Journal of Power Sources 110 (2002) 222–228

JOURNAL OF POWER SOURCES

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Fabrication and characterization of a YSZ/YDC composite electrolyte by a sol–gel coating method

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Received 17 April 2002; accepted 29 April 2002

Abstract

The compatibility of a composite electrolyte composed of a yttria stabilized zirconia (YSZ) film and a yttria-doped ceria (YDC) substrate in a solid oxide fuel cell (SOFC) that can be operated under 800 °C was evaluated. The YSZ film coated on a YDC substrate was derived from a polymeric YSZ sol using a sol–gel spin coating method followed by heat-treatment at 1400 °C for 2 h. The SEM and XRD analysis indicated that there were no cracks, pinholes, or byproducts. The composite electrolyte comprising a YSZ film of 2 μm thickness and a YDC substrate of 1.6 mm thickness was used in a single cell performance test. A 0.5 V higher value of open circuit voltage (OCV) was found for the composite electrolyte single cell compared with an uncoated YDC single cell between 700 and 1050 °C and confirmed that the YSZ film was an electron blocking layer. The maximum power density of the composite electrolyte single cell at 800 °C, 122 mW/cm^2 at 285 mA/cm^2, is comparable with that of a YSZ single cell with the same thickness at 1000 °C, namely 144 mW/cm^2 at 330 mA/cm^2. The hypothetical oxygen partial pressure at the interface between the YSZ film and the YDC substrate for the composite electrolyte with the same thickness ratio at 800 °C is 5.58×10^{-18} atm which is two orders of magnitude higher than the equilibrium oxygen partial pressure of Ce_2O_3/CeO_2, 2.5×10^{-20} atm, at the same temperature.

Keywords: Low temperature SOFC; Composite electrolyte; Sol–gel coating; YSZ thin film; Single cell performance

1. Introduction

Because of their high ionic conductivity, mixed electronic–ionic conductors (MIEC) such as ceria based solid solutions are considered as a potential electrolyte material for low temperature solid oxide fuel cells (SOFCs) which can operate under 800 °C [1]. It is expected that, by using metallic interconnects, the SOFC stack cost can be reduced. The electronic conductivity of ceria based solid solutions, however, not only reduce the cell performance but also cause mechanical breakdown of the cell. To reduce the unstability of MIEC, some research groups have fabricated a composite electrolyte composed of MIEC substrate and pure oxygen ion conductor film such as yttria stabilized zirconia (YSZ) [2–6]. The YSZ film in a composite electrolyte is an electron blocking layer and the stability of the composite electrolyte is determined by the interfacial oxygen partial pressure between the YSZ film and the ceria substrate. Virkar [2], Marques and Navarro [3] theoretically proved that the interfacial oxygen partial pressure was determined by the ratio of the thickness of two layers. Yahiro et al. [4], Eguchi et al. [5], and Mehta et al. [6] reported that the composite electrolytes showed an enhancement of single cell performance compared with cells using uncoated ceria electrolyte. The YSZ films on a ceria based substrate, however, are fabricated by costly gas-phase technology, such as sputtering or ion plating method. A more economical process for the fabrication of the composite electrolyte is required.

Among the various ceramic processes, sol–gel technology has unique advantages for the fabrication of ceramic films or fibers. It does not require costly equipment, allows a lower processing temperature, and can control microstructure and chemical composition easily. The sol suitable for the preparation of films or fibers is a polymeric sol that was fabricated through the partial hydrolysis of metal alkoxide. In the case of zirconium alkoxide, however, the hydrolysis

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0378-7753/02/$ – see front matter
PII: S0378-7753(02)00270-7

reaction proceeds quickly due to its high reactivity with water. One approach to overcome this problem is to use a chelating agent that makes it possible to control the extent and direction of the hydrolysis-condensation reaction by forming a strong complex with alkoxide. Some kinds of organic acids, β-dicarbonyls, and alkanolamines have been used as chelating agent in sol–gel processes [7]. Since the detailed chemical reaction between a metal alkoxide and a chelating agent is different, the optimization of the procedure for a metal alkoxide-chelating agent system is a matter of trial and error.

In the present research, we fabricated the YSZ coated yttria-doped ceria (YDC) composite electrolyte using a sol–gel coating method, and observed the SOFC single cell performance of the composite electrolyte. We paid special attention to evaluation of the stability of the composite electrolyte.

2. Experimental

2.1. Fabrication of a YSZ/YDC composite electrolyte

The polymeric zirconia sol was synthesized by the partial hydrolysis of zirconium *n*-butoxide (ZrO_2 28%, Alfa Aesar) using acetic acid (Duksan Pharmaceutical) and nitric acid (HNO_3 90–94%, Junsei Chemical) as a chelating agent and catalyst, respectively. Table 1 summarizes the initial composition of the reactants for synthesizing a zirconia sol. The YSZ sol was formed by mixing prepared zirconia sol with yttrium nitrate hexahydrate (Aldrich Chemical)-isopropanol (Showa Chemical) solution. The final composition of the YSZ sol corresponded to the stabilized zirconia, $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$. The detailed sol preparation process was reported previously [8]. To optimize the coating process on YDC substrate, the sol concentration was modified through solvent evaporation. The physical properties of the YSZ sol used for coating are listed in Table 2.

Table 1
Molar ratio of reactants for zirconia sol synthesis

Zr alkoxide	1
Isopropanol	30
H_2O	2
HNO_3	1.2
CH_3COOH	2

Table 2
Characteristics of YSZ sol

	Concentration (mol/l)	Density (g/cm^3)	Viscosity (cP)[a]
Before concentration	0.45	0.89	3.60
After concentration	0.80	0.95	5.90

[a] Measured at room temperature and 60 rpm shear rate.

To prepare the YDC substrate, the YDC powders with the composition of $Ce_{0.8}Y_{0.2}O_{1.9}$ were fabricated by the coprecipitation method emplying the protocol of Van herle et al. [9]. The coprecipitate of cerium and yttrium oxalate with the corresponding composition was obtained by the mixing oxalic acid (Junsei Chemical) solution and nitrate co-solution made with cerium nitrate (Kanto Chemical) and yttrium nitrate (Aldrich Chemical). During the coprecipitaton, the solution pH was maintained about 4 by the addition of ammonium hydroxide solution (Kanto Chemical). The washed and dried coprecipitates were calcined at 600 °C for 2 h followed by ball milling with a zirconia ball and isopropanol media in a polyethylene jar. The substrates were prepared by uniaxial pressing at 5000 psi followed by cold isostatic pressing at 20,000 psi of the calcined YDC powder. Sintering was performed at 1600 °C for 2 h. The surfaces of sintered substrates were polished with sand paper, diamond pastes, and γ-Al_2O_3 with 0.05 μm diameter before coating. The dimension of the YDC support after the polishing was 1.6 mm thickness with 2 cm diameter. Fig. 1 shows the microstructure of sintered YDC substrate used for the fabrication of the composite electrolyte.

YSZ thin films on YDC substrates were prepared by spin coating performed by placing a few drops of the YSZ sol in the middle of the substrate and spinning the sample at 2000 rpm for 20 s using a spin-coater (Laurell, WC-200-4NPP). After drying at room temperature for 12 h, the sample was heat-treated at 600 °C with a heating rate of 0.5 °C/min and maintained for 2 h, then cooled to room temperature at a rate of 2 °C/min. After the calcinations at 600 °C for 2 h, repetitive coating was performed up to six times to adjust the film thickness. The final heat-treatment condition of the composite electrolyte to get the dense YSZ film on YDC substrate was 1400 °C for 2 h with the heating rate of 2 °C/min and cooling rate of 5 °C/min. The surface and cross-sectional microstructure of composite electrolyte was observed with FE-SEM (Hitachi, S-4200), and the

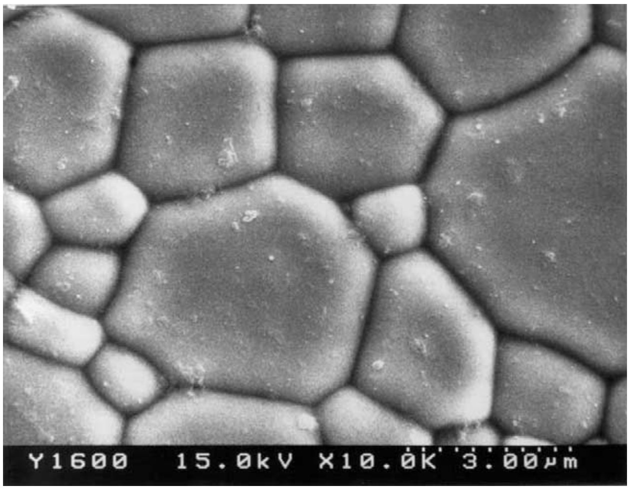

Fig. 1. SEM micrograph of YDC substrate sintered at 1600 °C for 2 h.

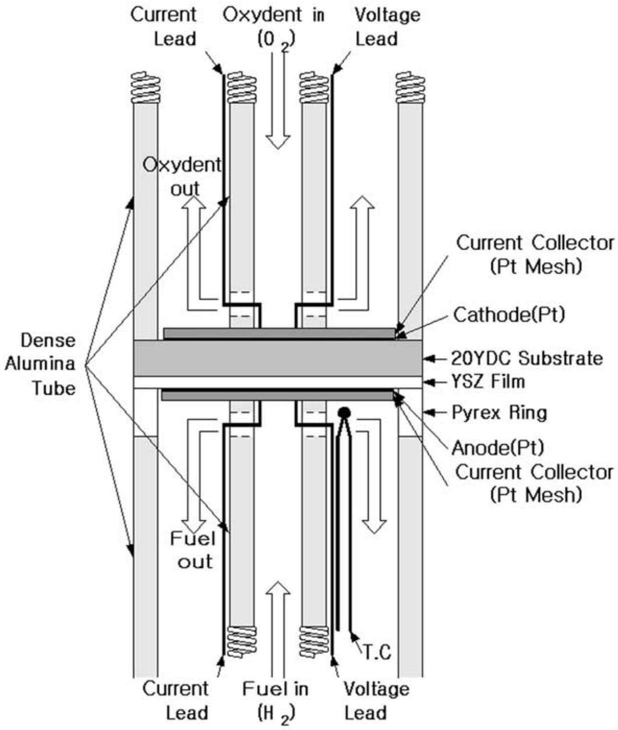

Fig. 2. Schematic diagram of single cell test equipment.

crystalline structure of that was examined using X-ray diffraction (Rigaku, D/Max3).

2.2. Single cell performance test

The single cell performance of the composite electrolyte was tested between 700 and 1050 °C. For preparing electrodes, both sides of an electrolyte disc were coated with Pt paste (TR-706, Tanaka) by a screen printing method followed by heat-treatment at 1200 °C for 2 h to remove the organic ingredients in the platinum paste and to reduce the contact resistance between the electrolyte and electrodes. The diameter of the electrode was about 1 cm after the heat-treatment. The four-probe single cell test equipment was composed of spring-loaded alumina tubes to improve the gas sealing of the Pyrex O-ring and the electric contact between the electrodes and the Pt mesh current collector (99.95%, John Matthey), as illustrated in Fig. 2. High purity Pt wires (>99.9%, Pyromation) were used for all current and voltage leads. The hydrogen fed through a water bubbler placed in a water bath was kept at 25 °C. The YSZ side of composite electrolyte was exposed to fuel in subsequent testing. Prior to a single cell performance test, the SOFC single cell assembly was heated to 1100 °C and kept for 1 h to make a gas tight sealing. Multimeter (2000, Keithley) and dc current source (228A, Keithley) were employed to measure the open circuit voltage (OCV) and the *I–V* characteristics. The same single cell performance tests were also performed with the uncoated YDC electrolyte and YSZ electrolyte.

3. Results and discussion

3.1. Microstructure of YSZ film on YDC substrate

The microstructural changes of the surface of YSZ films on YDC substrates as a function of heat-treatment temperature are shown in Fig. 3(a)–(c) when the heat-treatment time was fixed at 2 h. The YSZ thin film heat-treated at 1200 °C showed an underdeveloped microstructure with small grains of diameter under 0.1 μm, indistinct grain boundaries, and there are some pinholes. The grains with about 0.5 μm diameter and clear grain boundaries were found in the film heat-treated at 1300 °C. At that temperature almost all pinholes disappeared. When heat-treated at 1400 °C, the YSZ thin film was composed of grains of irregular shape. The grain size was varied from 1 to 10 μm without cracks or pinholes. Mehta et al. reported that the YSZ film prepared at room temperature by the RF-sputtering method showed some cracks after the heat-treatment at 900 °C and these cracks disappeared on the heat-treatment at 1500 °C [6]. Whether the cracks were generated or not was determined by the difference of thermal expansion coefficient between the YSZ film and the YDC substrate and the thermal history of the composites. The thermal expansion coefficient of YSZ and YDC is 10.8 and 14.5, respectively [10]. While if prepared at lower temperature it was under tensile stress during heating, therefore, the YSZ film prepared at higher temperature was under compressive stress during cooling. In general, ceramics show excellent mechanical strength under compressive stress but are easily broken under tensile stress. The stresses exerted on the substrate can be negligible when substrate is sufficiently thick. Fig. 3(d) shows the cross-sectional microstructure of the YSZ/YDC composite electrolyte prepared by a single coating followed by heat-treatment at 1400 °C for 2 h. The film had about a 280 nm thickness and good adhesion to the substrate. We have previously reported that the film thickness on a (1 0 0) Si wafer was about 160 nm [8] when the same YSZ sol and the same coating conditions were employed. Such a difference between two experiments originated from the differences of interfacial energy and the surface roughness between the YDC substrate and the (1 0 0) Si wafer. The film thickness increased linearly with repetitive coating and reached about 1.9 μm after the sixth coating as illustrated in Fig. 4.

As can see in Fig. 5, the result of XRD analysis for the YSZ/YDC composite electrolyte made by a single coating then heat-treatment at 1400 °C for 2 h, showed only peaks corresponding to cubic YSZ and YDC and there was no evidence that CeO_2–ZrO_2–Y_2O_3 was formed. It is known that the harmful byproduct of CeO_2–ZrO_2–Y_2O_3 which reduces the ionic conductivity of the electrolyte is formed over 1600 °C [11]. In this study, the heat-treatment required to obtain the dense YSZ film can be lowered at 1400 °C by employing the sol–gel process and therefore the formation of such a harmful byproduct was suppressed. The abnormally high intensity of the peak corresponding to the (1 1 1)

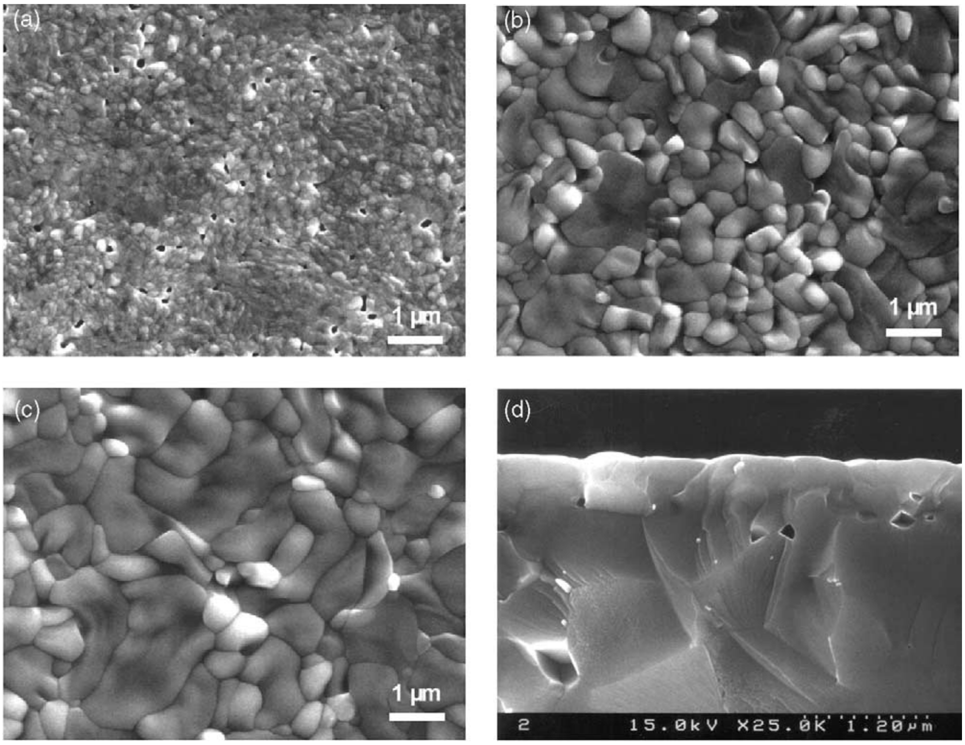

Fig. 3. Surface micrographs of YSZ films coated on YDC after the heat-treatment at (a) 1200 °C, (b) 1300 °C, and (c) 1400 °C for 2 h, and (d) cross-sectional micrographs of YSZ/YDC composite electrolyte prepared by single coating after the heat-treatment at 1400 °C for 2 h.

plane of YSZ meant the preferred orientation of the YSZ film on the YDC substrate was the (1 1 1) plane.

3.2. *OCV and current–voltage characteristics*

With the theoretical OCV value (Nernst Potential, E_N), the OCV values measured between 700 and 1050 °C for the single cells composed of YSZ, YDC, and three different composite electrolytes prepared by six coatings are shown in Fig. 6. The difference between E_N and the OCV of the YSZ single cell may come from the instrumental error such as the inaccuracy of temperature control of single cell test equipment or the water bubbler for fuel gas. Fig. 6 shows that the OCV of the YSZ/YDC single cell was 0.5 V higher than that of the YDC single cell. Such a result implies that the YSZ thin film on YDC substrate fabricated by the sol–gel method was an effective an electron blocking layer. The OCV measurement in our study are summarized in Table 3 with

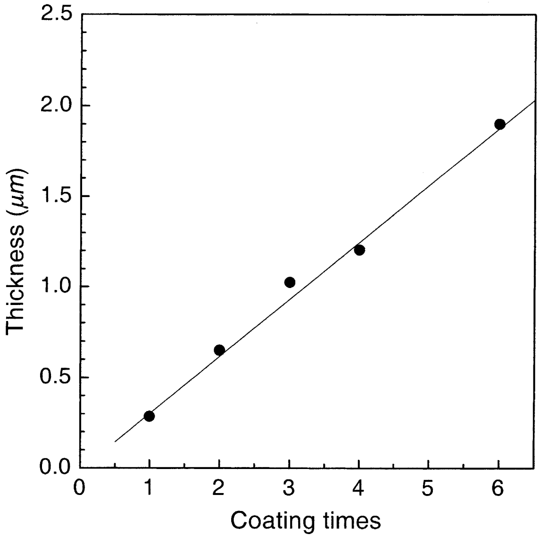

Fig. 4. Thickness of YSZ film coated on YDC substrate as a function of repetition times of coating procedure after the heat-treatment at 1400 °C for 2 h.

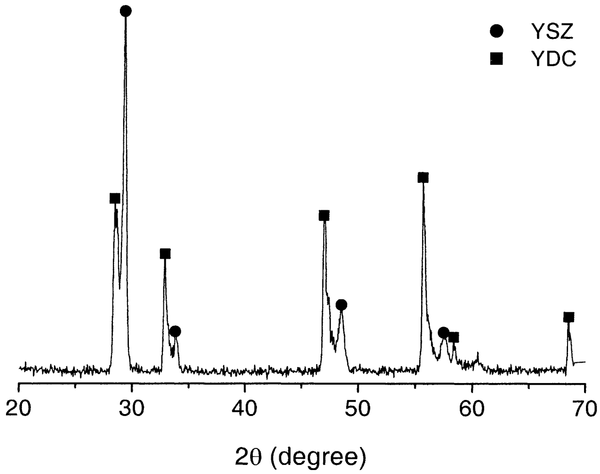

Fig. 5. XRD pattern of YSZ/YDC composite electrolyte after the heat-treatment at 1400 °C for 2 h.

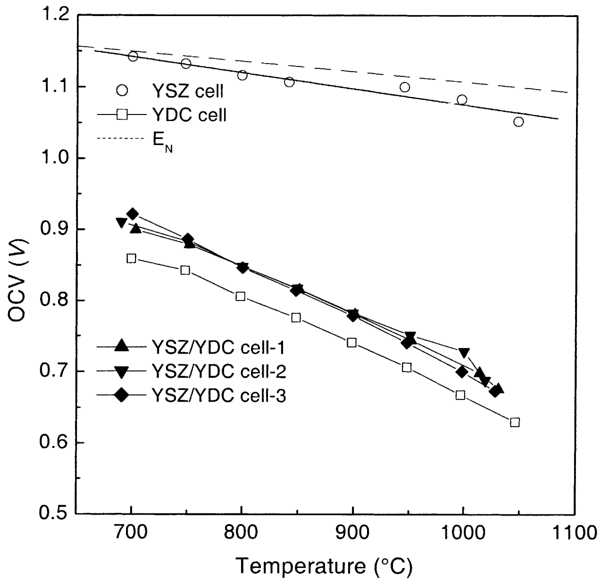

Fig. 6. OCV of various SOFC single cells vs. temperature.

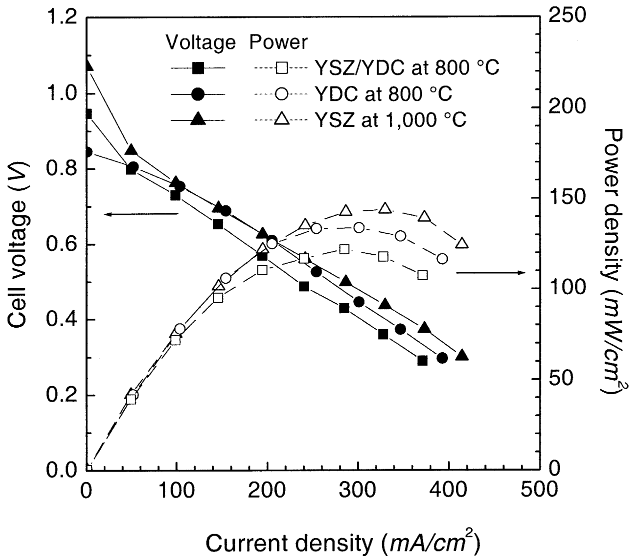

Fig. 7. Cell voltage and power density for YDC and YSZ/YDC single cells at 800 °C and YSZ single cell at 1000 °C as a function of current density.

the results from the literature [3–5]. In Table 3, "SDC" mean samaria doped ceria with the composition of $Ce_{0.8}Sm_{0.2}O_{1.9}$. All the data obtained for YSZ/YDC were well in accordance with each other. The higher OCV of the YSZ/SDC single cell compared with the YSZ/YDC was a result of the higher ionic conductivity and reduced resistance of SDC compared with the YDC [12]. The results of the OCV measurement confirmed that the composite electrolyte fabricated by the sol–gel method in this study had comparable performance to those made by costly gas-phase technology.

The current–voltage and current–power density characteristics of SOFC single cells made with YDC and composite electrolytes prepared with six coatings at 800 °C and those of YSZ single cell at 1000 °C are presented in Fig. 7. All electrolytes used for this experiment had the same thickness, 1.6 mm. The slope of the current–voltage curves shown in Fig. 7 are similar to each other because the resistivities of YDC and the composite electrolyte at 800 °C were nearly the same as that of YSZ at 1000 °C. The effect of YSZ film on resistivity of composite electrolyte is negligible due to its small thickness ratio of film to substrate. The maximum power density of YDC and YSZ/YDC single cells at 800 °C were 134 and 122 mW/cm^2 at 301 and 285 mA/cm^2 current density, respectively. Comparing that with a YSZ single cell at 1000 °C, 144 mW/cm^2 at 330 mA/cm^2, these are slightly smaller but comparable. The reason the maximum power density of YSZ/YDC single cell was lower than that of the YDC single cell in spite of their similar resistivity, was the difference in the catalytic activities of the fuel electrodes. Setoguchi et al. reported that the overpotential of Pt as a fuel electrode on ceria based oxide is smaller than that on YSZ [15]. Remember that the YSZ side of composite electrolyte was exposed to fuel in our study. We consider that the single cell performance for the composite electrolyte can be improved by further optimization of electrode-electrolyte compatibility.

Table 3
OCV values for SOFC single cells composed of various composite electrolytes

Temperature (°C)	Substrate		Film thickness (µm)	OCV (V)	Film preparation method	Reference
	Material	Thickness (mm)				
600	YDC	1.5	1	0.95	RF-sputtering	[4]
700				0.89		
800	SDC	0.685	2	1.05	Ion plating	[5]
800	YDC	1.0	3	0.84	RF-sputtering	[6]
700	YDC	1.6	2	0.92	Sol–gel coating	This work
800				0.85		
900				0.78		
1000				0.70		

3.3. *Stability of composite electrolyte*

To evaluate the stability of composite electrolytes, the interfacial oxygen partial pressure between the YSZ film and the YDC substrate was calculated theoretically. The temperature is assumed to be 800 °C. It is assumed that H_2O saturated H_2 at room temperature and O_2 were used for the fuel and the oxidant gas, respectively. The hypothetical equation derived by Virkar was employed for our calculation [2]. At the OCV condition, the external resistance become infinite and the original equation can be modified:

$$\ln pO_{2(\mathrm{i})} = \frac{R_{\mathrm{i}(2)} + R_{\mathrm{e}(2)}}{R_{\mathrm{i}(1)} + R_{\mathrm{i}(2)} + R_{\mathrm{e}(1)} + R_{\mathrm{e}(2)}} \ln pO_{2(\mathrm{I})} + \frac{R_{\mathrm{i}(1)} + R_{\mathrm{e}(1)}}{R_{\mathrm{i}(1)} + R_{\mathrm{i}(2)} + R_{\mathrm{e}(1)} + R_{\mathrm{e}(2)}} \ln pO_{2(\mathrm{II})} \quad (1)$$

where $R_{\mathrm{i}(1\,\mathrm{or}\,2)} = \delta_{(1\,\mathrm{or}\,2)}/\sigma_{\mathrm{i}(1\,\mathrm{or}\,2)}$ and $R_{\mathrm{e}(1\,\mathrm{or}\,2)} = \delta_{(1\,\mathrm{or}\,2)}/\sigma_{\mathrm{e}(1\,\mathrm{or}\,2)}$, $\delta_{(1\ \mathrm{or}\ 2)}$ is the thickness of each layer of composite electrolyte, σ_{i} and σ_{e} the ionic and electronic conductivity of each material, respectively, $pO_{2(\mathrm{i})}$ the interfacial oxygen partial pressure, and $pO_{2(\mathrm{I})}$ and $pO_{2(\mathrm{II})}$ the oxygen partial pressure at the fuel and air electrode, respectively. The ionic conductivity data were obtained from the literature [10,12]. Due to a lack of data, the electronic conductivity of YSZ was calculated from Eq. (2) that was originally derived for calcia stabilized zirconia (CSZ, $Zr_{0.9}Ca_{0.1}O_{1.9}$) by Etsell and Flengas [13]:

$$\sigma_{\mathrm{e}} = \sigma_{\mathrm{i}} pO_{2(\mathrm{I})}{}^{-1/4} \exp\left(-\frac{3.12 \times 10^4}{T} + 8.05\right) \quad (2)$$

where T is the temperature. The electronic conductivity of the YDC was calculated from the OCV value of the YDC single cell at 800 °C and E_{N} with Eq. (3) [2]:

$$t_{\mathrm{i}} = \frac{E}{E_{\mathrm{N}}} = \frac{\sigma_{\mathrm{i}}}{\sigma_{\mathrm{e}} + \sigma_{\mathrm{i}}} \quad (3)$$

where t_{i} is the ionic transport number and E the OCV of an electrolyte. From the calculation, the oxygen partial pressure of the fuel side of the YDC surface, i.e. interface between the YSZ film and the YDC substrate, can be deduced as 5.58×10^{-18} atm. The partial pressure of oxygen for the equilibrium of Ce_2O_3/CeO_2 at 800 °C is about 2.5×10^{-20} atm 4.34×10^{-22} [14]. If ceria is directly used in fuel cells, an increase in electronic conductivity may occur and decomposition of the electrolyte is possible due to the lower actual pO_2 than the equilibrium partial pressure. The decomposition of $CeO_2 \rightarrow (1/2)Ce_2O_3 + (1/2)O_2$ followed by a volume change can induce mechanical failure of the electrolyte. The oxygen partial pressure of the fuel side of the YDC surface in the composite electrolyte, however, increases up to 10^{-18} which is two orders of magnitude higher than the equilibrium oxygen partial pressure. The results of hypothetical calculation verified that the YSZ film coated YDC composite electrolyte had sufficient stability for low temperature SOFC operation at 800 °C. Under the same conditions, the $pO_{2(\mathrm{i})}$ for the composite electrolyte composed of a 0.5 mm thick YDC substrate and a 2 μm thick YSZ film was 1.31×10^{-20} atm which is lower than the thick YDC substrate but still sufficiently high to prevent the decomposition of CeO_2. Since the thick YDC substrate with 1.6 mm thickness was used in this study, the maximum obtained power density was relatively low as shown in Fig. 7. The stability of the composite electrolyte with 0.5 mm thickness YDC substrate, however, is sufficient to use for a low temperature SOFC operated at 800 °C. In our lab, therefore, we are attempting to prepare a thinner substrate by a slip casting or tape casting method to improve the single cell performance of a composite electrolyte.

4. Conclusion

A composite electrolyte comprising a YSZ film and YDC substrate was fabricated by the sol–gel method. The polymeric sol for coating with a YSZ composition was synthesized by the partial hydrolysis of zirconium *n*-butoxide and solvent evaporation. The YSZ film deposited by spin coating showed a crack and pinhole free microstructure after heat-treatment at 1400 °C for 2 h. The absence of CeO_2–ZrO_2–Y_2O_3 was confirmed by XRD analysis. The composite electrolyte with a 2 μm thick YSZ film and 1.6 mm thick YDC substrate was deposited by six repetitive coatings then heat-treated at 1400 °C for 2 h. The OCV of the composite electrolyte was 0.5 V higher than that of uncoated YDC electrolyte at 700–1050 °C. The maximum power density of the composite electrolyte single cell at 800 °C was 122 mW/cm^2 at 285 mA/cm^2. This value is lower than that of a YSZ single cell with the same thickness at 1000 °C, 144 mW/cm^2 at 330 mA/cm^2, but is comparable. The stability of the composite electrolyte was evaluated by theoretical calculation of the oxygen partial pressure at the interface between the YSZ films and the YDC substrate. When the thickness of the film and the substrate is 2 μm and 1.6 mm, respectively, the interfacial oxygen partial pressure is 5.58×10^{-18} atm which is two orders of magnitude higher than the equilibrium oxygen partial pressure of Ce_2O_3/CeO_2, 2.5×10^{-20} atm. From these results, it is confirmed that the YSZ/YDC composite electrolyte fabricated by the sol–gel coating method in this study is a suitable material with a high stability and comparable cell performance for low temperature SOFC operation.

References

[1] H.L. Tuller, A.S. Nowick, J. Electrochem. Soc. 122 (1975) 255–259.

[2] A.V. Virkar, J. Electrochem. Soc. 138 (1991) 1481–1487.

[3] F.M.B. Marques, L.M. Navarro, Solid State Ionics 90 (1996) 183–192.

[4] H. Yahiro, Y. Baba, K. Eguchi, H. Arai, J. Electrochem. Soc. 135 (1988) 2077–2080.

[5] K. Eguchi, T. Setoguchi, T. Inoue, H. Arai, Solid State Ionics 52 (1992) 165–172.

[6] K. Mehta, S.J. Hong, J.F. Jue, A.V. Virkar, in: S.C. Singhal, H. Iwahara (Eds.), Proceedings of the 3rd International Symposium on Solid Oxide Fuel Cells, Electrochemical Society, Pennington, NJ, 1997, pp. 92–103.

[7] C.J. Brinker, G.W. Scherer, Sol–gel Science: The Physics and Chemistry of Sol–Gel Processing, Academic Press, Boston, MA, 1990.

[8] S.-G. Kim, S.W. Nam, S.-P. Yoon, J. Han, T.-H. Lim, S.-A. Hong, S.-H. Hyun, J. Sol–Gel Sci. Technol., in press.

[9] J. Van herle, T. Horita, T. Kawada, N. Sakai, H. Yokokakwa, M. Dokiya, J. Am. Ceram. Soc. 80 (1997) 933–940.

[10] N.Q. Minh, Science and Technology of Ceramic Fuel Cells, Elservier, Amsterdam, 1995.

[11] Y. Mishima, H. Mitsuyasu, M. Ohtaki, K. Eguchi, J. Electrochem. Soc. 145 (1998) 1004–1007.

[12] R.T. Dirstine, R.N. Blumenthal, T.F. Kuech, J. Electrochem. Soc. 126 (1979) 264–269.

[13] T.H. Etsell, S.N. Flengas, J. Electrochem. Soc. 119 (1972) 1–7.

[14] L.B. Pankratz, Thermodynamic properties of elements and oxides, US Bureau of Mines, Bulletin B672 (1983).

[15] T. Setoguchi, K. Okamoto, K. Eguchi, H. Arai, J. Electrochem. Soc. 139 (1992) 2875–2880.