Short communication

Fabrication and performance of gadolinia-doped ceria-based intermediate-temperature solid oxide fuel cells

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Abstract

Anode-supported solid oxide fuel cells (SOFC) based on gadolinia-doped ceria (GDC) are developed in this study. A carbonate co-precipitation method is used to synthesize the nano-sized GDC powders. A dense GDC electrolyte thin film supported by a Ni–GDC porous anode is fabricated by dry-pressing and spin-coating processes, respectively. In comparison with dry pressing, it is easy to prepare a thinner electrolyte film by the novel spin-coating method. Cell performance is examined using humidified (3% H_2O) hydrogen as fuel and air as oxidant in the temperature range of 500–700 °C. Cell performance is strongly dependent on the electrolyte thickness. With a porous Ni–GDC anode, a dense 19-μm GDC electrolyte film and a porous $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$–GDC cathode, the cell exhibits maximum power densities of 130, 253, 386 and 492 mW cm^{-2} at 500, 550, 600 and 650 °C, respectively. It is also found that at the low operating temperature about 500 °C, the cell resistance is significantly dominated by the electrode polarization resistance.
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1. Introduction

Lowering the operating temperature to an intermediate temperature of 500–800 °C is the main challenge in current SOFC research activities. Such a reduction would greatly enhance the long-term performance stability, widen the material selection, lessen the sealing problem, enable the use of low-cost metallic interconnects, and eventually accelerate the commercialization of SOFC technology [1]. Significant barriers to intermediate-temperature SOFCs are the increase of electrolyte resistance and the high electrode polarization resistance for the reactions. To overcome these problems, the following approaches are normally adopted: decreasing the electrolyte thickness [2–4], developing alternative electrolyte materials with high ionic conductivity at intermediate temperature [5–7], and minimizing electrode polarization resistance [8–10]. In recent years, considerable effort has been devoted to the development of intermediate-temperature SOFCs based on a thin-film elec-

trolyte of doped ceria [11–16]. This is due to the much higher ionic conductivity of doped ceria than the conventional electrolyte material of yttria-stabilized zirconia (YSZ) at intermediate temperatures [7].

Currently, various processes have been developed for the preparation of thin electrolytes on porous electrode substrates, such as screen printing [12], dry pressing [13,14], spray coating [15], slurry spin coating [16], magnetron sputtering [17], and tape casting [11,18]. For instance, Doshi et al. [11] applied a multi-layer tape casting technique to fabricate a fuel cell that consisted of a 30-μm thick $Gd_{0.2}Ce_{0.8}O_{1.9}$ (GDC) electrolyte, a Ni–GDC anode and an ANLC-1 cathode. The cell generated a maximum power of 140 mW cm^{-2} at 500 °C when using hydrogen and air. Xia et al. [12] developed a screen-printing method to produce a $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) electrolyte film and demonstrated a peak power of 188 mW cm^{-2} at 500 °C for a cell with a Ni–SDC anode and a $Sm_{0.5}Sr_{0.5}CoO_3$ (SSC)–SDC cathode. Leng et al. [15] recently successfully prepared a 10-μm thick GDC electrolyte film by a spray-coating method. The cell, assembled with a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF)–GDC cathode and Ni–GDC anode, exhibited maximum power of 578 and 167 mW cm^{-2} at 600 and 500 °C, respectively. It is usually dif-

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ficult, however, to fabricate a thin GDC electrolyte film with a dense structure. One reason is associated with the fact that CeO_2-based materials are difficult to densify even when sintered at high temperatures ($\sim$1600 °C) for a long time [19]. In order to reduce the sintering temperature, nano-structure powders are desirable. Our previous work has successfully synthesized nano-sized GDC powders by a carbonate co-precipitation method [20,21]. The sintering temperatures of co-precipitated GDC powders can be reduced to 1300 °C. In this study, the nano-sized GDC powders are further investigated for the application in the fabrication of anode-supported, thin-electrolyte cells. A spin-coating method is adopted to prepare the thin GDC electrolyte layer. This is a simple and effective process to fabricate a thin electrolyte coating on the porous substrate. The process requires no strict baking and cooling rate, and only a few cycles are needed to obtain the designed thickness. By comparison, the fabrication and performance of a cell with a GDC electrolyte prepared by conventional dry pressing are presented in this paper.

2. Experimental

A carbonate co-precipitation method was used to synthesize a nano-sized powder of $Gd_{0.2}Ce_{0.8}O_{1.9}$. High-purity reagents ($Ce(NO_3)_3 \cdot 6H_2O$; $Gd(NO_3)_3 \cdot 6H_2O$; 99.9% purity, Sigma–Aldrich Chemical Company, US) were used as starting materials. Ammonium carbonate ($(NH_4)_2CO_3$; 99.99% purity, Alfa Aesar, Johnson Matthey, US) was employed as the co-precipitation medium. Stoichiometric amounts of nitrate salts were dissolved in distilled water, and then dropped into an ammonium carbonate solution under vigorous stirring. The resultant co-precipitate was washed for several times with distilled water and ethanol, respectively. After drying at 70 °C for 20 h, the co-precipitated powder was calcined at 700 °C for 2 h to yield the nano-sized oxide particles. Details of the synthesis process can be found in our previous publications [20,21]. Phase analysis of the synthesized powder was conducted by means of X-ray diffraction (XRD) to confirm the formation of the correct fluorite structure. The morphology of the powder was examined with transmission electron microscope (TEM, JEOL 2010, Japan).

The anode-supported fuel cells were fabricated by dry-pressing and spin-coating methods. The anode powder was prepared by ball-milling NiO powder (J.T. Baker, US) and the GDC powder in a composition ratio of 65%:35% by weight. Graphite (10 wt.% of the solid content) was used as a pore former. The resulting NiO–GDC mixture was then pressed uni-axially at 100 MPa in a steel die of 24-mm diameter. For the dry-pressing process, the nano-sized GDC powder was dispersed uniformly on to the pre-pressed green NiO–GDC substrate which was contained in the die. The GDC powder and the anode substrate were then co-pressed at 200 MPa to form a green bilayer and subsequently co-sintered at 1350 °C for 4 h to obtain a dense electrolyte film. The film thickness can be controlled with the amount of GDC powder. For the spin-coating process, the green NiO–GDC anode discs were pre-sintered at 1000 °C for 1 h to coarsen the microstructure and to strengthen the mechanical property of the anode substrates. A stable sus-

pension of 10 wt.% GDC was prepared by mixing the GDC powder in iso-propanol solution with suitable organic additives. The GDC suspension was spin coated on to the anode substrate at 1200 rpm for 15 s. The electrolyte film was dried at room temperature and the spin-coating process was repeated to obtain the designed thickness. The bilayer of GDC film and NiO–GDC anode was then co-sintered at 1350 °C for 4 h.

To prepare the cathode, commercial $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ powder (Nextech Materials Ltd., US) was mixed with GDC powder in a weight ratio of 60%:40% to form the composite cathode powder. The composite powder was then mixed with polyethylene glycol 400 to form the cathode paste. The paste was applied at the centre of the electrolyte side of the bilayer by screen printing and sintered at 975 °C for 2 h to form a completed cell. The thickness of the cathode was $\sim$30 μm and the cathode area was 0.5 cm^2.

Cell performance was evaluated using a built-in-house SOFC test station. The anode side of the cell was sealed between two alumina tubes with ceramic paste. During the
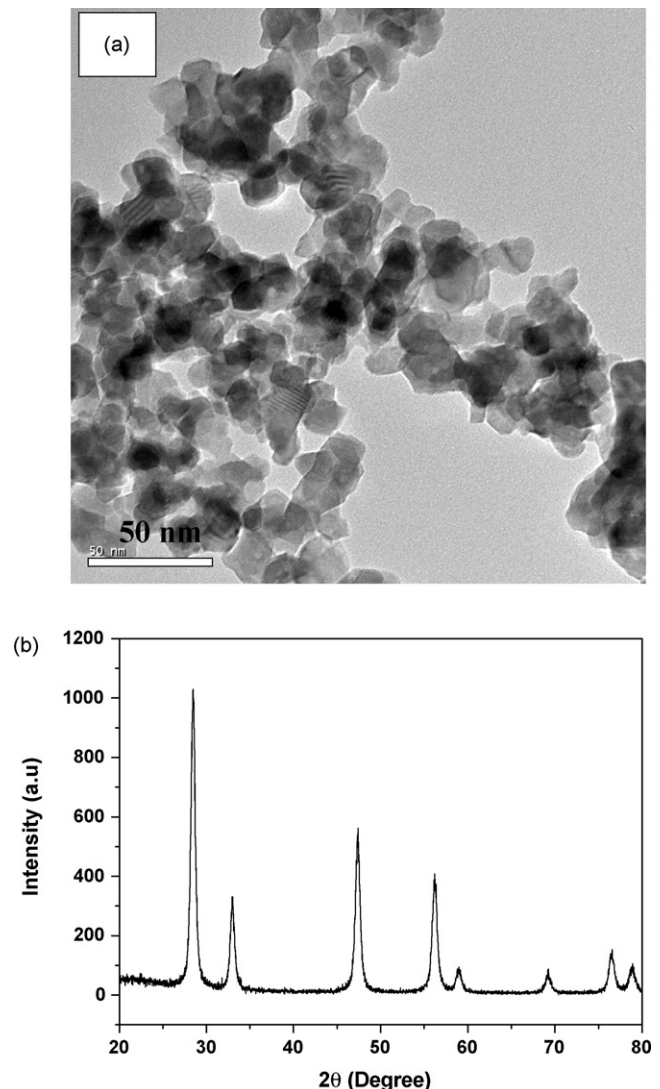

Fig. 1. (a) TEM micrograph and (b) XRD pattern of GDC powder after calcination at 700 °C for 2 h.

test, hydrogen humidified at room temperature (3% H_2O) was fed to the anode chamber at a flow rate of 70 ml min^{-1}, while the cathode was exposed to the static air. Platinum gauze was used as the current-collector for both the anode and the cathode. Electrochemical measurements were performed using a Solartron 1260 frequency response analyzer in conjunction with a 1287 electrochemical interface. The current–voltage characteristics of the cell were measured using linear sweep voltammetry at a scan rate of 5 mV s^{-1} over a temperature range of 500–700 °C. The overall cell impedance was determined in the frequency range of 100 kHz to 0.1 Hz with a signal amplitude of 10 mV under open-circuit conditions. The ohmic resistance was measured from the high-frequency intercept and the electrode polarization resistance was directly obtained from the difference between the high-frequency and the low-frequency intercept in the impedance spectra. After testing, the microstructure of the cell was examined by scanning electron microscopy (SEM, JEOL 6360, Japan).

3. Results and discussion

Fig. 1 shows a TEM micrograph and the XRD pattern of the $Gd_{0.2}Ce_{0.8}O_{1.9}$ powder synthesized through a carbonate co-precipitation method (calcined at 700 °C for 2 h). All the peaks of XRD pattern (Fig. 1b) correspond to the fluorite structure of CeO_2, which demonstrates a single crystalline phase of the powder synthesized. Fine grain size of the GDC powder can be expected from the very wide diffraction peaks in the XRD pattern. The TEM observation (Fig. 1a) revealed that the obtained

GDC powders have mean particle size around 20 nm after calcination at 700 °C for 2 h.

To reduce the electrolyte resistance in the intermediate temperature range, many approaches have been adopted to fabricate the anode-supported cell, as described above. Among the developed methods, the dry-pressing process is a simple handling and cost-effective approach [13]. Fig. 2 shows cross-sectional micrographs of an anode-supported cell fabricated by a dry-pressing process, which consisted of porous Ni–GDC anode support (bottom), a dense GDC electrolyte (middle) and a porous LSCF-GDC cathode (top). It is observed that the GDC electrolyte layer is well adhered to the porous Ni–GDC anode support. The thickness of the GDC electrolyte is ∼98 μm. The dense structure of electrolyte layer is clearly seen in Fig. 2b. The GDC layer appears to be almost fully dense except for some isolated pores, but no cross-layer pinholes or cracks are observed. This indicates that a dense electrolyte film has been successfully prepared from the nano-sized GDC powders even though it is sintered at a comparatively low temperature. In contrast to the dense electrolyte layer, both the anode and cathode are highly porous, as shown in Fig. 2c and d. The average grain size of the Ni–GDC anode and the LSCF-GDC anode is about 0.7 and 0.1 μm, respectively. The retained fine grain-size of the electrodes after sintering at a low temperature will significantly increase the active sites for the electrode reactions, and thus improve the electrochemical performance of the cell.

The voltages and power densities of a cell with a 98-μm GDC electrolyte film as a function of current density at different measuring temperatures are shown in Fig. 3. An open-circuit voltage
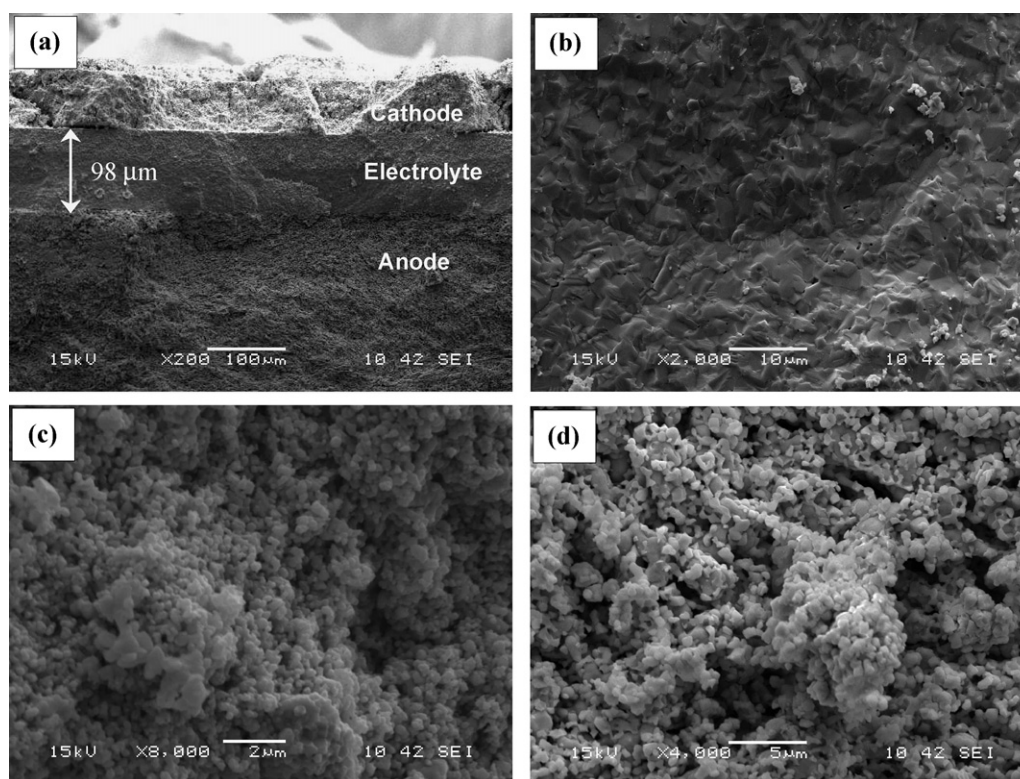

Fig. 2. Cross-sectional SEM micrographs of anode-supported cell: (a) overview of entire cell (top layer: cathode; middle layer: electrolyte; bottom layer: anode); (b) GDC electrolyte; (c) LSCF–GDC cathode; (d) Ni–GDC anode.
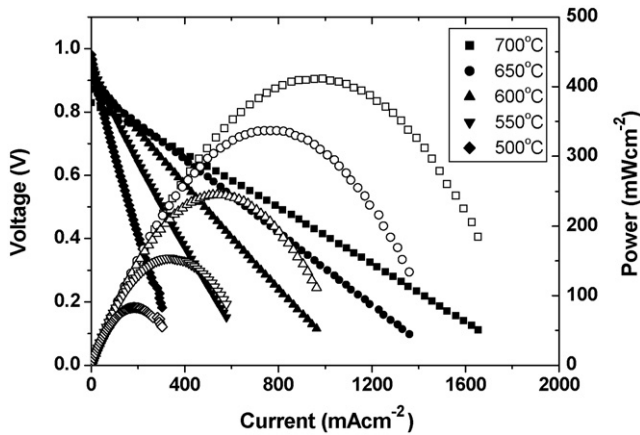
Fig. 3. Cell voltages and power densities as a function of current density of a fuel cell with a 98-μm thick GDC electrolyte.

(OCV) of 0.981 V was measured at $500\,^{\circ}\text{C}$. This is 130 mV higher than that of the cell reported by Leng et al. [15] that had a GDC electrolyte with the same thickness, and also 60 mV higher than that of the cell with a 26-μm GDC electrolyte prepared via a pressing process by Xia and Liu [13]. This implies that a dense electrolyte film is prepared in this study and this is in agreement with the microstructural observation (Fig. 2b). Nevertheless, the OCV value still shows a large difference from the theoretical value, i.e., 1.155 V at $500\,^{\circ}\text{C}$. The difference between the measured OCV and the theoretical values increases with increase in operating temperature. This is due to the increasing electronic conductivity of doped ceria materials in reducing atmospheres [22,23]. At $700\,^{\circ}\text{C}$, the measured OCV is 0.831 V, i.e., much lower than the theoretical value of 1.121 V. This shows clearly that the cell with a doped ceria electrolyte is unsuitable for application above $700\,^{\circ}\text{C}$. The maximum power density of the cell is 83, 155, 245, 337 and 412 mW cm^{-2} at temperatures from 500 to $700\,^{\circ}\text{C}$ at intervals of $50\,^{\circ}\text{C}$. These results are comparable with those for the cell reported by Xia and Liu [13], which consisted of a Ni–SDC anode, a 26-μm thick GDC electrolyte and a SSC–GDC cathode. However, such results were still lower than those for cells a with thinner electrolyte film reported in the literature [9,15,16].

Fig. 4 shows the cell impedance at different temperatures under open-circuit conditions and the corresponding total electrode polarization resistance and ohmic resistance. The latter two parameters were determined from the impedance spectra. All the resistances decrease with increase in temperature. Obviously, electrode polarization dominates the total cell resistance at the low temperatures, while the effect of ohmic resistance on the total cell resistance increases with the increase in temperature. For example, the ohmic resistance of the present cell is $\sim$0.52 Ω cm^2 at $600\,^{\circ}\text{C}$ while the polarization resistance is $\sim$0.41 Ω cm^2. The performance of the cell is significantly limited by the ohmic resistance at high temperatures. Therefore, it is critical to reduce the thickness of the electrolyte layer. It is difficult, however, to obtain a thin electrolyte film of less than 50 μm by the dry-pressing process although a GDC electrolyte film as thin as 8 μm has been obtained by a similar process by Xia et al. [14]. The problems with a dry-pressing process are dif-
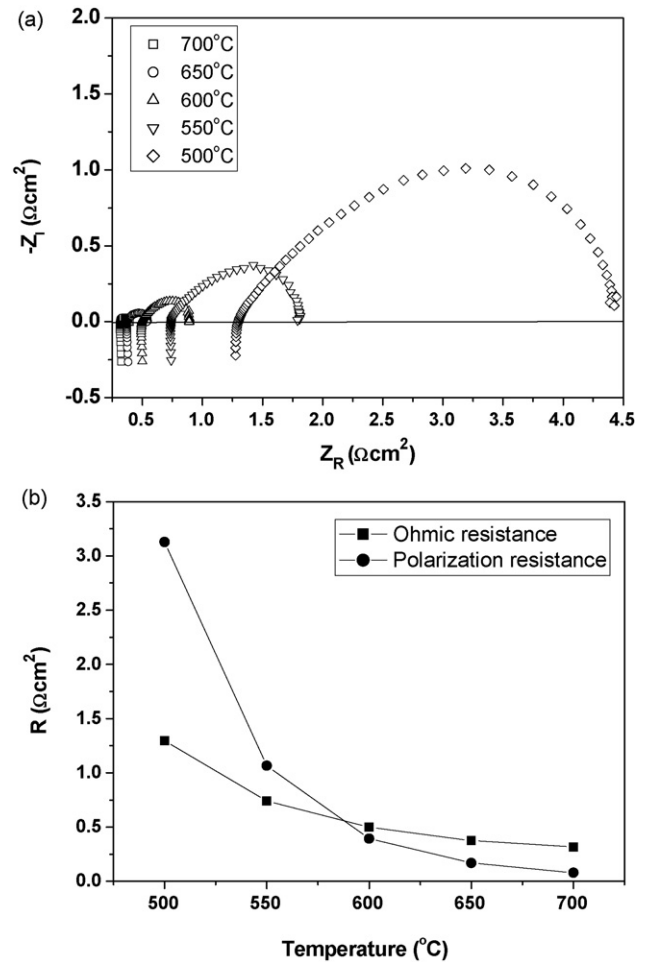

Fig. 4. (a) Impedance spectra and (b) total electrode polarization resistance and ohmic resistance of a cell with a 98-μm thick GDC electrolyte under open-circuit conditions at various temperatures.

ficulty in controlling the amount and uniform distribution of the GDC powders on to the green NiO–GDC substrate. Thus a spin-coating method has been adopted to prepare the thin electrolyte film in this study.

Fig. 5 shows the cross-sectional SEM images of a cell fabricated by a spin-coating process. The GDC electrolyte film is about 19-μm thick. Good adhesion can be seen at both the cathode|electrolyte and anode|electrolyte interfaces. Fig. 6 compares the microstructures of the GDC electrolytes prepared by the dry-pressing and the spin-coating methods. Similar to that prepared by a dry-pressing method, the GDC electrolyte prepared by spin coating is almost dense, as shown in Fig. 6a and c, with few residual pores mainly located along the grain boundaries. The grain size increases significantly to about 1.5 μm after sintering at $1350\,^{\circ}\text{C}$ for 4 h. On the other hand, few pores are observed inside the electrolyte film (Fig. 6d). The pores occur at some specific zones, where is most likely the interface area between the layers during the coating cycles. However, no cross-film pore is observed. This shows that the 19-μm thick electrolyte film is successfully prepared on the anode support by the spin-coating process. As compared with that prepared by the dry-pressing method, the thickness of the electrolyte film is
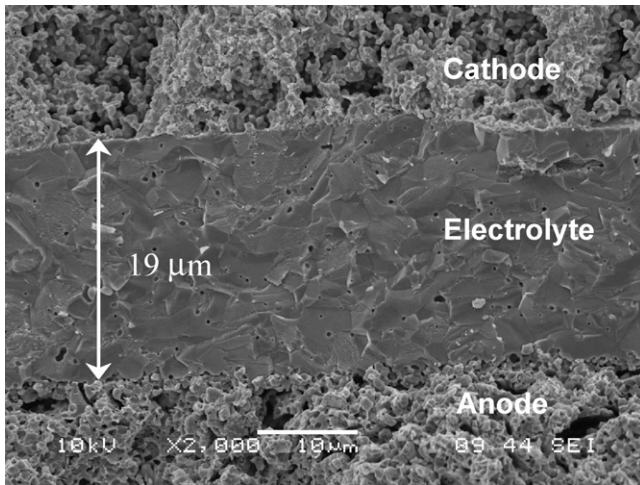
Fig. 5. Cross-sectional SEM micrograph of an anode-supported cell with a 19-μm thick GDC electrolyte.

Fig. 7. Cell voltages and power densities as a function of current density of a fuel cell with a 19-μm thick GDC electrolyte.

easily controlled by adjustment of the spin-coating cycles. In the current study, an electrolyte film of 19-μm thick is obtained after eight time cycles. It is clear that a thinner film can be prepared by reducing the spin-coating cycles. On the other hand, a recent study by Wang et al. [24] shows that it is difficult to obtain a dense electrolyte film when the thickness of the film is less than 5 μm. They prepared the electrolyte film by a slurry spin-coating process and concluded that a suitable thickness of electrolyte film is about 10 μm for obtaining low ohmic resistance and high OCV. In the present study it is found that the sintered electrolyte
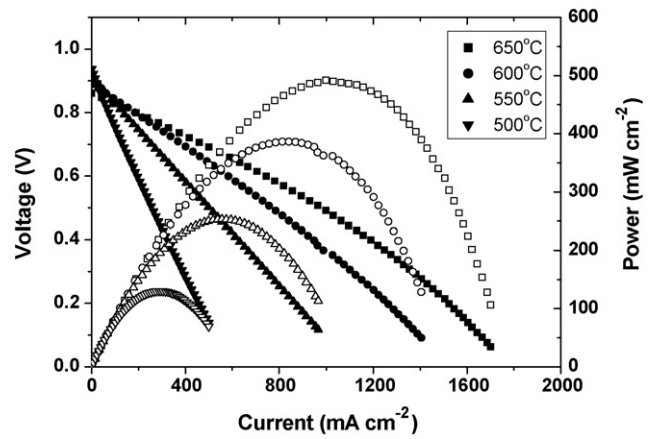
film is uneven and has many pores after five cycles of coating treatment. The final OCVs of such cells are much lower than the theoretical value, indicating a porous electrolyte layer.

The performance of a cell with a 19-μm GDC electrolyte thin film at different temperatures is given in Fig. 7. The OCV is 0.945 V at 500 °C, which is lower than that of a cell prepared by dry pressing. This implies the possible leakage of the electrolyte film for the gas transportation although the SEM image shows a dense structure. The maximum power density of the current cell is 130, 253, 386 and 492 mW cm^{-2} at 500, 550, 600 and 650 °C, respectively. The cell exhibits greater performance than a cell with a thicker electrolyte (Fig. 4). As the other components of
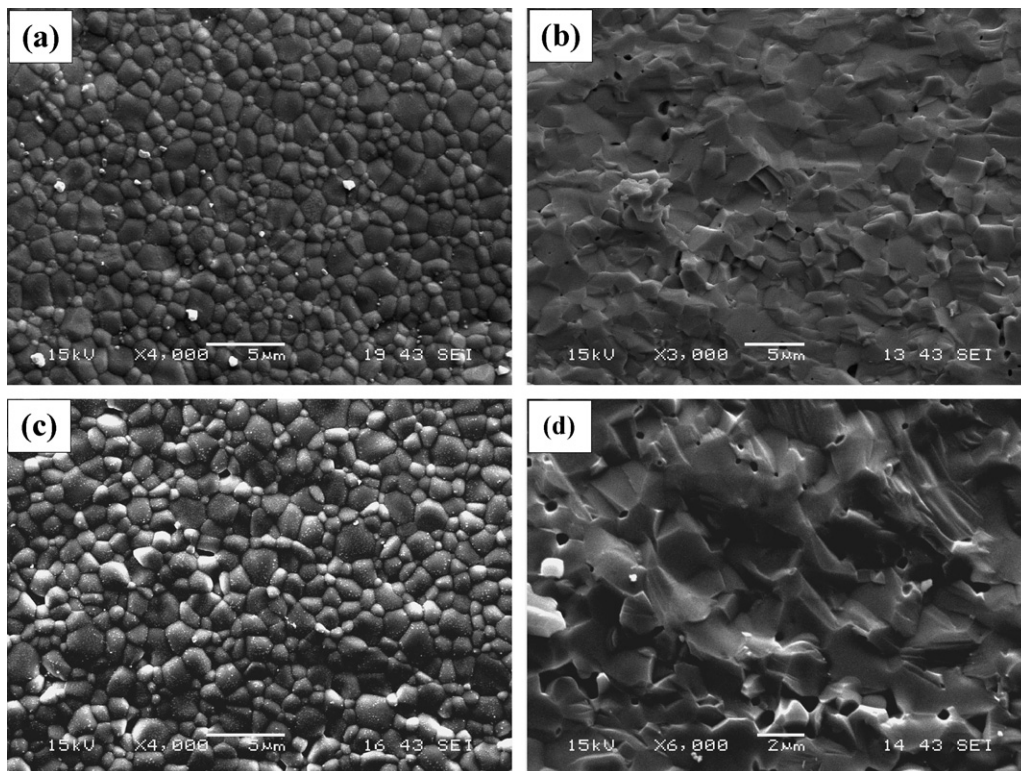

Fig. 6. SEM micrographs of (a and c) surface and (b and d) cross-section of GDC electrolyte prepared by dry-pressing (a and b) and spin-coating (c and d) methods, respectively.
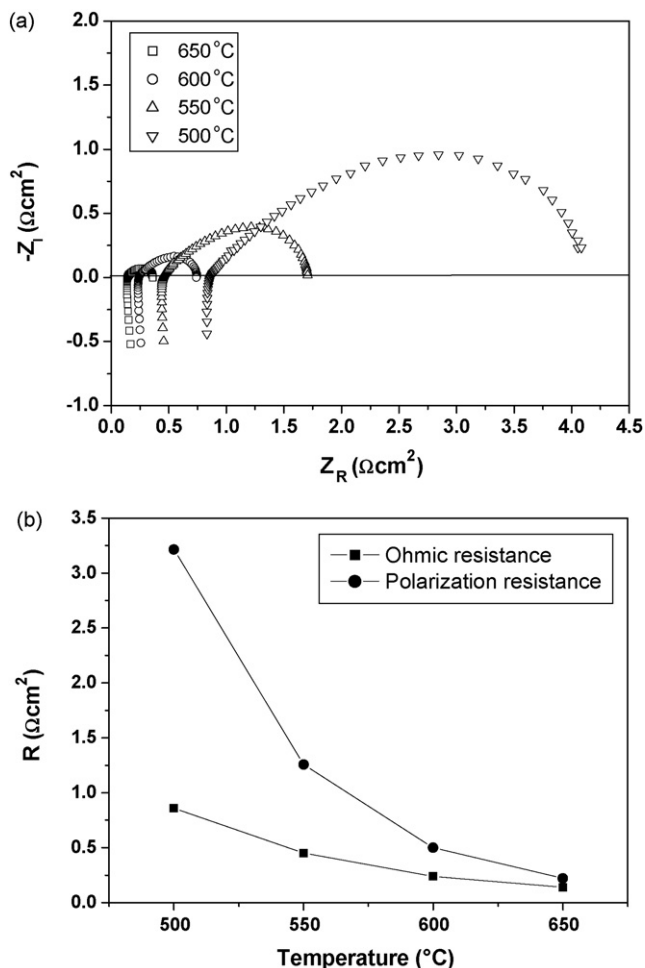
Fig. 8. (a) Impedance spectra and (b) total electrode polarization resistance and ohmic resistance of a cell with a 19-μm thick GDC electrolyte under open-circuit conditions at different temperatures.

the cells, i.e. the anode and the cathode, are basically the same in both cases, the improvement in cell performance is clearly attributed to a decrease in electrolyte thickness. The impedance of a cell with a 19-μm thick electrolyte measured at different temperatures and the corresponding electrode polarization resistance and ohmic resistance are given in Fig. 8. Obviously, the ohmic resistance of the cell decreases significantly. For example, the ohmic resistance at $600\,^\circ C$ is $0.24\,\Omega\,cm^2$, i.e., much smaller than that of $0.52\,\Omega\,cm^2$ of a cell with a 98-μm electrolyte film at the same temperature. Thus, the improved power output is mainly due to the use of a thinner electrolyte. It is feasible to prepare a thin electrolyte film by spin coating for an anode-supported SOFC.

Although the cell developed in this study displays much better performance when using a thinner electrolyte, the value is still low for practical applications, especially at a low operating temperature range, i.e., $\sim500\,^\circ C$. A forecast given by Steele [7] on a GDC electrolyte-based SOFC is that the peak power is about $400\,mW\,cm^{-2}$ at $500\,^\circ C$ for a cell with 25-μm thin GDC electrolyte film. Recent studies show that cell performance at low temperature is mainly dominated by the cathode polarization resistance rather than the ohmic resistance [9,13,16]. Thus to improve the cell performance, it is important to develop novel electrocatalytic cathode materials and improve the electrode structure. Performance improvement with a modified cathode material will be presented in a further study.

4. Conclusion

Nano-sized GDC powders have been synthesized by a carbonate co-precipitation method. Dense GDC thin-film electrolytes are successfully fabricated on anode substrates by dry-pressing and spin-coating processes, respectively. Using the spin-coating process, it is easy to prepare a thinner electrolyte film. The cell performance is critically related to the electrolyte thickness. With a Ni–GDC anode and a LSCF-GDC cathode, a cell with ~19-μm GDC electrolyte film generates maximum power densities of 386 and $130\,mW\,cm^{-2}$ at 600 and $500\,^\circ C$, respectively.

References

[1] N.P. Brandon, S. Skinner, B.C.H. Steele, Annu. Rev. Mater. Res. 33 (2003) 183–213.
[2] S. de Souza, S.J. Visco, L.C. de Jonghe, J. Electrochem. Soc. 144 (1997) L35–L37.
[3] J.W. Kim, A.V. Virkar, K.Z. Fung, K. Mehta, S.C. Singhal, J. Electrochem. Soc. 146 (1999) 69–78.
[4] J. Will, A. Mitterdorfer, C. Kleinlogel, D. Perednis, L.J. Gauckler, Solid State Ionics 131 (2000) 79–96.
[5] T. Ishihara, T. Shibayama, M. Honda, H. Nishiguchi, Y. Takita, J. Electrochem. Soc. 147 (2000) 1332–1337.
[6] K. Huang, J.H. Wan, J.B. Goodenough, J. Electrochem. Soc. 148 (2001) A788–A794.
[7] B.C.H. Steele, Solid State Ionics 129 (2000) 95–110.
[8] C. Xia, M. Liu, Adv. Mater. 14 (2002) 521–523.
[9] Z.P. Shao, S.M. Haile, Nature 431 (2004) 170–173.
[10] S.P. Jiang, S. Zhang, Y.D. Zhen, W. Wang, J. Am. Ceram. Soc. 88 (2005) 1779–1785.
[11] R. Doshi, V.L. Richards, J.D. Carter, X. Wang, M. Krumpelt, J. Electrochem. Soc. 146 (1999) 1273–1278.
[12] C. Xia, F. Chen, M. Liu, Electrochem. Solid-State Lett. 4 (2001) A52–A54.
[13] C. Xia, M. Liu, Solid State Ionics 144 (2001) 249–255.
[14] C. Xia, M. Liu, J. Am. Ceram. Soc. 84 (2001) 1903–1905.
[15] Y.J. Leng, S.H. Chan, S.P. Jiang, K.A. Khor, Solid State Ionics 170 (2004) 9–15.
[16] N. Ai, Z. Lu, K. Chen, X. Huang, B. Wei, Y. Zhang, S. Li, X. Xin, X. Sha, W. Su, J. Power Sources 159 (2006) 637–640.
[17] P.K. Srivastava, T. Quach, Y.Y. Duan, R. Donelson, S.P. Jiang, F.T. Ciacchi, S.P.S. Badwal, Solid State Ionics 99 (1997) 311–319.
[18] T. Misono, K. Murata, T. Fukui, J. Chaichanawong, K. Sato, H. Abe, M. Naito, J. Power Sources 157 (2006) 754757.
[19] T. Kudo, H. Obayashi, J. Electrochem. Soc. 122 (1975) 142–147.
[20] A.I.Y. Tok, L.H. Luo, F.Y.C. Boey, Mater. Sci. Eng. A 383 (2004) 229–234.
[21] A.I.Y. Tok, L.H. Luo, F.Y.C. Boey, J.L. Woodhead, J. Mater. Res. 21 (2006) 119–124.
[22] M. Mogensen, N.M. Sammes, G.A. Tomsett, Solid State Ionics 129 (2000) 63–94.
[23] L. Navarro, F. Marques, J. Frade, J. Electrochem. Soc. 144 (1997) 267–273.
[24] J. Wang, Z. Lu, K. Chen, X. Huang, N. Ai, J. Hu, Y. Zhang, W. Su, J. Power Sources 164 (2007) 17–23.