Journal of The Electrochemical Society, **151** (8) A1230-A1235 (2004) 0013-4651/2004/151(8)/A1230/6/\$7.00 © The Electrochemical Society, Inc.



Fabrication and Characterization of Anode-Supported Tubular SOFCs with Zirconia-Based Electrolyte for Reduced Temperature Operation

Tuong Lan Nguyen,^{a,z} Takeo Honda,^a Tohru Kato,^a Youko Iimura,^a Ken Kato,^a Akira Negishi,^a Ken Nozaki,^a Mitsunobu Shiono,^b Akihisa Kobayashi,^b Kan Hosoda,^b Zifu Cai,^b and Masayuki Dokiya^{b,*}

^aNational Institute of Advanced Industrial Science and Technology, Energy Electronics Institute, Fuel Cell Group, Tsukuba, Ibaraki 305-8568, Japan ^bGraduate School of Environmental and Information Sciences, Yokohama National University, Hodogaya, Yokohama 240-8501, Japan

An anode-supported tubular solid oxide fuel cell (SOFC) with a thin electrolyte film for reduced temperature operation was fabricated by a wet cofire process. Instead of the traditional extrusion method, the anode substrate was formed by a tape-cast method. This allows design the substrate with some advantageous configurations that can improve the performance of SOFCs. Sc_2O_3 and Y_2O_3 -stabilized zirconia electrolyte films were fabricated on the substrate by a modified slurry dip-coating method and then cofired. In order to use $(La_{0.6}Sr_{0.4})CO_3$ cathode, a thin $(CeO_2)_{0.9}(GdO_{1.5})_{0.1}$ interlayer was also fabricated by the slurry dip-coating method. The fabricated tubular cell generated electricity successfully between 600 and 850°C. Power density of *ca*. 170 and 220 mW/cm² was achieved at 600 and 700°C, respectively, however, the ohmic resistance was larger than expected. Because $(CeO_2)_{0.9}(GdO_{1.5})_{0.1}$ interlayer was used, ohmic resistance could be high due to the formation of a layer of $(Zr,Ce)O_2$ solid solution at the zirconia/ceria interface. The gaseous diffusion resistance governed the performance between 700 and 850°C. Better performances of the anode-supported tubular SOFCs can be achieved by further optimizations for the zirconia/ceria interface, control of both porosity and thickness of the anode substrate, as well as improvement of the $(La_{0.6}Sr_{0.4})CO_3$ cathode. (© 2004 The Electrochemical Society. [DOI: 10.1149/1.1768131] All rights reserved.

Manuscript submitted November 4, 2003; revised manuscript received February 13, 2004. Available electronically July 2, 2004.

In order to make solid oxide fuel cells (SOFCs) suitable for practical use such as in compact cogeneration systems and transportation applications, reduced temperature SOFCs have been extensively studied. Operation at around 750°C or less retards materials degradation and hence prolongs stack lifetime, reducing cost by utilization of metallic materials, simplifying the system. Reducedtemperature SOFCs can be realized in two parallel ways: employing materials with high functional properties and/or fabricating SOFCs with novel thin-film concepts. Among basic SOFC designs, anodesupported SOFCs with thin-film electrolyte are better suited for operation at reduced temperature. Many groups have investigated the planar anode substrate SOFC due to its high specific power output and volumetric power density. However, works on tubular SOFCs have shown that the tubular designs have an advantage of being capable of coping with thermal stresses.¹ Siemens Westinghouse multiple tubular cell tests have been successfully conducted for almost 70,000 h.² Small-scale tubular SOFCs, as described by Kendall and Prica,³ and Mizusaki et al.,⁴ could endure rapid heating/cooling and quickly respond to load variation within 1 min at an operating temperature of 800°C. Therefore, it can be expected that a tubular design can be applied to anode substrate SOFCs for cogeneration and transportation applications.⁵⁻⁸ In such cases, a benefit on sealing the stack is expected because the sealing length can be reduced.⁹ Previously, Kato *et al.*^{7,8} estimated the performance at medium temperature of lightweight Ni porous substrate tubular SOFC with electrolyte film fabricated by plasma spraying. Because single tubular cells can be joined by alloy interconnection to build SOFCs modules and stacks, the weight and cost of SOFC systems can be reduced drastically. We have investigated the possibility of fabricating the tubular anode supported SOFC by a wet cofire process, because it has the potential for mass production and cost reduction for SOFCs. The cofired cell has the basic configuration: Ni cermet anode-supported tube/electrolyte film/cathode. In an advanced cell, the substrate thickness can be reduced or it can be replaced by cheaper ceramic, Ni, or alloy porous tubes. In general, the extrusion method is used to prepare a tubular ceramic substrate,

whereas the tape-casting method has been widely adopted for fabricating a planar ceramic substrate. In this study we modified the tape-casting method for preparing the tubular NiO-yttria-stabilized zirconia (YSZ) cermet anode substrate, because it is not only adequate to a laboratorial scale but also is capable of mass producing. There are some available wet methods for fabricating a ceramic thin film such as dip-coating, screen printing, spraying, tape casting, or electrophoretic depositing. However, we have selected the dipcoating method because it is reasonable to expect that the method is most appropriable for a tubular shape. Furthermore, because both methods require only simple equipment and also avoid waste of materials, reduction of fabrication cost is expected.

This paper reports the primary results of fabricating reduced temperature, tubular anode-supported SOFCs by a wet cofire process. Advantages of 10 mol % Sc₂O₃ (10SSZ) and 3 mol % Y₂O₃ (3YSZ)-stabilized ZrO₂ electrolyte thin films, $(CeO_2)_{0.9}(GdO_{1.5})_{0.1}$ interlayer, and (La_{0.6}Sr_{0.4})CoO₃ cathode were combined to promote the electricity generation at reduced temperature. 10SSZ and 3YSZ were chosen among various stabilized ZrO2 electrolytes because SSZ electrolytes present the highest oxide ionic conductivity, whereas 3YSZ has the highest mechanical strength. Such properties are needed for the thin electrolyte film. In addition, because 10SSZ is expensive, replacement of 10SSZ by 3YSZ in a Ni cermet allows not only strengthening the substrate but also cutting down expense of material. Use of $(La_{0.6}Sr_{0.4})CoO_3$ is desirable because this material exhibits high cathodic performance at reduced temperature. In order to suppress the reaction between $(La_{0.6}Sr_{0.4})CoO_3$ and electrolyte, the fabrication of $(CeO_2)_{0.9}(GdO_{1.5})_{0.1}$ (GDC) as an interlayer on stabilized ZrO₂ films by dip-coating was investigated in detail. Performance characteristics of the cells were evaluated between 600 and 850°C. Based on the evaluated performance characteristics, the problems of materials and fabrications can be clarified for this type of SOFC.

Experimental

Preparation of Ni cermet substrate tube.—A mixture of 45 vol % nickel oxide and 55 vol % 3YSZ (Tosoh Co.) powders was used to make an anode substrate. Nickel oxide powder was obtained by grinding NiCO₃·2Ni(OH)₂·nH₂O (High Purity Chemical Co.) in an

^{*} Electrochemical Society Active Member.

^z E-mail: lan-nguyentuong@aist.go.jp

alumina mortar and then thermally decomposed at 600°C. A green substrate tube was fabricated by tape-casting. An anode slurry tape with gauze immersed inside was prepared by doctor blading organic-based slurry of anode powders. The slurry is comprised of anode powders, pore former (poly-methyl-metha-acrylate, Souken Kagaku Co.), and organic ingredients such as binder (poly vinyl butyral), dispersant (oil fish), plasticizer (di-n-butyl-phthalate), bubble-killing reagent (Triton-X), and solvents (isopropanol and toluene).¹⁰ The used cotton gauze was 12×12 threads per cm² netting (type I, Hakujuji Co., Japan). Cotton threads were ca. 100-130 µm diam. Slurry tape was wound to form a tube with precise dimensions and then calcined at 900°C in air by a properly controlled temperature program. Because the thermal gravimetric analysis (TG/DTA) has shown that organic components are burned out between 150 and 350°C, a slow heating rate of 0.5°C/min was applied within this range, and a faster heating rate of 2.5°C/min was used outside this temperature range.

Preparation of electrolyte film, GDC interlayer, and $(La_{0.6}Sr_{0.4})CoO_3$ cathode.—Powder of 10 mol % Sc₂O₃ and 1 mol % CeO₂-stabilized ZrO₂ (10SSZ, Daiichi Kigenso Kogyo Kagaku) and 3YSZ was used to prepare electrolyte films. Particle size of 10SSZ and 3YSZ powders was smaller than ca. 0.5 and 0.1 µm, respectively. Electrolyte powder was dispersed into organic ingredients to form slurries by using a ball mill. Organic ingredients were similar with those of the anode slurry. Electrolyte films were prepared by the slurry dip-coating method. In the traditional slurry dip-coating method, the substrate is coated with electrolyte film by dipping it several times into a slurry tank and then withdrawing at an appropriate speed. Here the technique was modified. The green tube was vertically fixed inside a tank. A green slurry film was deposited on the outside face of the tube when the slurry was flooded and then emptied out through a slurry outlet located at the bottom of the tank. The pressure inside the substrate tube was slightly decreased by vacuum pump. This breaks away microbubbles of air that could be trapped between the surface of the tube and the slurry. In this work, the green electrolyte film was deposited by only one time coating. The contact time of slurry with the green substrate anode tube was ca. 5 s. After drying at room temperature in air, the green electrolyte films were cofired on the substrate at 1300°C in air for 3 h.

As a protective layer for stabilized ZrO_2 electrolyte films from unfavorable solid-state reactions with $(La_{0,6}Sr_{0,4})CoO_3$ cathode, a GDC film (Anan Kasei Co.) was also fabricated by the dip-coating method. The slurry of GDC was prepared in the same way as that of electrolytes. A green GDC interlayer was either subsequently coated to the green electrolyte film and then cofired in air at 1300°C, or a GDC green film was deposited on the dense electrolyte film and fired at a lower temperature in the secondary step. The latter allows suppressing unfavorable solid-state reactions between electrolyte films and GDC.

Single-phase ($La_{0.6}Sr_{0.4}$)CoO₃ (LSC) cathode powder was prepared by the coprecipitation method.¹¹ The LSC cathode was deposited by brush painting a LSC paste, which consists of LSC powder, cellulose acetate, and turpentine oil, on the GDC interlayer followed by firing at 1000°C for 1 h in air. The heating and cooling rate of each firing process was 2.5°C/min. The microstructure of samples was examined by scanning electron microscopy (SEM).

Measurement of the interfacial conductivity (σ_E) of LSC electrode in a 10SSZ pellet/GDC interlayer/LSC half-cell.—In order to examine the possibility of GDC interlayer for suppressing the unfavorable solid-state reaction between LSC and the electrolyte film as well as to attain a maximum cathodic activation of LSC, we examined the influences of firing temperature of the GDC interlayer to the interfacial conductivity, σ_E , of LSC electrode in 10SSZ pellet/GDC interlayer/LSC half-cells. 10SSZ disks (15 mm/diam; 2 mm thick) were used as the solid electrolyte. GDC films were prepared by coating GDC slurry on both faces of 10SSZ disks and then firing between 1000 and 1300°C in air for 2 h. LSC electrodes of 6 mm



Figure 1. Photograph of green NiO-3YSZ anode substrates, of which the slurry tapes were (a) spirally and (b) cylindrically would around a mandrel.

diam were screen printed at the center on GDC films and then fired at 950°C for 1 h in air. The $\sigma_{\rm E}$ of LSC electrodes was examined by a three-probe method using a frequency analyzer (Solatron 1260) and a potentiostat (Solatron 1286) over the frequency range of 1 MHz to 10 mHz using ±10 mV excitation voltage between 600 and 800°C in air. A Pt reference electrode was set on the side of SSZ pellets. Pt lead wires and Pt mesh current collectors were used. The interfacial resistance ($R_{\rm E}$) of LSC electrodes was deduced from the complex impedance plots.¹² The $\sigma_{\rm E}$ was calculated from $R_{\rm E}$ as

$$\sigma_{\rm E} = \frac{1}{AR_{\rm E}}$$
[1]

where A is area of LSC electrode, and $R_{\rm E}$ is interfacial resistance. For clarifying the effects of the GDC interlayer, $\sigma_{\rm E}$ of LSC on a GDC disk was also measured.

Performance characteristics of tubular SOFCs.—The performance characteristics were evaluated for both cases of 10SSZ and 3YSZ electrolyte cells. The effective cathode area of 10SSZ and 3YSZ cells was *ca.* 10 and 5.6 cm², respectively. Glass O-rings were used to seal the cell between H₂ and air sites. H₂ was passed at a rate of 8-15 mL/min/cm² and humidified at room temperature. Current-voltage and ac impedance measurements were made by a two-probe method between 600 and 850°C by the potentiogalvanostat (Toho Technical Research P/G-stat-2000) and a frequency analyzer (NF-S-5720C) over the frequency range of 1 MHz to 10 mHz using ± 10 mV excitation voltage. Pt lead wires were used with a four-terminal configuration. Current collectors were Pt and Ni meshes at the cathode and anode side, respectively.

Results and Discussion

Fabrication of NiO-3YSZ supported tubular SOFC .-- In this study, instead of the traditional extrusion method, tubular anode substrates were manufactured by tape-casting. The slurry tape was strong because cotton gauze was immersed inside the slurry. This allows winding the sheet around a polished steel mandrel to form a tubular shape. Cotton gauze and other organic ingredients were burned out and removed during the calcinations to obtain a NiO-3YSZ green tubular substrate. The design of the green substrate tube can be altered by changing the size of the slurry sheet and the mandrel, and also by changing the way of rolling the sheet around the mandrel. Figure 1 shows an example of the appearance of tubes with two open ends. The green anode substrate tubes were annealed at 900°C in air for 2 h. The tube was shaped by rolling the tape spirally (Fig. 1a) or cylindrically (Fig. 1b). The former technique is suitable for mass producing long tubes. These green tubes were fabricated with the thickness of ca. 0.5-1 mm. This is required because the tubular substrate should have sufficient mechanical strength for supporting the thin electrolyte film in a finished product. However, the thickness of the substrate can be reduced by utilizing a corrugated design.

The 10SSZ and 3YSZ electrolyte films were fabricated on the green anode substrate tube by a slurry dip coat and cofire process.

A1232



Figure 2. Photograph of cofired NiO-3YSZ anode supported tubular SOFCs: (a, b) anode-supported electrolyte film half-cells, (c) an SOFC with GDC interlayer, (d) a half-cell with corrugated substrate, and (e) a half-cell combined with a Ni porous substrate tube.

The success of fabricating the film depends on both electrolyte slurry coating and cofiring processes. An electrolyte green film should be thin, flawless, and adhere well to the substrate. In order to avoid cracking of electrolyte film due to possible stress induced by the cofiring process, shrinkages of the substrate and electrolyte film were carefully investigated.¹³ Photographs of cofired samples are given in Fig. 2. The half-cells with the basic structure as thick NiO-3YSZ anode-supported tube/thin electrolyte film are shown in Fig. 2a and b. A finished product with GDC interlayer and LSC cathode is given in Fig. 2c. These samples have a good appearance with straight length and round cross section. The outer diameter and thickness are 6-10 and 1 mm, respectively. In this work, tubular cells were fabricated with a longest length of ca. 25 cm, which was limited by the size of the furnace. Figure 2d shows a cofired half-cell with a corrugated substrate. The thickness of the anode layer, which is adjacent to the electrolyte film, was reduced to around 150 µm. It can be expected that the resistance of gaseous diffusion on the anode side can be improved with the reduction of the thickness of anode substrate.¹⁴ Figure 2e shows a half-cell that was cofired with a Ni porous substrate tube.^{7,8} In order to combine the SOFC with the Ni substrate tube into one, the NiO-3YSZ green substrate was precisely prepared with consideration of its shrinkage coefficient. The thickness of the cell and the Ni substrate tube was ca. 0.3 and 0.9 mm, respectively. Because the cell was cofired in air, the Ni substrate tube was oxidized to NiO, but it keeps in touch firmly with the SOFC. This confirms the possibility of developing metallic substrate-supported thin electrolyte film SOFCs in a cost-effective way. Details of the fabricating process and properties of this type of SOFC have been under further investigation and will be reported elsewhere.

SEM observations of cofired tubular NiO-3YSZ/10SSZ/GDC/ LSC and NiO-3YSZ/3YSZ/GDC/LSC cells are shown in Fig. 3. The dense electrolyte films were successfully fabricated upon porous substrate. As shown in Fig. 3a and b, surfaces of 10SSZ and 3YSZ electrolyte films did not exhibit cracks or pinholes. The grain sizes of 10SSZ varied between ca. 3 and 7 µm (Fig. 3a), whereas 3YSZ particles were submicrometer (Fig. 3b). Grain growth rate of 10SSZ was relatively higher than that of 3YSZ. For achieving better mechanical strength of very thin ceramic film, suppression of grain grown during the cofire process is important. Hence, there is a need to further reduce the particle sizes of 10SSZ powder. Cross sections of the 10SSZ and 3YSZ electrolyte cells are shown in Fig. 3c and d, respectively. GDC interlayer and LSC cathode were subsequently deposited on electrolyte films and fired at 1200 and 1000°C, respectively. Dense, thin, and uniform electrolyte films adhered well to the porous anode substrate and GDC interlayer. Electrolyte films can be fabricated thinner than 10 µm. Because the 3YSZ particles are submicrometer, further reduction in thickness of 3YSZ electrolyte film is expected by reducing the amount of 3YSZ powder dispersed in the slurry. Thin electrolyte film with few closed submicrometer pores was fabricated by sintering at 1300°C without using any sintering aid. This is achieved by optimizing the compositions of slurry and also the coating technique to form a uniform and high-packed green film. Figure 3e and f shows the microstructures of ca. 3 µm



Figure 3. SEM observations of cofired anode-supported tubular SOFCs: (a) surface of SSZ film, (b) surface of 3YSZ film, (c) cross section of 10SSZ electrolyte cell, (d) cross section of 3YSZ electrolyte cell, (e) surface of GDC interlayer fired at 1200°C, and (f) cross section of 10SSZ electrolyte film and GDC interlayer at a high magnification.

GDC interlayer, which was deposited upon dense 10SSZ film of NiO-3YSZ/10SSZ/LSC cell, then fired at 1200°C for 2 h. Cracks were not found on the GDC interlayer. The GDC particles were sintered. However, because the half-cell with an electrolyte film previously cofired at 1300°C did not contract further at 1200°C, only GDC particles shrunk. Therefore, openings occurred in the sintered GDC interlayer. This is different in the case of double layers of electrolyte and GDC cofired on the NiO-3YSZ substrate. In that case, as shown in Fig. 4, despite that close pores remained inside, a dense GDC interlayer was also obtained. SEM observations also show that despite its large thermal expansion coefficient, porous LSC cathodes with a thickness of *ca*. 20-30 μ m were also attached stably to triplet substrates.

Influences of GDC interlayer on the interfacial conductivities, σ_E , of LSC.—Figure 5 shows the Arrhenius plots of σ_E of LSC electrode measured between 600 and 800°C in air on 10SSZ/GDC/LSC half-cells. The firing temperature of LSC electrode was fixed at 950°C, but the firing temperature of the GDC interlayer was var-



Figure 4. SEM observation of 10SSZ and GDC double layer cofired on a NiO-3YSZ substrate at 1300°C: (a) surface of GDC and (b) cross section of the cofired 10SSZ/GDC double layers.



Figure 5. Arrhenius plots of interfacial conductivity, σ_E , measured between 600 and 800°C in air of LSC electrode on 10SSZ disk/GDC interlayer. The GDC interlayer was fired at (∇) 1000, (\triangle) 1100, (\bigcirc) 1200, and (\Box) 1300°C. (•) LSC on a GDC disk.

ied between 1000 and 1300°C. $\sigma_{\rm E}$ increased when the firing temperature of the GDC layer was increased to 1200°C ($\sigma_{\rm E,1200} > \sigma_{\rm E,1300} > \sigma_{\rm E,1300} > \sigma_{\rm E,1300}$). $\sigma_{\rm E,1300}$ and $\sigma_{\rm E,1200}$ are higher than that of LSC deposited on a dense GDC disk. The activation energy ($E_{\rm a}$) also showed a reduced tendency with increasing GDC firing temperature ($E_{\rm a,1200} = 1.39 \, {\rm eV} < E_{\rm a,1300} = 1.47 \, {\rm eV} < E_{\rm a,CGO} = 1.50 \, {\rm eV} < E_{\rm a,1100} = 1.61 \, {\rm eV} < E_{\rm a,1000} = 1.98 \, {\rm eV}$). The results reveal that the GDC interlayer successfully suppressed the unfavorable solid-state reaction between LSC and stabilized ZrO₂ electrolyte films. Preparation of GDC films at a temperature between 1200 and 1300°C gives full scope to the cathodic performance of LSC on stabilized ZrO₂ electrolyte SOFCs. The microstructure of GDC films fired between 1000 and 1300°C are shown in Fig. 6. Together



Figure 6. SEM observations of surface of GDC interlayer fired at various temperatures on 10SSZ disks. The firing temperatures were (a) 1000, (b) 1100, (c) 1200, and (d) 1300°C.



Figure 7. Performance curves of a cofired, anode-supported tubular with SSZ electrolyte film Ni-3YSZ/SSZ/GDC/LSC SOFC at 800°C.

with the increase of firing temperature, GDC particles were further sintered and became larger. The openings were also enlarged. For cases of the interlayer fired at 1200 and 1300°C, the size of the largest opening was ca. 100 and 200 nm, respectively. With the thickness of a few micrometers, the interlayer with such small openings should be effective to keep electrolyte film from unfavorable solid-state reactions with LSC. The grain growth of GDC particles reinforced their connections. Such improvements in microstructure of the GDC interlayer enhances the oxygen reduction reaction occurring at the triple-phase boundary of LSC-GDC-air. Consequently, in this study the firing temperature of the GDC layer was kept at 1200°C. However, if the solid-state reaction and interdiffusion phenomena at the interface of zirconia in contact with the GDC, of which the ionic conductivity of the product is lower by two orders of magnitude than stabilized ZrO2, are taken into consideration, it is preferable to fire GDC upon zirconia at as low as possible temperature.¹⁵ Further optimizations for preparing the GDC interlayer have been under examination.

Tubular cell performance test.—Preliminary cell performance tests were carried out on tubular cells with the basic configuration as shown in Fig. 2c. The cell with 10SSZ electrolyte film showed an open-circuit voltage (OCV) of *ca.* 1.0 V and a power density of 150 mW/cm² at 800°C (Fig. 7). Because the OCV was lower than the theoretical value of 1.1 V, gas leakages were recognized in this cell. Reasons for this may be a defect in the glass seal, or during the reduction of NiO in the substrate some microcracks were yielded on the 10SSZ film. Further investigations are required for improving the tubular Ni-3YSZ/10SSZ/GDC/LSC SOFC.

Performances of the cell with 3YSZ electrolyte film are shown in Fig. 8. The cell generated electricity reproducibly with thermal recycles between 600 and 850°C. OCV values were ca. 1.1 V, higher than that of the SSZ case, and in good agreement with theoretical values. This indicated that the 3YSZ electrolyte thin film was perfectly fabricated. This is expected because 3YSZ is tougher and stronger than other electrolyte materials.¹⁶ Furthermore, the utilized 3YSZ particles were not only fine but also had a low growth rate. Maximum power densities were ca. 170 mW/cm² (600°C), 195 mW/cm² (650°C), 220 mW/cm² (700°C), 220 mW/cm² (750°C), 230 mW/cm² (800°C), and 225 mW/cm² (850°C). The power density at around 600°C is satisfactory because it is higher than that of other SOFCs, which were composed of Ni-10SSZ anode substrate, 10SSZ electrolyte film, and different cathode materials such as 100 mW/cm² of Ni-10SSZ/10SSZ/Pt-10SSZ,¹⁰ 60 mW/cm² of Ni-10SSZ/10SSZ/Ag-Pt-10SSZ,13 and it is comparable with the power output of 190 mW/cm² achieved for a small disk-type Ni-3YSZ/10SSZ/GDC/LSC SOFC.¹⁷ However, when increasing temperature.



Figure 8. (left) Cell voltage and (right) power density as a function of current densities for a cofired, anode-supported tubular with 3YSZ electrolyte film Ni-3YSZ/3YSZ/GDC/LSC SOFC between 600 and 850°C: (+) 600, (∇) 650, (\diamond) 700, (\triangle) 750, (\bigcirc) 800, and (\square) 850°C.

the power densities did not increase much. This means that in this case performances of the cell were mainly affected by less- or non-thermal activating processes.

Shown in Fig. 9 are the complex impedance plots measured at the open-circuit condition. The plots show two arcs. As the first arc varied but the second arc did not vary much with temperature, we can attribute the Cole-Cole plots to ohmic resistance, R_b (left intercept on z axis), polarization resistance of electrodes (first arc at high frequency), R_1 , and gaseous diffusion resistance, R_2 , (second arc at low frequency). Such behavior of the gaseous diffusion resistance was also shown in some other studies on anode-supported planar



Figure 9. Impedance spectra at open-circuit state of the Ni-3YSZ/3YSZ/GDC/LSC SOFC (3% humidified H_2 vs. air).



Figure 10. (\triangle) Ohmic resistance, R_b , (\Diamond) polarization resistance of electrodes, R_1 , (\bigcirc) gaseous diffusion resistance, R_2 , and (\square) total resistances, R_{total} as determined from the impedance spectra. (×) Ohmic resistance of 15 μ m thickness of 3YSZ film.

SOFCs.^{18,19} The resistances are plotted in Fig. 10 as a function of temperature. $R_{\rm b}$ is larger than both R_1 and R_2 . $R_{\rm b}$ is also larger than the theoretical value calculated for 15 μm thick 3YSZ film. In addition, temperature dependence of $R_{\rm b}$ was less than that of 3YSZ electrolyte. The apparent activation energy (E_a) of 0.3 eV was calculated for $R_{\rm b}$, while the 3YSZ shows an $E_{\rm a}$ of 0.8 eV.¹⁶ The observations show that ohmic losses other than electrolyte losses are significant. Because GDC interlayer was deposited upon the 3YSZ layer, formation of a very thin layer of (Zr,Ce)O2 solid solution can be the reason for such behavior of $R_{\rm b}$. This suggests that further control of fabrication of GDC interlayer is required. Because the current collector was a Pt mesh, limited contact between the cathode and the Pt mesh may also have contributed to the ohmic resistance. Regarding the processes occurring on electrodes, because R_2 did not vary much with the change of temperature, below 700°C R_1 is greater than R_2 , but at higher temperatures R_1 is lesser than R_2 . Together with less dependence of R_b on temperature, this can explain why more electricity cannot generate when the operating temperature is increased to between 700 and 850°C. The cause of gaseous diffusion resistance can be attributed to low porosity of the thick anode substrate and also to a stagnant gas layer existing out-side the porous anode substrate.¹⁸ The low anodic activity of Ni-3YSZ should also be noted. The control of porosity and thickness of the anode substrate are other key issues for the cofire cell. In addition, further improvement of the LSC cathode is also expected for improving cell performance.

Conclusions

The present investigation has confirmed the high technological feasibility of the wet cofired process for fabricating reduced-temperature operable anode-supported tubular SOFCs. Because the process is simple and does not require complicated equipment, it is useful for mass producing cost-effective, tubular-type SOFCs.

It was possible to use Co-based perovskite oxides as cathode materials with zirconia-based electrolyte in conjunction with a GDC interlayer, which was prepared by the slurry dip-coating method. The performance of LSC cathode was enhanced by optimizing the microstructure of the GDC interlayer. However, because a layer of $(Ze,Ce)O_2$ solid solution with very low conductivity at the ZrO_2/GDC interface can be formed, which in turn increases the ohmic loss, the fabrication of GDC interlayer should be further optimized.

The cofired anode substrate tubular SOFC with stabilized ZrO_2 electrolyte films, GDC interlayer, and LSC cathode showed high performance at reduced temperature. The performance is able to be improved by suppressing the influences of gaseous diffusion at the anode side, and solid-state reaction at the interface of the electrolyte and interlayer, and also by further improving the cathodic activities.

The National Institute of Advanced Industrial Science and Technology, Japan, assisted in meeting the publication costs of this article.

List of Symbols

- A area of (La_{0.6}Sr_{0.4})CoO₃ cathode
- R_E interfacial resistance
- σ_E interfacial conductivity
- $E_{\rm a}$ activation energy
- $R_{\rm b}$ ohmic resistance of a tubular cell
- R_1 polarization resistance of electrodes of a tubular cell
- R_2 gaseous diffusion resistance of a tubular cell
- R_{total} total resistance of a tubular cell

References

- 1. N. Q. Minh, J. Am. Ceram. Soc., 76, 563 (1993).
- M. Williams, in *Solid Oxide Fuel Cells VII*, H. Yokogawa and S. C. Shinghal, Editors, PV 2001-16, p. 3, The Electrochemical Society Proceedings Series, Pennington, NJ (2001).
- K. Kendall and M. Prica, in *The First European Solid Oxide Fuel Cell Forum* Proceedings, Vol. 1, p. 163, U. Bossel, Editor, Lucerne, Switzerland (1994).
- N. Yamada, K. Yashiro, A. Kaimai, Y. Nigara, T. Kawada, and J. Mizusaki, Extended Abstracts of the 10th Symposium on Solid Oxide Fuel Cells in Japan, p. 31,

the Solid Oxide Fuel Cell Society of Japan, Tokyo, Japan (2001).

- J. Van Herle, R. Ihringer, N. M. Sammes, G. Tompsett, K. Kendall, K. Yamada, C. Wen, T. Kawada, M. Ihara, and J. Mizusaki, *Solid State Ionics*, **132**, 333 (2000).
- R. H. Song, E. Y. Kim, D. R. Shin, and H. Yokogawa, in *Solid Oxide Fuel Cells VI*, S. C. Shinghal and M. Dokiya, Editors, PV 99-19, p. 845, The Electrochemical Society Proceedings Series, Pennington, NJ (1999).
 T. Kato, S. Wang, A. Negishi, S. Nagata, and K. Nozaki, in *The Fourth European*
- T. Kato, S. Wang, A. Negishi, S. Nagata, and K. Nozaki, in *The Fourth European* Solid Oxide Fuel Cell Forum Proceedings, A. J. McEvoy, Editor, Vol. 2, p. 553, Lucerne, Switzerland (2000).
- T. Kato, S. Wang, N. Iwasita, T. Honda, T. Kaneko, A. Negishi, S. Nagata, and K. Nozaki, in *Solid Oxide Fuel Cells VII*, H. Yokogawa and S. C. Shinghal, Editors, PV 2001-16, p. 1065, The Electrochemical Society Proceedings Series, Pennington, NJ (2001).
- 9. W. Winkler and J. Kruger, J. Power Sources, 71, 244 (1998).
- T. L. Nguyen, K. Kobayashi, Z. Cai, I. Takahashi, K. Yasmoto, M. Dokiya, S. Wang, and T. Kato, in *Solid Oxide Fuel Cells VII*, H. Yokogawa and S. C. Shinghal, Editors, PV 2001-16, p. 1042, The Electrochemical Society Proceedings Series, Pennington, NJ (2001).
- S. Wang, T. Kato, S. Nagata, T. Honda, T. Kaneko, N. Iwasita, and M. Dokiya, Solid State Ionics, 146, 203 (2002).
- M. Shyono, K. Kobayashi, T. L. Nguyen, K. Hosoda, T. Kato, K. Ota, and M. Dokiya, *Solid State Ionics*, Submitted.
 Z. Cai, T. L. Nguyen, S. Wang, and M. Dokiya, *Solid State Ionics*, 152-153, 583
- Z. Cai, T. L. Nguyen, S. Wang, and M. Dokiya, *Solid State Ionics*, **152-153**, 583 (2002).
- J. W. Kim and A. V. Virkar, in *Solid Oxide Fuel Cells VI*, S. C. Shinghal and M. Dokiya, Editors, PV 99-19, p. 830, The Electrochemical Society Proceedings Series, Pennington, NJ (1999).
- A. Tsoga, A. Gupta, A. Naoumidis, and P. Nikolopoulos, Acta Mater., 48, 4709 (2000).
- N. Q. Minh and T. Takahashi, *Science and Technology of Ceramic Fuel Cells*, pp. 90-92, Elsevier Science B.V., Amsterdam (1995).
- T. L. Nguyen, T. Kato, M. Shiono, A. Kobayashi, K. Hosoda, and M. Dokiya, in 2002 Fuel Cell Seminar, p. 391, Palm Springs, CA (2002).
- 18. S. Primdahl and M. Mogensen, J. Electrochem. Soc., 146, 2827 (1999).
- P. V. Hendriksen, S. Koch, M. Mogensen, Y. L. Liu, and P. H. Larsen, in *Solid Oxide Fuel Cells VIII*, S. C. Shinghal and M. Dokiya, Editors, PV 2003-07, p. 1147, The Electrochemical Society Proceedings Series, Pennington, NJ (2003).