, KEYENCE Corp., Japan) to evaluate the aspect ratio of the printed anode convex structures. It should be noted that the temperature control technique was employed only on the printed substrates in this study; therefore, the temperature of the ink flowing inside the micronozzle is unaffected and kept at room temperature.

2.4. Full-cell fabrication

A spin coating technique was used to deposit the materials of the anode functional layer (AFL), the YSZ electrolyte layer, and the gadolinium-doped ceria (GDC, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$) barrier layer. The homemade binder described in section 2.1 was used to prepare spin-coating slurries. The identically prepared anode slurry was used in forming the anode ridge structures and AFL to create a crack-free electrolyte film by matching their thermal shrinkage ratios during the high-temperature sintering [14]. The weight ratios of the YSZ and GDC powders (GDC-10(AU), Shin-Etsu Astech Co., Ltd., Japan) in their electrolyte slurries were 25 wt%. All the slurries were prepared by planetary ball milling at 500 rpm for 12 h to ensure homogeneity.

An appropriate amount of the NiO–YSZ AFL slurry was painted onto the disc surface where the anode ridge structures were formed, followed by spin coating at 8000 rpm for 60 s. After drying the AFL slurry at 200 °C on a hot plate for 1 min, the YSZ electrolyte slurry was then spin-coated onto the AFL and dried in the same way, followed by a sintering process in the air at 1400 °C for 5 h with heating and cooling rates of 120 and 200 °C h⁻¹, respectively. Onto the YSZ electrolyte layer, a GDC barrier layer was spin-coated to prevent a chemical reaction between the YSZ and the lanthanum strontium cobalt ferrite (LSCF) material in the cathode. The conditions for spin coating the GDC barrier layer were the same as those for the AFL and YSZ electrolyte, and sintering was performed in air at 1250 °C for 2 h with heating and cooling rates of 200 °C h⁻¹.

The cathode material was deposited by a screen printing technique. A cathode paste consisting of 60 wt% LSCF (La_{0.6}Sr_{0.4})_{0.97}Co_{0.2}Fe_{0.8}O₃, LSCF-6428-N, Kceracell Co., Ltd., Korea)–GDC mixed powder (LSCF: GDC = 50:50 wt%) and a 40 wt% commercial ink vehicle (VEH, Nexceris, LLC, USA) was prepared by planetary ball milling at 600 rpm for 1 h. The obtained cathode paste was screen-printed on the GDC barrier layer with a mask thickness of 60 µm, followed by sintering in the air at 950 °C for 5 h with heating and cooling rates of 200 °C h⁻¹. The final apparent geometrical area of the cathode was ca. 0.785 cm².

The purpose of applying the AFL is to enable a fair comparison between the flat and patterned cells. Since the ASL was fabricated with the pore former with the size of ca. 8 µm, its structure has a higher porosity and hence lower TPB density than those of the

anode ridge structures. Therefore, without the AFL, the TPB density in the active reaction area near the anode–electrolyte interface would be significantly different between the flat and the patterned cells.

2.5. Electrochemical measurement and microstructure analysis

The prepared cells were electrochemically evaluated by a fuel cell evaluation system (Microtrac MRB, Japan). The tested cell was fixed between two alumina tubes with Pyrex glass rings attached at the end of the tubes for gas sealing. More details can be found elsewhere [24]. The operating temperature of the cells was controlled using an electric furnace. The electrode surfaces were painted with silver paste (Nexceris, LLC, USA) for better electrical connection, and a platinum mesh was used to collect the current. The current–voltage (i – V) and AC impedance characteristics were measured using a Solartron 1455A frequency response analyzer and a Solartron 1470E potentio/galvanostat electrochemical interface (AMETEK Inc., USA).

A reduction treatment for NiO in the anode was carried out before the electrochemical measurement. The cell was heated to 800 °C, and H₂–N₂ mixture gas with a total flow rate of 100 sccm was supplied. The proportion of H₂ was gradually increased from 0 to 100% over 1 h and then kept at 100% for a further 1 h. The electrochemical measurement was conducted at 600 and 700 °C with 100 sccm of 20% humidified H₂ as fuel and synthetic dry air (N₂:O₂ = 79:21) as an oxidant. The electrochemical impedance analysis was performed at the open-circuit voltage (OCV) with an applied current amplitude of 10 mA and a frequency range of 10⁻¹ to 10⁵ Hz. After testing, the cell was cooled to room temperature in a reducing atmosphere.

Scanning electron microscopy (SEM, Miniscope TM3000, Hitachi High-Tech Science Corp., Japan) was used to observe the cross-section of the anode convex structures. The tested cells were impregnated with epoxy resin (EpoFix, Struers, Denmark) under an atmosphere of 34 kPa at room temperature for 10 min. This helps to identify the solid and pore phases in the anodes. After curing, the samples were cut and polished to expose the cross-section.

3. Results and Discussion

3.1. Rheological characteristics of anode ink

The rheological properties of anode ink are shown in Fig. 2. The square block symbols in Fig. 2(a) show the shear stresses of the anode ink obtained in the experiment at 10, 25, and 50 °C as a function of the shear rate. It is found that the shear stress is nonzero when the shear rate is zero. This indicates that the anode ink can flow only if the applied shear stress exceeds the yield stress. In addition, when the shear stress is larger than the yield stress, the anode ink shows a shear-thinning behavior, meaning that the gradient in the graph, corresponding to the viscosity of the ink, decreases with the shear rate. These rheological behaviors allow the anode ink to be extruded smoothly during printing as long as shear stress greater than the yield stress is applied and also to retain its shape after printing when the shear stress is removed. The viscosity of the ink is found to decrease with temperature, indicating that the temperature dependency of the fluid proposed by Andrade [25] is also valid in the ink with a high solid volume fraction (18.6%). Similar trends were reported in the literature [26-29], although most fluids analyzed had solid volume fractions below 10%.

The solid lines in Fig. 2(a) show the curves fitted to the data measured using the generalized model of non-Newtonian fluids, the Herschel–Bulkley model, which considers the yield stress and the shear thinning behavior:

$$\tau = \tau_0 + K\dot{\gamma}^n \quad (1)$$

where τ is the shear stress, τ_0 is the yield stress correlated with the viscoelasticity of the fluid, K is the fluid consistency, $\dot{\gamma}$ is the shear rate, and n is the flow index. Table 3 shows the fitted results for each temperature. It is found that the yield stress τ_0 and the flow index n decrease with temperature. This indicates that the anode ink can be smoothly extruded from the nozzle when the temperature of the ink is increased. In addition, if the extruded ink is immediately cooled after deposition, the ink is expected to show an improved shape retention capability for the deposited anode ridge structures.

Fig. 2(b) shows the measured contact angles of the anode ink with a porous anode substrate and a dense alumina substrate at various temperatures. First, it can be seen that the contact angle with the anode disc is always greater than that with an alumina substrate, which indicates a lower wettability of the anode ink to the porous anode disc. This means that the surface energy of the anode disc is lower than that of the alumina substrate; the lower surface energy prevents the adhesion of the deposited anode ink, resulting in better shape retention. Furthermore, it can be seen that the temperature of the disc and substrate affects the wettability of the anode ink. The contact angle increases in both cases as the temperature of the disc/substrate decreases, indicating better shape retention. The contact angle of the anode ink with the anode disc at 5 °C is about 82°.

In summary, the viscosity and wettability of the anode ink are reduced at lower temperatures, resulting in the improved shape retention of the deposited structure on the substrate. Therefore, from the rheological results obtained in this section, better shape retention is expected to be achieved by lowering the temperature of the printed anode substrate. In addition, warming the ink in the micronozzle can decrease the ink viscosity and hence avoid clogging, although it was not employed in this study.

3.2. Ridge structure

After studying the rheological properties of the anode ink, the temperature-controlled microextrusion was applied to fabricate the anode ridge structures on an anode support disc to extend the anode–electrolyte interfacial area. Fig. 3 shows the measured outer shapes of the anode ridge structures fabricated on the anode support disc using a micronozzle with an inner diameter of 100 μm . The support disc temperature was varied at 5, 15, and 30 $^{\circ}\text{C}$. The graph clearly shows that the anode ridge structures become higher and narrower (the aspect ratio becomes greater) as the temperature of the anode disc decreases. Specifically, when the temperatures of the anode support disc are 5, 15, and 30 $^{\circ}\text{C}$, the widths of the anode ridge structures printed by the micronozzle with an inner diameter of 100 μm are about 120, 134, and 156 μm and their heights are about 118, 104, and 95 μm , respectively; thus, their aspect ratios are calculated to be 0.98, 0.78, and 0.61, respectively. Note that these are the values just after printing. Therefore, these results verify that the proposed temperature control method can improve the capability for shape retention. Further increase in the aspect ratio of the ridge structures can be expected at even lower temperatures; however, the ink binder may freeze at around 0 $^{\circ}\text{C}$, which makes it challenging to carry out the drying process after printing. In addition, water

condensation from the ambient air may occur on the anode disc, which may damage the fabricated ridge structures. Therefore, in the following section, the anode ridge structures in PTN_LT were fabricated at 5 °C.

The SEM images of PTN_RT and PTN_LT were obtained to observe the anode ridge structures. Figure 4(a) shows the cross-sectional SEM image of the flat cell and Figs. 4(b) and (c) show those of the anode ridge structures in the patterned cells. They clearly show that narrower and taller structures are successfully formed in PTN_LT than in PTN_RT. The width and height of the anode ridge structures in PTN_RT are 156 and 26 μm and those in PTN_LT are 131 and 37 μm , respectively; thus, the aspect ratios of the anode ridge structures are 0.16 and 0.28 in PTN_RT and PTN_LT, respectively. The figures also show that the YSZ electrolyte is densely formed in both patterned cells without any observable defects. The electrolyte thickness at the top of the ridge structures is slightly smaller than that between the ridge structures. This is because the viscosity of the YSZ electrolyte slurry for spin coating was low for pursuing a thin uniform electrolyte layer and hence tended to flow from the top of the ridge structures to the bottom before being dried. A perfectly uniform electrolyte thickness might be obtained by employing other fabrication techniques that enable uniform formation on a complex surface, such as radiofrequency sputtering [3]. Also, the cathode layer is successfully fabricated without any visible defect or delamination.

Because narrower ridge structures can be fabricated in PTN_LT by temperature-controlled microextrusion printing, a shorter pitch of the anode filaments on the same printing area was realized in PTN_LT, as shown by the double-headed white arrows in

Figs. 4(b) and (c). This results in an interface enlargement on the anode side of about 25% in PTN_LT, which is greater than that in PTN_RT (ca. 18%) and almost double of those in the patterned cells in our previous studies [10, 14]. Since the electrolyte thickness, including the dense YSZ electrolyte and the porous GDC barrier layer, is 5~10 μm , the cathode-electrolyte interfacial area is also enlarged by a similar percentage. It can be seen in Fig. 4(c) that there is space remaining to further shorten the pitch. However, the YSZ electrolyte between the ridge structures tended to break during the sintering process when the ridge structures were too close to each other. The YSZ electrolyte breakage problem could also be fixed by radiofrequency sputtering since it is a sintering-free process, which will be the focus of our future work. After several attempts, a pitch length of 240 μm was determined for PTN_LT. The

3.3. Electrochemical performance

Figure 5 shows the i - V and i - P characteristics of the cells at the operating temperatures of 700 and 600 $^{\circ}\text{C}$ with 80% H_2 -20% H_2O as fuel. Table 4 shows the theoretical and measured OCVs. The measured OCVs of the cells are close to the theoretical values calculated from the Nernst equation at each operating temperature. It is worth noting that the OCVs of the patterned cells are almost the same as those of the flat cell, which indicates that the YSZ electrolyte with a thickness of no more than 5 μm has been successfully densified even on the ridge structures, providing sufficient gas tightness during electrochemical testing. This is because of the excellent match of the thermal shrinkage ratios of the anode ridge structures and AFL, which was also found in our previous study [14]. The electrochemical performance of the patterned cells is significantly enhanced at both operating temperatures compared with that of the flat cell

because of the increase in the electrode–electrolyte interfacial area. Moreover, PTN_LT exhibits further enhanced performance compared with PTN_RT. The peak power density achieved with PTN_LT (ca. 1.28 W cm⁻²) is 7.6% greater than that of PTN_RT (ca. 1.19 W cm⁻²) at 700 °C. Furthermore, from Fig. 5(b), the peak power density of PTN_LT (ca. 0.44 W cm⁻²) is enhanced by 30.6 % compared with that of PTN_RT (ca. 0.34 W cm⁻²) at 600 °C. This is because the effect of the interface enlargement becomes more significant at lower operating temperatures, which is because the reduction in cell overpotential becomes larger with decreasing operating temperature. This agrees with the conclusion of our previous studies [10, 14].

Figure 6 shows the Nyquist plots of the electrochemical impedance spectroscopy (EIS) results measured under the OCV condition at the operating temperatures of 700 and 600 °C with 80% H₂–20% H₂O as a fuel. The results were analyzed by fitting with the equivalent circuit model shown in Fig. 7(a). With this model, the internal resistance of the cells was separated into three components: ohmic resistance (R_0) and polarization resistance in the high and low-frequency regions (R_1 and R_2). L is the inductance of the wiring for the current collection, and CPE is the constant phases element. Figures 7(b) and (c) show the area-specific resistances obtained by equivalent circuit fitting analysis at 700 and 600 °C, respectively. As clearly shown in the figures, R_0 and R_1 in the patterned cells are reduced, while R_2 is not significantly changed under both operating temperature conditions, compared with that of the flat cell. In the patterned cells, R_0 in PTN_LT is further reduced compared with that in PTN_RT. For instance, R_0 is 0.11 Ω cm² in PTN_RT and 0.094 Ω cm² in PTN_LT, whereas it is 0.13 Ω cm² in FLT at 700 °C; thus, the decreases in R_0 of PTN_RT and PTN_LT relative to FLT are calculated to be 15%

and 28%, respectively. The reduction in the ohmic resistance R_0 is mainly because of the decreased local ionic current density in the electrolyte. A more detailed mechanism and its theoretical analysis are reported in our previous report [10]. It has been shown in Fig. 4 that PTN_LT has a greater interface enlargement than PTN_RT. Therefore, the local current density in PTN_LT is smaller for the same current density, leading to a more reduced ohmic resistance. The inhomogeneity of the electrolyte thickness also reduces the ohmic resistance further, as discussed in our previous study [30].

The polarization resistance in the high-frequency region, R_1 , is also reduced in the patterned cells compared with that in the flat cell, as shown in Fig. 7. It can be considered that R_1 is associated with the activation resistance of the electrodes [10, 11]. The reduction in R_1 also becomes greater with increasing interfacial area: e.g., it is calculated to be about 29% in PTN_RT and 42% in PTN_LT at 700 °C. The larger interfacial area leads to a reduced local current density; thereby, the charge-transfer current per unit reaction site decreases, which results in the reduction in R_1 [10]. On the other hand, the polarization resistance in the low-frequency region (R_2) is almost the same in the three cells. The impedance in this region can be associated with the gas transport in the anode support layer [10, 11] because the thicknesses of the AFL and cathode layer are negligibly small compared with that of the anode support layer (*ca.* 450 μm). Since the materials and the fabrication techniques of the anode support layer were identical in the tested cells, the gas diffusion resistance is almost the same. In other words, the ridge structure on the anode substrate does not significantly change the gas diffusion pathways.

As discussed above, it can be concluded that the performance enhancement in the patterned cells is mainly contributed by the reductions in R_0 and R_1 . The reductions in R_0 and R_1 become greater with increasing the electrode–electrolyte interfacial area. Consequently, the performance of PTN_LT is the highest among the three tested cells, and this superiority is a result of using the temperature-controlled microextrusion printing technique proposed in this study.

4. Conclusions

A temperature control method was applied to the microextrusion process to improve the capability of the fabricated structures for shape retention, and anode-supported SOFCs were fabricated. Structures with an increased aspect ratio were successfully obtained, and a shorter pitch was realized in the same printing area. Consequently, the electrode–electrolyte interfacial area was further increased, leading to an enhanced electrochemical performance of the SOFC. Firstly, we experimentally investigated the temperature dependence of the rheological properties of the anode ink. The results suggest that an improved capability for shape retention can be achieved by printing the anode ink on a cooled anode support disc. Then, we applied the temperature control method to fabricate PTN_LT, and a further increased electrode–electrolyte interfacial area (ca. 25%) was obtained compared with PTN_RT (ca. 18%) fabricated without the temperature control method. A YSZ electrolyte provided sufficient gas tightness, and an LSCF–GDC cathode was successfully fabricated without delamination on the surface-modified cells. PTN_LT shows superiority in terms of electrochemical performance, which is a result of the greater interface enlargement. It is also considered that the temperature control method can be

applied not only in patterned SOFC fabrication but also in other fields in which microextrusion printing is used.

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Table with legends

Table 1: Composition of NiO–YSZ anode slurry.

Powder			Solvent	Dispersant	Binder	Plasticizer	
/ wt. %			/ wt. %	/ wt. %	/ wt. %	/ wt. %	
NiO	YSZ	PMMA	Ethanol	Triton	PVB	PEG 400	Glycerine
28.6	19.1	5.30	33.8	1.06	6.36	2.89	2.89

Table 2: Printing parameters for patterned cells.

Parameter	PTN_RT	PTN_LT
Stage speed / mm s ⁻¹		3.0
Extrusion flow rate / $\mu\text{L min}^{-1}$		3.0
Micronozzle inner diameter / μm		100
Temperature of anode support disc / °C	24	5
Pitch length / μm	300	240

Table 3: Rheological properties of anode ink at different temperatures.

Temperature / °C	τ_0 / kPa	K / kPa s ⁻ⁿ	n / -
10	0.435	0.350	0.495
24	0.342	0.214	0.412
50	0.203	0.118	0.298

Table 4: Theoretical and measured OCVs at 600 and 700 °C with 80% H₂.

Temperature / °C	Theoretical value / V	FLT / V	PTN_RT / V	PTN_LT / V
600	1.06	1.04	1.02	1.04
700	1.03	1.02	1.01	1.01

Figures

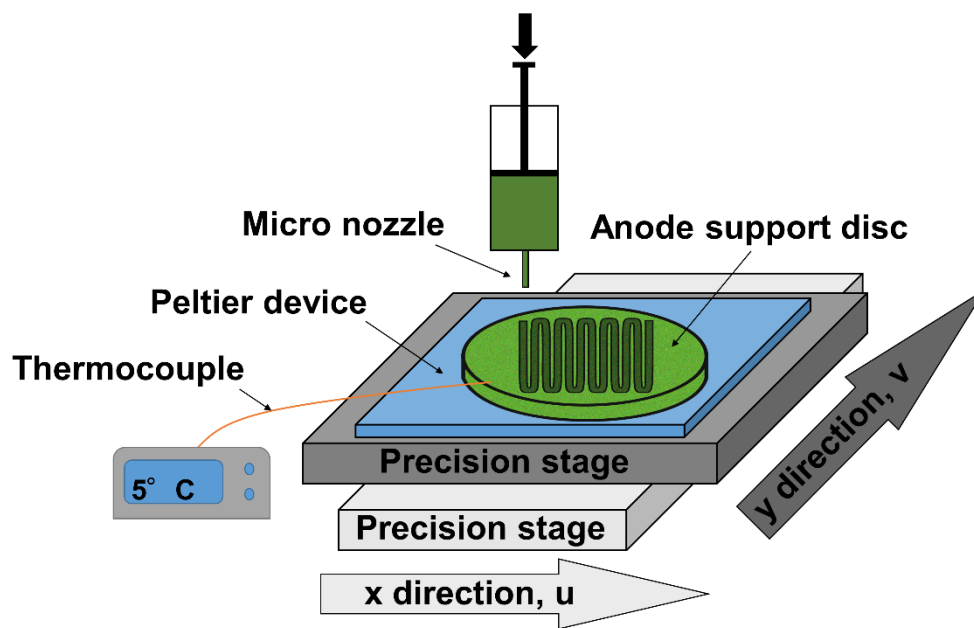


Figure 1: Schematic image of temperature-controlled microextrusion printing.

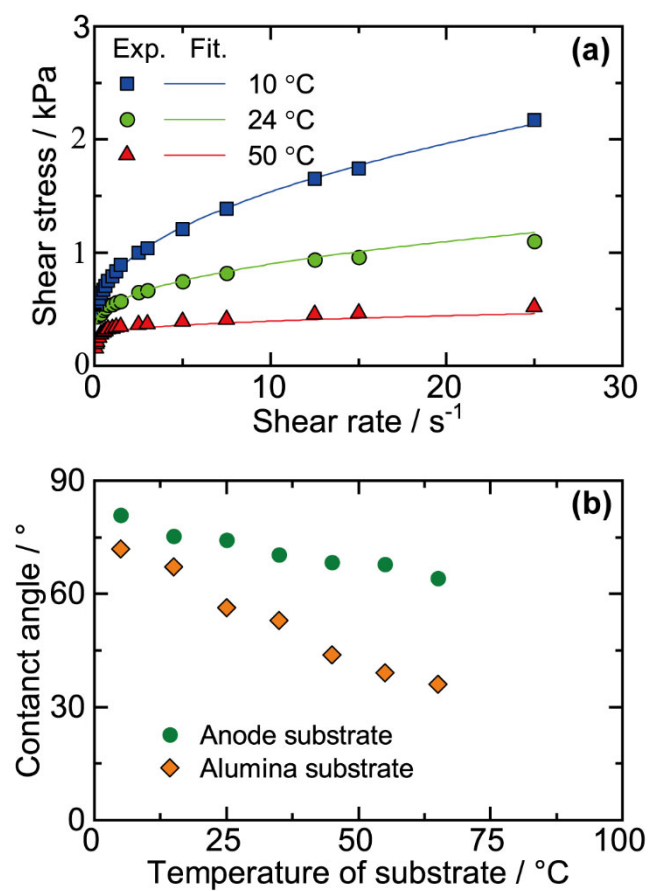


Figure 2: Rheological properties of anode ink at various temperatures: (a) shear stresses and (b) contact angles of anode ink droplet with the anode support disc and alumina substrate.

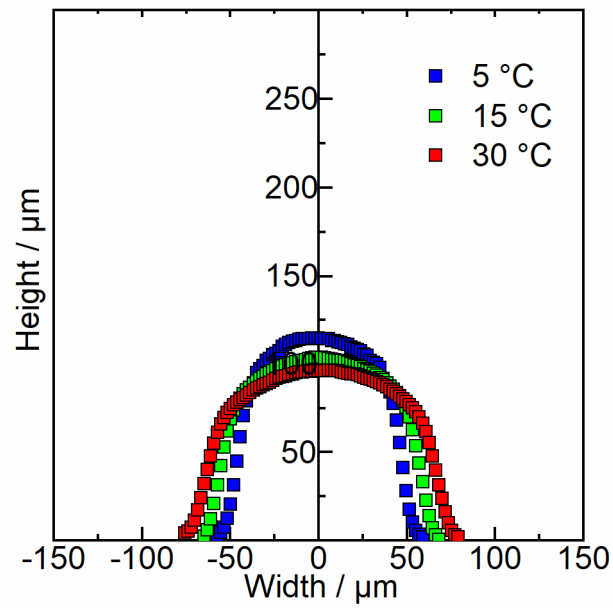


Figure 3: Outer shapes of anode ridge structures fabricated on anode support disc at temperatures of 5, 15, and 30 °C using a micronozzle inner diameter of 100 μm .

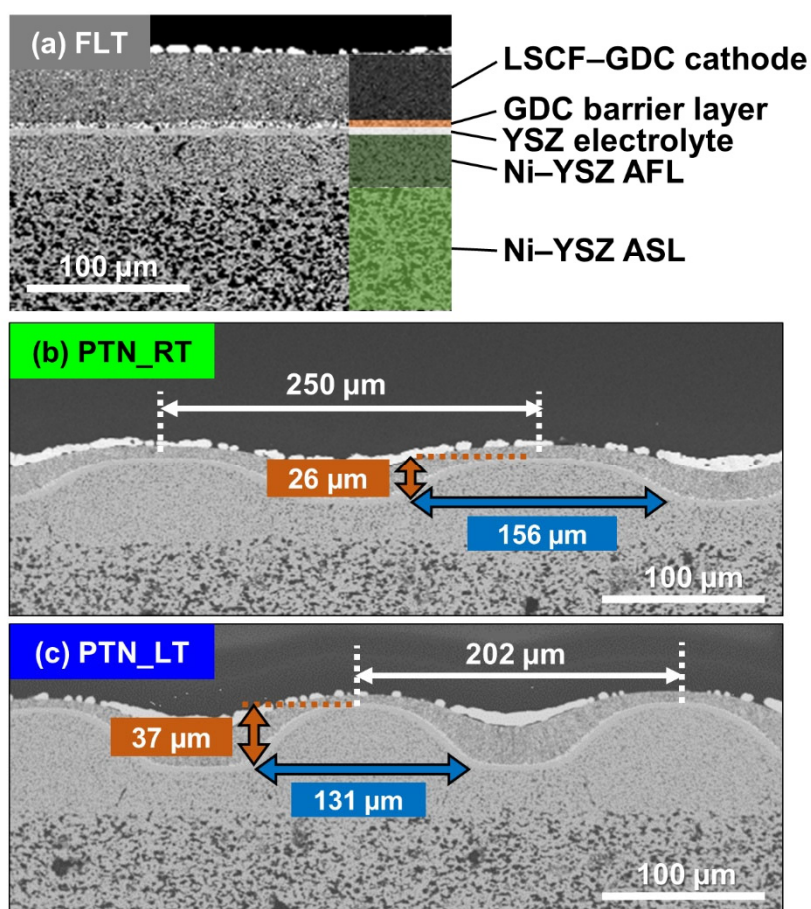


Figure 4: Cross-sectional SEM images of (a) flat and (b), (c) patterned cells: (b) anode ridge structure fabricated at room temperature (24 °C) and (c) anode ridge structure fabricated at low temperature (5 °C).

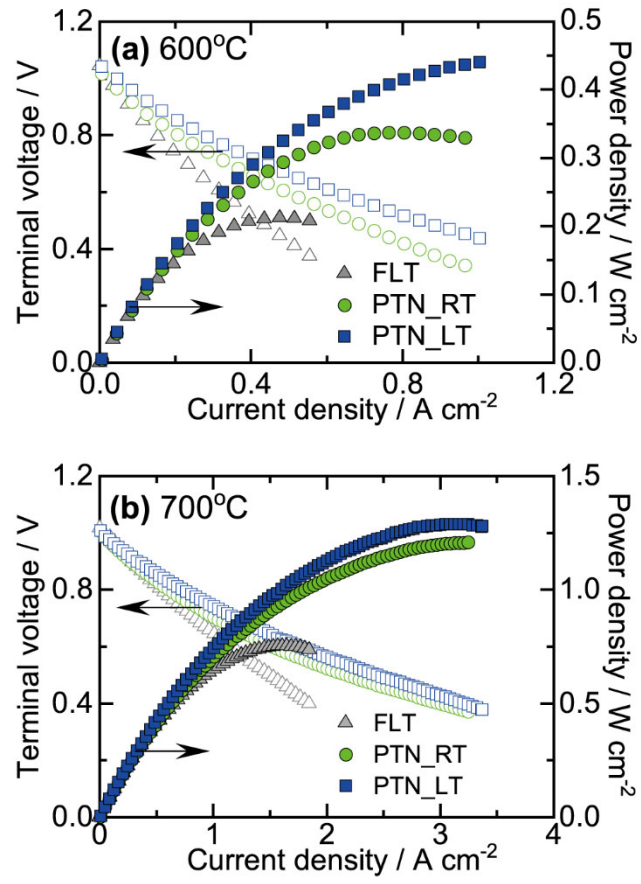


Figure 5: i - V - P curves of the cells tested at the operating temperatures of (a) 700 °C and (b) 600 °C with 80% H₂-20% H₂O.

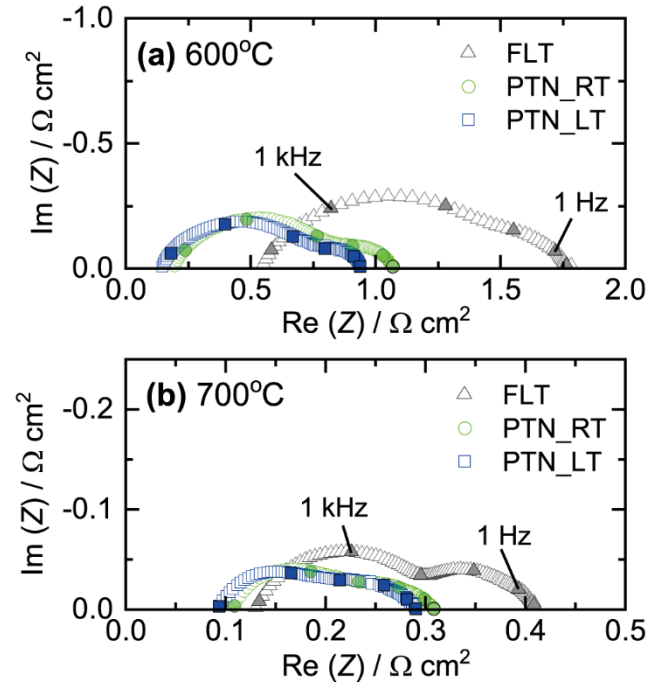


Figure 6: Nyquist plots of EIS of cells at (a) 700 °C and (b) 600 °C with 80% H₂–20% H₂O under OCV condition.

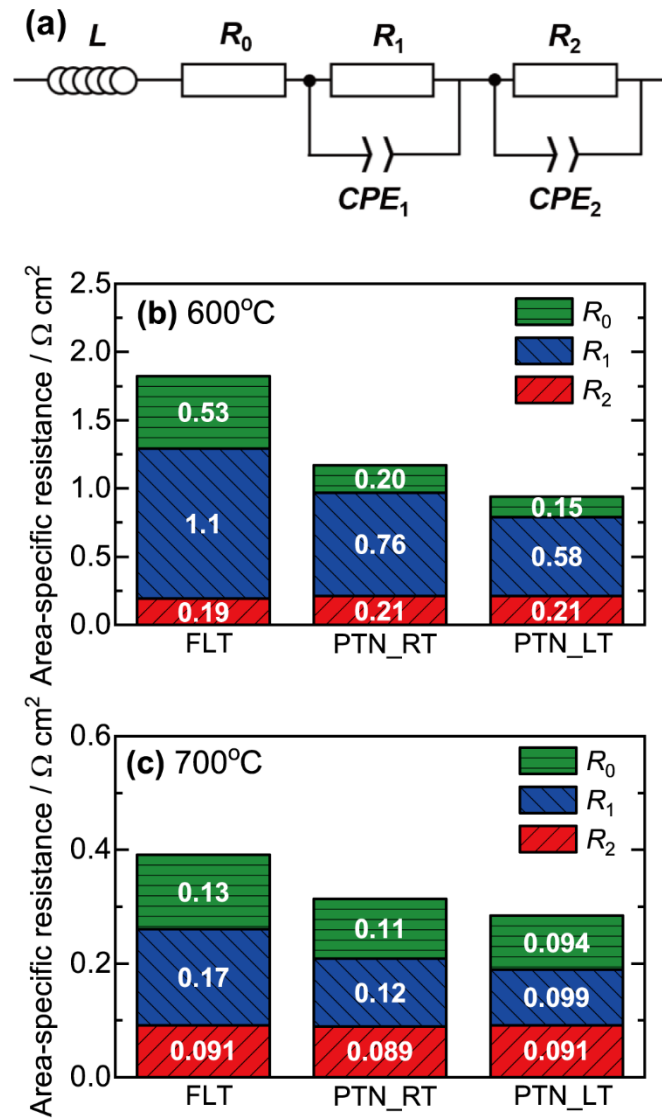


Figure 7: (a) Equivalent circuit model for the fitting analysis and area-specific resistances of cells at (b) 700 °C and (c) 600 °C with 80% H₂–20% H₂O as fuel.