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Preparation of YSZ/YDC and YSZ/GDC composite electrolytes by the tape casting and sol-gel dip-drawing coating method for low-temperature SOFC

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The composite electrolytes for low-temperature solid oxide fuel cells were fabricated via coating the YSZ sol on tape-casted substrates of yttria doped ceria (YDC) and gadolinia doped ceria (GDC). The doped ceria substrates with 98% of relative density were prepared by the tape-casting method followed by the sintering at 1,500°C for 2 hours. The YSZ polymeric sol for dip-drawing coating was synthesized by the partial hydrolysis of Zr-n-butoxide. The optimum dip-drawing coating rate for obtaining pinhole and crack free YSZ film was 2 cm/min using YSZ polymeric sol with 1.13 mol/ℓ of concentration. After 10 times coating on ceria substrates with YSZ followed by the heat-treatment at 1,400°C for 2 hours, the fully densified YSZ film with 2.0 μm of thickness without pores, cracks, or chemical reactions could be obtained. The results of single cell tests shows that YSZ layer coated doped ceria composite electrolyte prepared by the sol-gel dip-drawing method has an superior single cell performance to YSZ electrolyte without dissociation of ceria substrate.

1. Introduction

Solid oxide fuel cells (SOFC) are expected to provide a highly efficient power-generation system for future application [1, 2]. However, SOFCs based on YSZ (yttria stabilized zirconia) operate at around 1,000°C due to the limitation of the conductivity of solid electrolyte. Such a high operating temperature results in high material costs for interconnect materials and insulation as well as in fast system degradation due to the reactions at the interfaces between cell components. These problems can be overcome by lowering the operating temperature from 1,000°C to 800°C. The advantages of a reduced-temperature operation for SOFCs include wider material choice, longer cell life, improved reliability, and potentially reduced fuel cell cost.

In order to operate a SOFC at a lower temperature with high power output, the higher ionic conductive material should be used such as doped ceria, $BaCeO_3$, or $LaGaO_3$ [3–7]. Among them, doped ceria is considered as a solid electrolyte that is possibly competitive with stabilized zirconia for use in reduced-temperature SOFCs because of its having higher ionic conductivity. At low oxygen partial pressures, however, doped ceria shows a mixed conducting behavior exhibiting both ionic and electronic conductivity. Moreover, cerium dioxide (CeO_2) is easily dissociated to cerous oxide (Ce_2O_3) at high temperature in low oxygen partial pressure atmosphere followed by the pore formation or mechanical failure due to the difference of the lattice volume between two phases [3–5]. Researches, therefore, have been done to repress the electronic conduction and enhance the chemical stability of doped ceria by coating with pure ionic conducting material such as YSZ [8–10].

In this work, the characteristics of composite electrolytes prepared by a dip-drawing coating of thin YSZ film on tape-casted doped ceria substrates have been investigated as a basic research of the development of a new electrolyte material for reduced-temperature SOFCs. Among the various thin film process, the sol-gel process was chosen by virtue of its low processing temperatures, homogeneity, possibility of coating on substrates with large areas, and low cost.

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TABLE I Slurry composition for tape casting of substrates

Materials	Solid	Solvent		Binder	Plasticizer	Dispersant	Homogenizer
	Doped ceria	Toluene	2-propanol	Polyvinylbutyral	Dibutylphthalate	Menhaden fish oil	Triton-X
Supplier	–	Duksan Phar. Co., Korea	Yakuri Pure Chem. Co., Japan	Sigma-Aldrich Chem. Co., USA	Junsei Chem. Co., Japan	Sigma-Aldrich Chem. Co., USA	Duksan Phar. Co., Korea
Content	100 g	45 ml	90 ml	20 g	20 ml	2 ml	2 ml

2. Experimental

2.1. Fabrication of doped ceria substrate by the tape-casting method

Homogeneous yttria-doped ceria ($Ce_{0.8}Y_{0.2}O_{1.9}$, YDC) powder was obtained by the calcination at 600°C for 2 hours of oxalate co-precipitates synthesized by the method described in the literature [11, 12]. Gadolinia-doped ceria ($Ce_{0.8}Gd_{0.2}O_{1.9}$, GDC) powder was purchased from Praxair Specialty Ceramics (USA). To improve the sinterability of the powders, dry ball-milling was performed using zirconia balls in polypropylene containers for 3 days and the particle size was examined with a laser diffraction particle size analyzer (Par-III, Otsuka, Japan).

The slurry compositions for tape casting of doped ceria substrates were summarized in Table I. After the mixing of ingredients, de-airing was conducted with a mechanical vacuum pump for several minutes in order to control the viscosity of slurry in the range of 5,000–6,000 cP and to eliminate the dissolved air. After the tape-casting and drying, green sheets were punched into disk units ($\phi = 26$ mm, after sintering). Thermal analysis for dried tape was examined in order to determine the heating schedule for eliminating the organic components without the development of warpage or cracks using TG/DTA apparatus (TGDTA92, Setaram, France). To determine the optimum sintering temperature, the apparent densities of the sintered substrates heat-treated at 1,300–1,600°C for 2 hours were measured by the Archimedes method (ASTM C 373-88). The microstructures present were observed by scanning electronic microscopy (S-2000, Hitachi, Japan).

2.2. Preparing of composite electrolyte by sol-gel dip-drawing coating

Stable YSZ polymeric sols for dip-drawing coating were synthesized by the partial hydrolysis of zirconium n-butoxide followed by the addition of yttrium nitrate as described in the literature [10, 13]. The concentration and viscosity of YSZ polymeric sol for coating was controlled using vacuum evaporator. The viscosity of prepared sols were measured using B-type viscometer (DV-II$^+$, Brookfield, UK). The dip-drawing coating method was used to deposit thin YSZ films on the doped ceria substrates. We varied the drawing speed in up to 10.0 cm/min. After drying, the pre-heat-treatment was performed at 600°C for 2 hours. The dip-drawing coating, drying, and pre-heat-treatment procedures were repeated up to 10 times to control the thickness of YSZ layer. Finally, specimens were heat-treated at 1,400°C for 2 hours to densify the deposited film. The surface morphology of the composite electrolytes was observed using scanning electronic microscopy, and interfacial chemical reaction between films and substrates was examined using X-ray diffraction apparatus (D/MAX Rint 2000, Rigaku, Japan).

2.3. Single cell tests

YSZ coated ceria, uncoated ceria and YSZ substrates were tested at 900°C and 1,000°C in a fuel cell mode using single cell test equipment shown in Fig. 1 with hydrogen through a bubbler placed in ice-water bath of which temperature was maintained at 0°C and with oxygen as the fuel and oxidant gas, respectively. The single cell test equipment was designed using spring-loaded alumina tubes to improve the gas sealing of Pyrex O-ring and the electric contact between electrodes and current collector. For preparing electrodes, both sides of an electrolyte disc were coated with platinum paste (TR-706, Tanaka, Japan) by a screen printing method followed by the heat-treatment at 1,200°C for 2 hours to remove the organic ingredients in platinum paste and to reduce the contact resistance between electrolyte and electrodes. In the case of composite electrolytes, the YSZ side was exposed to fuel in subsequent testing. Multimeter (2000, Keithley, UK) and DC current source (228A, Keithley, UK) were used to measure the open circuit voltage (OCV) and I-V characteristics.

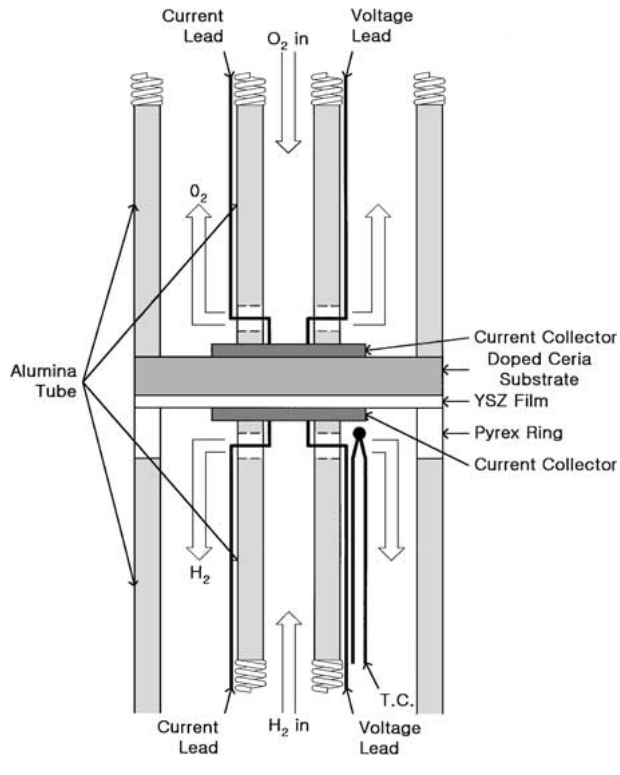

Figure 1 Schematic diagram of single cell test equipment.

3. Results and discussion

3.1. Sintering of tape-casted doped ceria substrates

In order to obtain a good result by tape-casting, that is a crack-free, flat, homogeneous and dense substrate, organics listed in Table I should be effectively burned out without a deformation of the green-sheet. So, thermal analysis was performed and the results are shown in Fig. 2. An exothermic peak at 280°C with the 12.5% of weight loss is corresponded to the decomposition of plasticizer, dispersant, and homogenizer while another one at 310°C with 5.3% of weight loss the decomposition of binder. As seen in Fig. 2, it was found that most of organic component of green tape were burned out in the narrow range of 200–350°C and terminated below 400°C. To avoid the development of warpages and cracks, therefore, the burning-out stage was conducted at a heating rate of 0.5°C/min from room temperature to 400°C and at a holding of 250°C, 300°C, and 400°C for 3 hours, respectively.

Fig. 3 shows the relative densities of YDC and GDC substrates sintered at various temperatures. Higher than 98% of theoretical density was obtained when samples were sintered at 1,500°C for 2 hours in both. It is considered that the density difference between two samples was caused by the difference of their average particle size; that of YDC powder is about 500 nm while GDC about 750 nm. We determine the optimum firing condition of sintering at 1,500°C for 2 hours based on the result of Fig. 3 and the appearance of dense microstructures as can see in Fig. 4.

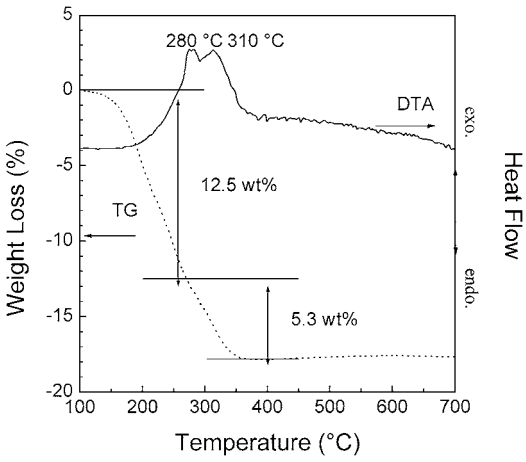

Figure 2 TG/DTA curves of a green tape.

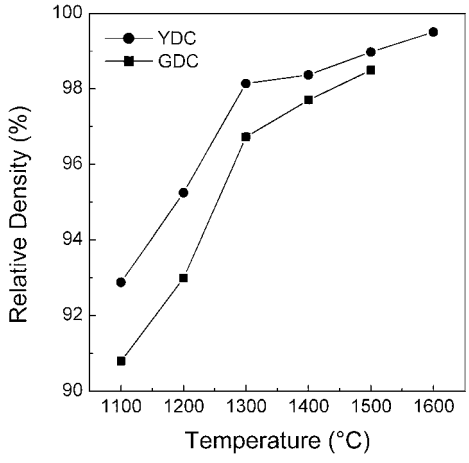

Figure 3 Density variations of doped ceria electrolytes as a function of sintering temperature.

3.2. Coating of YSZ layer on doped ceria substrate by dip-drawing

Table II shows the properties of the three YSZ polymeric sols with the different concentrations used in this research. When the YSZ polymeric sol was concentrated, the viscosity of the sol was increased but no gelation or precipitation was observed. Being stored at −20°C for 1 year, moreover, the YSZ sol had not undergone a increase in its viscosity. Fig. 5 shows the viscosity variation of the YSZ sol with the shear rate. It is well known that, to produce a defect-free gel fiber or gel coating layer, the sol with a chain-like structure of which viscosity would not change with shear rate was recommended [14]. The chain-like sol particle can easily slip down each other during drying without significant internal strain that causes defect in gel film. It could be seen from Fig. 5 that the YSZ polymeric sol was composed of chain-like polymers at a sol concentration of less than 1.13 mol/ℓ.

YSZ films were prepared on the sintered doped ceria substrates made by tape casting by a dip-drawing coating at 2.0 cm/min of drawing speed using the sols described in Table II. The coated side was the plane of substrate contact with carrier film during the tape-casting process. Coated samples were dried at room temperature over 12 hours and heated at a rate of 1°C/min to 600°C in order to prevent the crack generation due to the difference in the thermal expansion coefficient between films and substrates. Fig. 6a shows the thickness variation of YSZ films coated as a function of sol concentration after the heat-treatment at 600°C for 2 hours. The thickness of film increased linearly with the increase of sol concentration. It is found that the films annealed at 600°C were transparent when sol concentration was smaller than 1.13 mol/ℓ. The thickness of each coating layer is approximately 240 nm when use the sol of which concentration is 1.13 mol/ℓ. But, thicker films prepared using more concentrated sol tended to have some cracks. The appearances of the films using the sol of which concentration is 1.13 mol/ℓ after being heat-treated at 600°C for 2 hours at different dip-drawing speeds presented in Fig. 6b show that the film thickness increased linearly with drawing speed and the films of which thickness was over 200 nm became cracked. It can be seen that a slow rate, 2.0 cm/min, was preferable for the preparation of crack-free films. Much thicker films can be obtained by repeating the coating

TABLE II Characteristics of various YSZ sols

Sol	Concentration (mol/ℓ)	Viscosity (cP)[a]
Y1	1.00	6
Y2	1.13	8
Y3	1.31	12.5

[a]Values were at room temperature & 60 rpm shear rate.

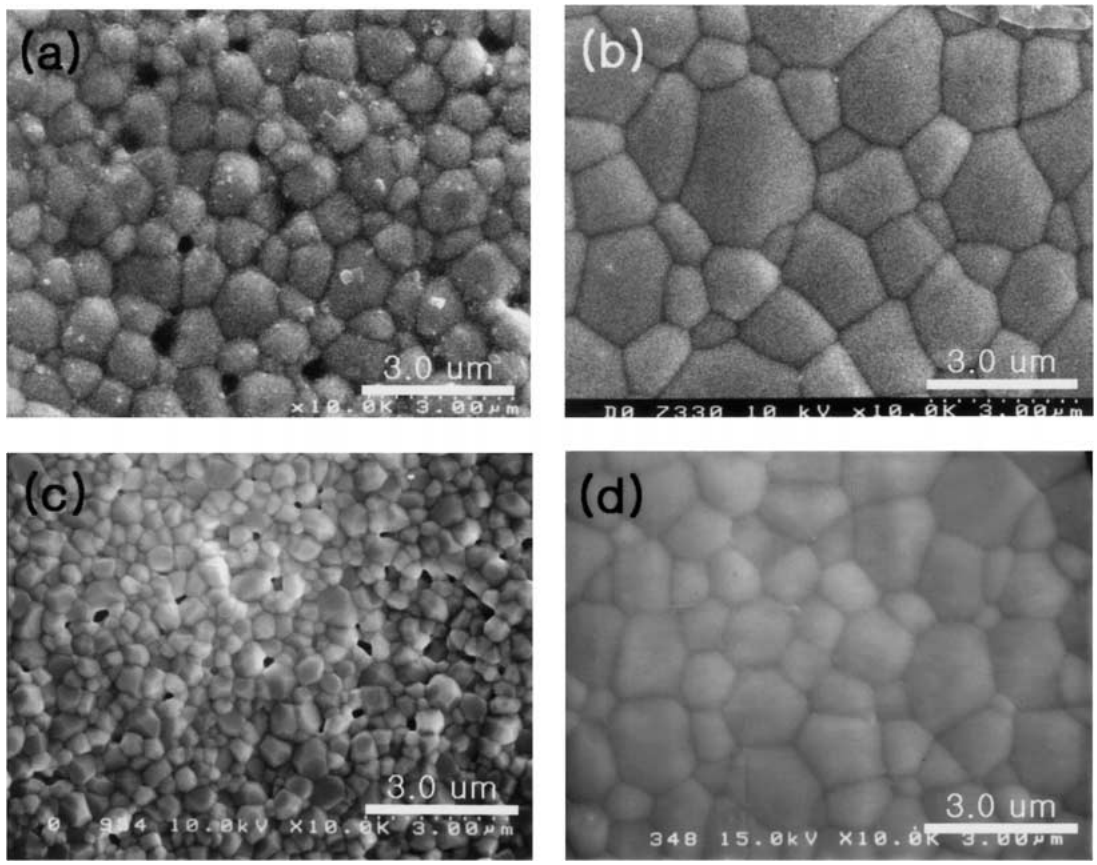

Figure 4 SEM micrographs of YDC substrate sintered at (a) 1,400°C and (b) 1,500°C, and GDC substrate sintered at (c) 1,400°C and (d) 1,500°C for 2 h.

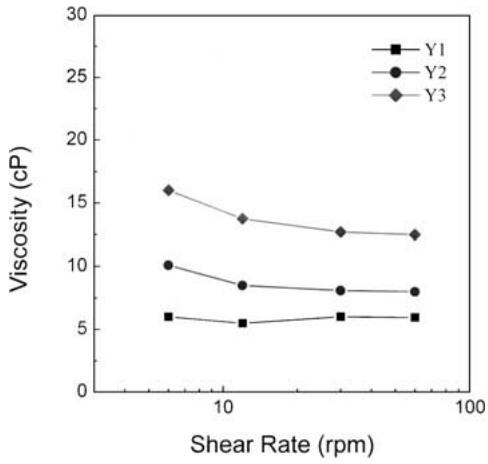

Figure 5 Viscosity of YSZ sols versus solid content and shear rate.

cycle composed of dip-drawing, drying, and pre-heat-treatment. The linear relationship between the number of coatings and the YSZ film thickness were observed. The composite electrolyte for further studies were fabricated with 10 times coating because it was reported that the thickness of YSZ film must be over 2.0 μm to prevent the dissociation of cerium dioxide to cerous oxide and suppress the electronic conductivity [15, 16].

3.3. XRD patterns and microstructures of composite electrolytes

It had reported that the reaction gave a cubic fluorite phase of yttria-doped ceria-zirconia (YCZ) solid solution initiated at 1,500°C or higher temperature [17]. The presence of YCZ phase that is poor electrolyte with low ionic conductivity degraded the performance of single cell. Hence, the YSZ film should be densified under 1,500°C to suppress the formation of YCZ phase at interface between doped ceria substrate and YSZ film. In our research, therefore, the composite electrolytes were heat-treated at 1,400°C for 2 hours. The XRD patterns of calcined xerogel, YDC and GDC powder, and YSZ/YDC and YSZ/GDC composite electrolytes are shown in Fig. 7. These results confirmed that composite electrolytes after a heating at 1,400°C were consisted of the two cubic fluorite phases, doped ceria and YSZ, and the solid state reaction between two phases did not proceed at this heat-treatment temperature.

The SEM micrographs of the surface and a cross-section of the composite electrolyte coated 10 times after heat-treatment are shown in Fig. 8. The surface microstructure of composite electrolyte proves that no pores and cracks were generated and fully densified YSZ films were obtained after heat-treatment at 1,400°C for 2 hours. The thickness of the YSZ layer after 10 coatings was around 2 μm and the interface between YSZ film and doped ceria substrate was well developed as can see in the micrographs of cross-section.

3.4. Single cell characteristics of composite electrolytes

A cell with YSZ/GDC, YSZ/YDC, YDC, GDC, and YSZ electrolytes were tested in a fuel cell mode. The open-circuit voltage for each temperature is

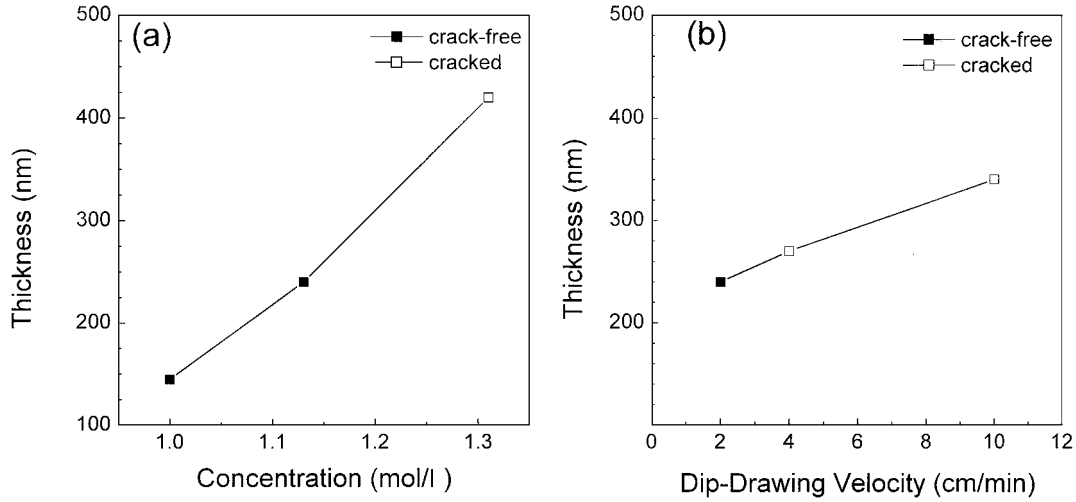

Figure 6 YSZ film thickness as a function of (a) sol concentration, and (b) dip-drawing speed after the heat-treatment at 600°C for 2 h.

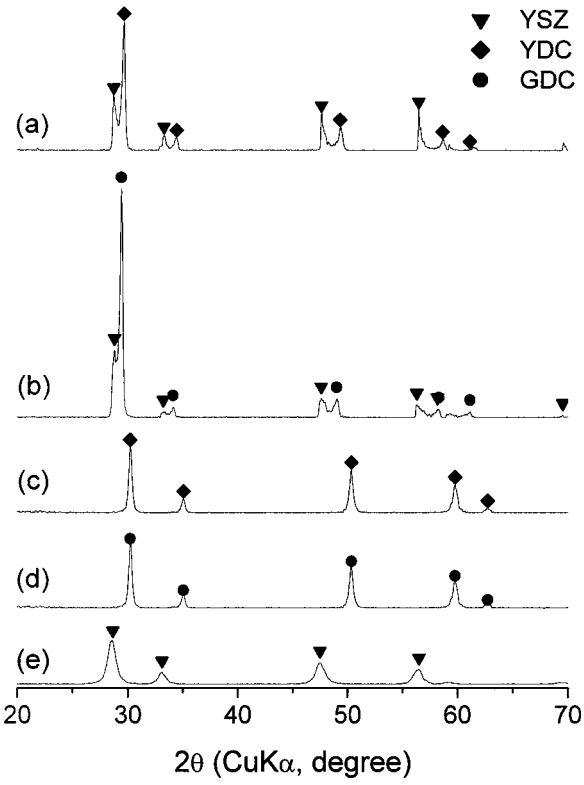

Figure 7 XRD patterns of (a) YSZ/YDC and (b) YSZ/GDC composite electrolyte heat-treated at 1,400°C for 2 h, (c) YDC powder calcined at 600°C, (d) GDC powder, and (e) YSZ xerogel heat-treated at 1,000°C.

summarized in Table III. The YSZ single cell was also prepared by tape casting. The OCV values for the single cells with composite electrolytes were higher than that for the doped ceria electrolyte without YSZ layer. These clarify that the electronic conductivity of ceria is restrained from YSZ layer and the oxygen partial pressure of the interface between YSZ layer and doped ceria substrate ($pO_{2,\,Inter}$) was increased [15, 16]. The equilibrium oxygen partial pressure for the Ce_2O_3/CeO_2($pO_{2,\,Eq}$) in $Ce_{0.8}Gd_{0.2}O_{1.9}$ solid solution is about 2.5×10^{-20} atm [18] and the oxygen partial pressure at anode side of the single cell test equipment illustrated in Fig. 1 ($pO_{2,\,Anode}$) was 1.87×10^{-21} atm. When using uncoated GDC as electrolyte, therefore, the anode side of electrolyte becomes being dissociated because $pO_{2,\,Anode}$ is an order of magnitude lower than $pO_{2,\,Eq}$. The YSZ/GDC composite electrolyte, however, can be used as an electrolyte without such a dissociation because the calculated value of $pO_{2,\,Inter}$ using the equations in literature [15, 16] is as high as 4.0×10^{-4} atm that is sixteen order of magnitude higher than $pO_{2,\,Eq}$.

TABLE III Performance of single cells

Temperature	Electrolyte	OCV (V)
1000°C	YSZ	1.170
	GDC	0.598
	YSZ/YDC	0.659
	YSZ/GDC	0.673
950°C	YSZ	1.176
	GDC	0.634
	YSZ/GDC	0.695
900°C	YSZ	1.179
	GDC	0.670
	YSZ/GDC	0.725

The YSZ single cell shows higher cell voltage at low current density region under 100 mA/cm^2. Since doped ceria is more oxygen ionic conductive than YSZ, however, the cell voltage of YSZ/GDC and GDC single cells became higher than that of YSZ single cell at high current density region over 100 mA/cm^2. The cell voltage difference between YSZ/GDC and GDC single cell can be negligible due to the thin thickness and well-developed microstructure of YSZ layer as shown in Fig. 8. While the maximum power density of YSZ single cell is 100 mW/cm^2 at 300 mA/cm^2, that of YSZ/GDC single cell is 160 mW/cm^2 at the current density of 400 mA/cm^2 which value is the limitation of out single cell test equipment, and the improved results is expected at the higher current density region. The results mentioned above imply that YSZ layer coated doped ceria composite electrolyte prepared by the sol-gel dip-drawing method shows superior single cell performance to YSZ electrolyte by virtue of the high oxygen ionic conductivity without dissociation because of higher oxygen partial pressure of the anode side of doped ceria substrate.

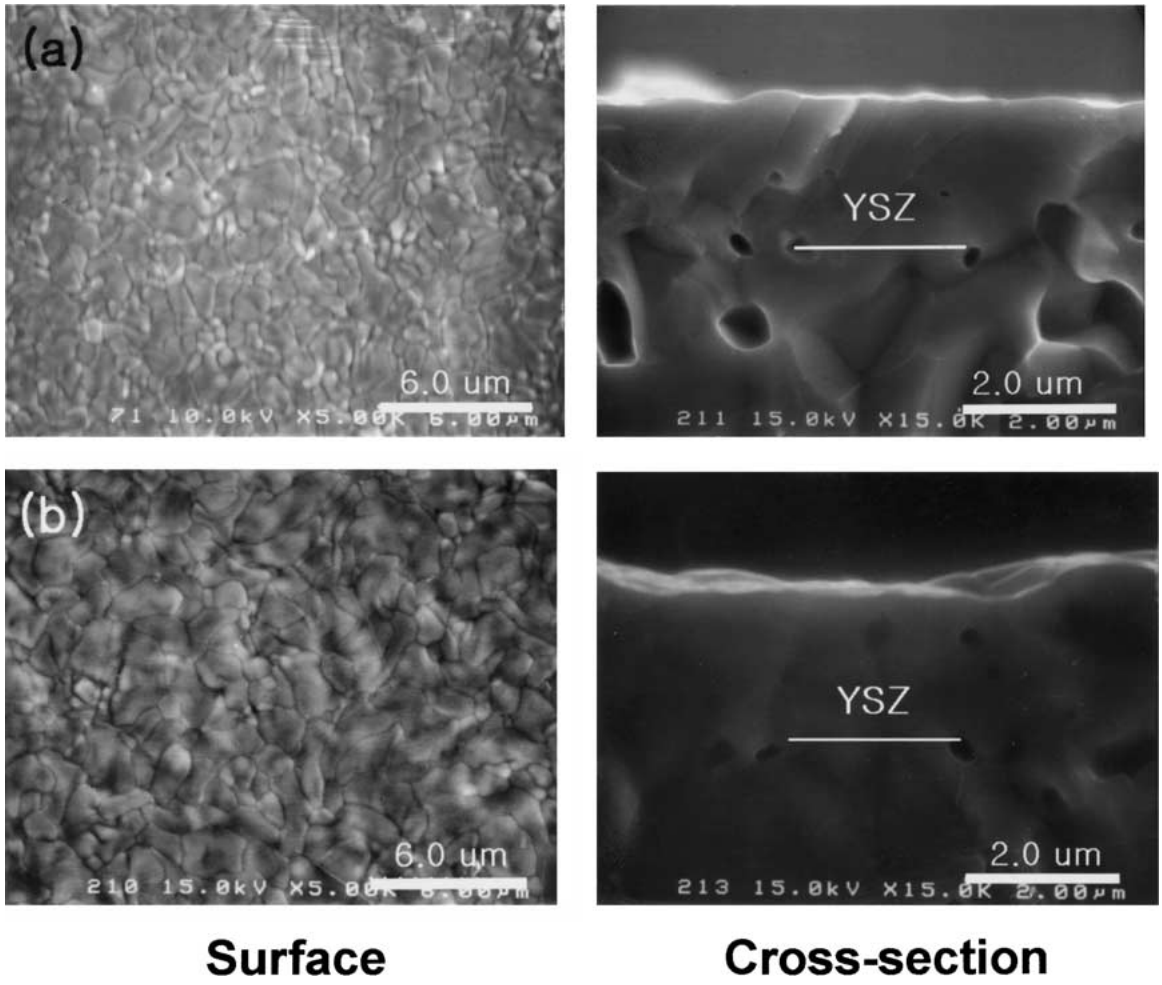

Figure 8 Surface and cross-sectional SEM micrographs of composite electrolytes heat-treated at 1,400°C for 2 h: (a) YSZ/YDC and (b) YSZ/GDC.

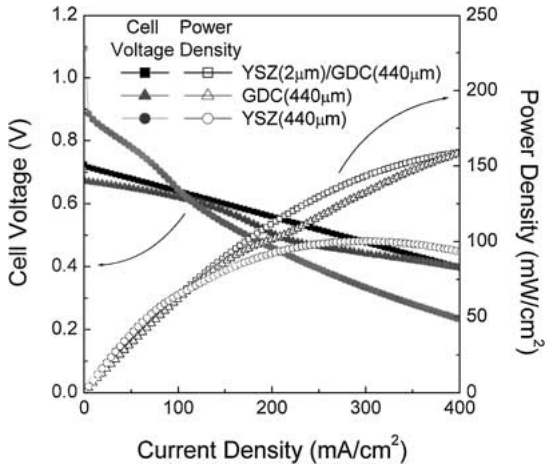

Figure 9 Cell voltage and power density versus current density of YSZ, GDC, and YSZ/GDC single cells at 900°C.

4. Conclusions

From the research about the fabrication of YSZ layer coated doped ceria composite electrolyte by the tape casting and the sol-gel dip-drawing method, and its single cell performance, the following conclusions are drawn.

The fully densified YSZ film with 2.0 μm of thickness without pores, cracks, or chemical reactions can be obtained after 10 times dip-drawing coating on ceria substrates with YSZ sol followed by the heat-treatment at 1,400°C for 2 hours. The higher OCV values for the single cells with composite electrolytes than that for the doped ceria electrolyte without YSZ layer shows that the electronic conductivity of ceria is restrained from YSZ layer and the oxygen partial pressure of the interface between YSZ layer and doped ceria substrate is increased to the region where the dissociation of ceria does not occur. The single cell performance of composite electrolyte is the same that of uncoated GDC electrolyte and superior to YSZ electrolyte. From these results, it is concluded that the coating of YSZ layer on GDC substrate by the sol-gel process using a dip-drawing coating method is an effective way to prepare the electrolyte material with high cell performance and high chemical stability for low temperature SOFC.

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