Available online at www.sciencedirect.com

Journal of the European Ceramic Society 27 (2007) 173–178

www.elsevier.com/locate/jeurceramsoc

Electrophoretic deposition for fabrication of YSZ electrolyte film on non-conducting porous NiO–YSZ composite substrate for intermediate temperature SOFC

Takushi Hosomi, Motohide Matsuda*, Michihiro Miyake

Department of Environmental Chemistry and Materials, Faculty of Environmental Science and Technology, Okayama University, Tsushima-Naka, Okayama 700-8530, Japan

Received 22 February 2006; received in revised form 19 April 2006; accepted 29 April 2006
Available online 14 June 2006

Abstract

Electrophoretic deposition (EPD) of YSZ electrolyte films onto porous NiO–YSZ composite substrates that had been pre-coated with graphite thin layers was carried out in the following two means for solid oxide fuel cell application: one was EPD based on electrophoretic filtration by which YSZ films were formed on the reverse sides without the graphite layers; the other was EPD on a graphite thin layer pre-coated on the substrates. Dense YSZ electrolyte thin films were successfully obtained in both means, although it was difficult to form YSZ films that were strongly adherent to the substrates using the latter means. The densification of YSZ films was assisted by shrinkage of the substrates during co-firing. A single cell was constructed on ca. 5 μm thick dense YSZ films fabricated using the EPD based on electrophoretic filtration. Maximum power densities over 0.06, 0.35, 1.10 and 2.01 W/cm^2 were attained, respectively, at 500, 600, 700 and 800 °C on the cell.

Keywords: Electrophoretic deposition (EPD); Electrolyte film; YSZ; SOFC; Electrical properties

1. Introduction

Much effort has been paid to development of solid oxide fuel cells (SOFCs) operating at or below 800 °C because lowering the operation temperature engenders long life and reduced costs of the total system. For reduced-temperature operating SOFCs, the electrolyte should be as thin as possible to minimize the internal ohmic loss. Although several techniques,[1] including electrochemical vapor deposition, have been used to form thin electrolyte films, it is desirable to develop cost-effective processes for broad commercial applications of SOFCs.

Electrophoretic deposition (EPD) is a colloidal process by which ceramic films are shaped directly onto substrates from a colloidal suspension in a DC electric field. The EPD has been used for SOFC applications.[2–19] The EPD is a suitable method for forming electrolyte thin films for intermediate temperature SOFCs with various stack designs, such as a tubular cell stack. The process is very simple; it also includes some technological advantages such as uniformity of deposition, even for complex and large forms, along with high deposition rates. However, the EPD requires conducting substrates for deposition. For that reason, few attempts have been made on non-conducting substrates, such as NiO–YSZ composites, that are useful as an anode in SOFC. In the present work, thin layers of graphite have been coated onto porous NiO–YSZ composite substrates to facilitate conduction on the surface. This paper deals with EPD of YSZ electrolyte films on the non-conducting porous substrates pre-coated with graphite layers. In addition, this paper reports influences of sinterability of the NiO–YSZ composite substrates on densification of YSZ films that are thus formed electrophoretically.

2. Experimental

Green sheets of NiO–YSZ composite substrates were fabricated by tape-casting a slurry on polyethylene films. The slurry was prepared by mixing NiO–YSZ (8 mol% Y_2O_3) composite powders, synthesized by Hosokawa Powder Technology Research Institute, with a dispersant (AKM-0531; NOP Corp.),

---

* Corresponding author. Tel.: +81 862518907; fax: +81 862518907.
E-mail address: mm@cc.okayama-u.ac.jp (M. Matsuda).

0955-2219/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2006.04.175

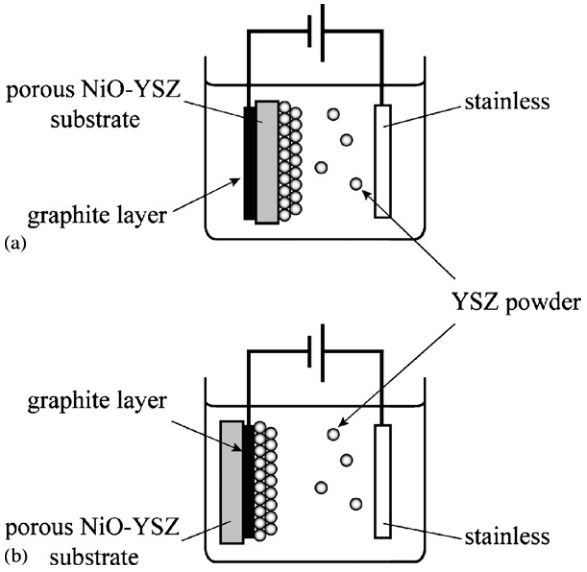

Fig. 1. Experimental setups for (a) EPD of YSZ powders onto porous NiO–YSZ composite substrates whose reverse sides were pre-coated with graphite thin layers and (b) EPD of YSZ powders onto graphite thin layers on porous NiO–YSZ composite substrates.

poly(vinylbutyral) as a binder, and di-*n*-butyl sebacate as a plasticizer in ethanol. The resultant slurry was used after de-airing. The green films' thickness was ca. 700 μm. Circular sheets cut from the green sheets were heated at 500 °C for 4 h to decompose and evaporate the organic additives and then at temperatures of 900–1200 °C for 2 h in air. Respective porosities of the substrates prepared by heating at 900, 1000, 1100 and 1200 °C were approximately 57, 55, 50 and 40%. Graphite layers with thickness of 0.6–1 μm were put onto the surface of the NiO–YSZ composite substrates using a commercial graphite spray.

In this work, the following two processes were used for the EPDs using the porous substrates pre-coated with graphite layers: one means (method 1) was EPD of dispersed YSZ ceramic powders onto the substrates; the other (method 2) was EPD onto the graphite layers on the substrates. Fig. 1 shows the difference in the experimental setups between the two methods. In method 1, the substrate specimen side without the graphite layer was placed, facing the stainless counter electrode. On the other hand, the graphite layer side was set to face the counter electrode in method 2. A distance of 1 cm was maintained between the graphite layer and counter electrode. A DC voltage of 400 V was applied between the graphite layer and counter electrode in suspensions containing 0.2 g of commercial YSZ (8 mol% Y_2O_3) powders (Tosoh Corp.). The resultant deposits were co-fired with the substrates at 1350 °C for 2 h in air. In this paper, the method 1 based on electrophoretic filtration was denominated as direct-EPD.

Microstructures of the deposits on the substrates were observed before and after co-firing using scanning electron microscopy (SEM). Single cells were constructed to examine performance of the YSZ electrolyte films thus fabricated on the porous NiO–YSZ composite substrates. A $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-x}$ (LSCF) compound was used as a cathode in the single cells. The LSCF was prepared using a conventional solid state reaction of La_2O_3, $SrCO_3$, Co_3O_4 and Fe_2O_3 powders. The mixture of those powders with cation stoichiometry was heated at 1000 °C, ground, and then re-heated at 1100 °C in air. The resulting powders were sufficiently ground using a micronizing milling machine. The average size of the LSCF powder used was around 0.5 μm, which was determined from particle-size distribution measurements using a laser scattering technique. The LSCF powders were screen-printed on the YSZ electrolyte films, and then heated at 850 °C in air. The obtained single cells were placed in an experimental system and sealed on an alumina tube with 9 mm inner diameter and 13 mm outer diameter. Fuel-cell performances were measured at 500–800 °C with a galvanostat and a digital voltmeter. Humidified (3% H_2O) hydrogen and air were supplied as a fuel and an oxidant. Single cells were heated in situ at 800 °C in flowing hydrogen gas to reduce NiO in the anode substrates into metallic Ni prior to the cell performance tests.

3. Results and discussion

3.1. *Direct-EPD of YSZ film on porous NiO–YSZ composite substrate pre-coated with graphite layer*

Fig. 2 shows cross-sectional SEM images of YSZ films formed electrophoretically before and after co-firing with the porous substrates. The YSZ powders were deposited on the negative electrode. The obtained deposits comprised densely packed YSZ powders. No crack was observed in the deposits. The deposits' thickness can be controlled as ca. 5–23 μm using EPD parameters including applied voltage and time. The deposits were transformed into a dense body that adhered strongly to the substrates after co-firing. The films' thickness was decreased ca. 37% by co-firing. Some closed pores were observed in the cross-section, but no large pores existed across the films. On the other hand, the substrates were highly densified after co-firing. Nevertheless, the substrates were restored into a porous body by in situ reduction in flowing hydrogen gas before the cell performance tests.

In the present work, ethanol was used as a suspension medium for method 1. According to previous papers,[2–4,7,8] iodine-dissolved acetylacetone is an effective solvent for EPD of YSZ. The iodine-dissolved acetylacetone was used instead of ethanol as the suspension medium for the direct-EPD. The iodine-dissolved acetylacetone had much lower resistance than the ethanol. Therefore, the applied voltages were lowered to 50 V to depress evolution of gases on the negative electrode. Although migration of the YSZ powders toward the negative electrode was observed in the iodine-dissolved acetylacetone similar to in the ethanol, no deposits were obtained. In general, EPD characteristics are based on a combination of two steps.[20] One is migration of charged powders toward an electrode with opposite charge in a DC electric field. The other is coagulation of the powders on the electrode after discharge. The EPD of ceramic powders such as YSZ is often dominated by the latter step. According to a previous paper,[21] the coagulation step is promoted only slightly in low electric field. The magnitude of applied voltage might, therefore, cause a difference between

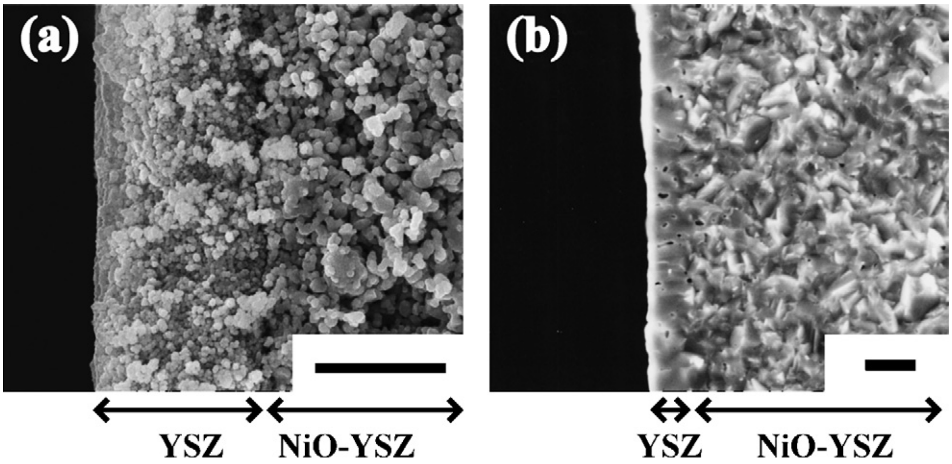

Fig. 2. SEM images of cross-section for YSZ films deposited by direct-EPD (a) before and (b) after co-firing with porous NiO–YSZ composite substrates (bars = 5 μm).

ethanol and iodine-dissolved acetylacetone in direct-EPD characteristics. High voltages were applied in the iodine-dissolved acdetylacetone to investigate the influence of applied voltage on the direct-EPD characteristics. However, no YSZ films were formed on the substrates as a result of gas-evolution.

Fig. 3 shows SEM images of free surfaces for the YSZ co-fired with the porous substrates prepared by pre-heating the green sheets at temperatures of 900–1200 °C. Although no significant difference was apparent among the deposits' microstructure before co-firing, the microstructures of co-fired YSZ films varied according to the substrates used. Densification of YSZ films tended to be degraded on the substrates prepared from green sheets with increasing pre-heating temperature from 900 to 1200 °C. A few small pores remained in the YSZ films on the substrates prepared by pre-heating at 900 °C, but YSZ films were denser than those formed on the substrates with pre-heating temperatures of 1100 and 1200 °C. The dense YSZ films showed good transparency.

In Table 1, linear shrinkage of the substrates with YSZ films after co-firing is shown along with the porosities of those substrates before co-firing. The linear shrinkage of the substrates prepared by pre-heating the green sheets at 900 °C was much greater than that by pre-heating at 1200 °C. This seems to be reasonable because the substrates with pre-heating at 1200 °C were denser than those at 900 °C. The diameter of substrates with pre-heating temperature of 900 °C decreased by ca. 22%

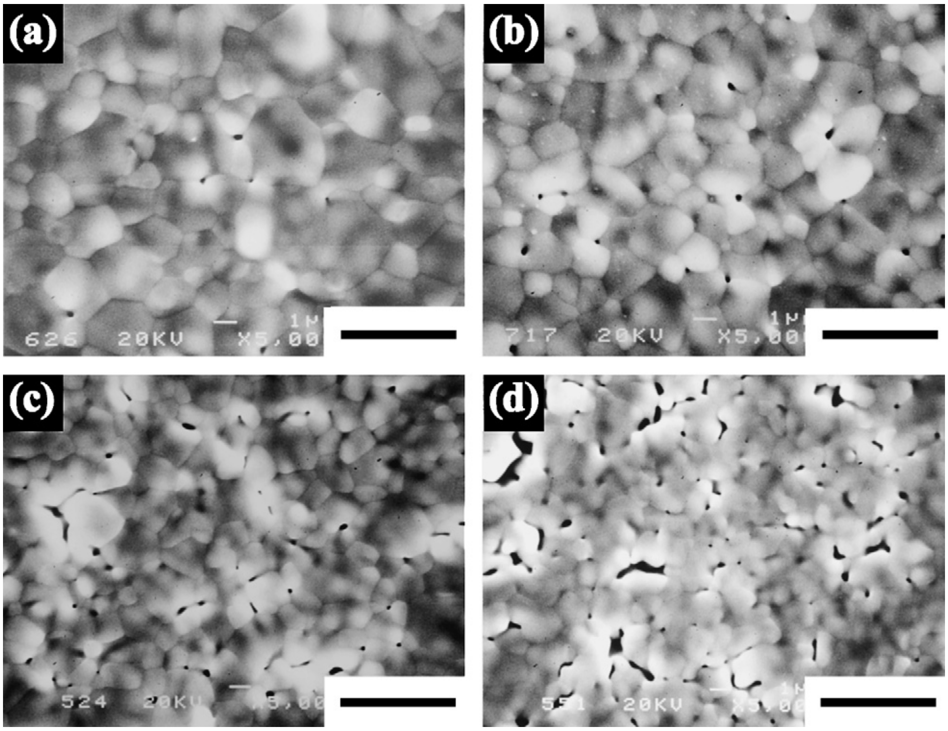

Fig. 3. SEM images of free surface for YSZ films co-fired with substrates prepared by pre-heating green sheets at (a) 900, (b) 1000, (c) 1100 and (d) 1200 °C, respectively (bars = 5 μm).

Table 1
Porosities of NiO-YSZ composite substrates prepared by pre-heating green sheets at 900–1200 °C for 2 h, and linear shrinkages of the substrates with YSZ films after co-firing at 1350 °C for 2 h

	Pre-heating temperature(°C)			
	900	1000	1100	1200
Porosity (%)	56.6	55.2	50.3	39.6
Linear shrinkage (%)	21.8	20.2	18.9	12.3

during co-firing, thereby assisting densification of the YSZ films. This result indicates that the sinterability of substrates affected the densification of the supported YSZ films. Therefore, the sinterability of the substrate used as a supporter, as well as EPD process parameters, was an important factor in fabricating dense YSZ films on the NiO–YSZ composite substrates by the direct-EPD.

3.2. EPD of YSZ film on a graphite layer pre-coated on porous NiO–YSZ composite substrate

In method 2, the EPDs were carried out using acetone as a solvent. Thin films were not obtained, even with short EPD time, because of high deposition rate when ethanol was used. The reason for the greatly enhanced EPD that was provided by method 2 using ethanol remains unclear.

Fig. 4 shows cross-sectional SEM images for the YSZ films formed on the graphite layers on the substrates before and after co-firing. The deposits were composed of densely packed YSZ powders on the graphite layers. Microstructures of YSZ films resembled those formed by direct-EPD in method 1. The graphite layers were burnt out during co-firing. Furthermore, no intermediate compound existed at the interface between the YSZ films and substrates. However, an opening was partly observed at the interface. The opening lowered the adhesion of co-fired YSZ films to the substrates. A thinner graphite layer might improve the connection between the electrolyte films and substrates. However, it is difficult to use a commercial graphite spray to produce thinner graphite layers by controlling the thickness. Therefore, it seemed that method 1 based on the direct-EPD was more convenient than method 2 for electrophoretic formation of YSZ electrolyte thin films on porous NiO–YSZ composite substrates.

3.3. Performance of a single cell constructed on a dense YSZ thin film supported by a NiO–YSZ composite substrate

For cell performance tests, dense YSZ electrolyte films were fabricated using the substrates with pre-heating at 900 °C

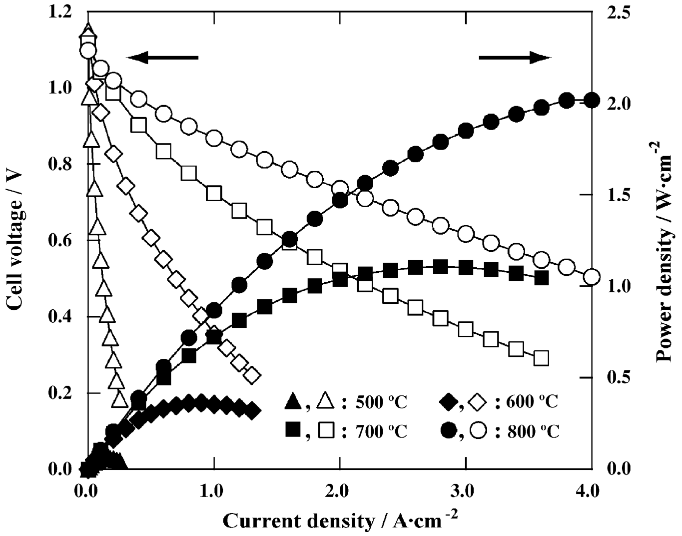

Fig. 5. Cell performance in a temperature of 500–800 °C for a single cell with ca. 5 μm thick dense YSZ film fabricated by direct-EPD of YSZ powders followed by co-firing with NiO–YSZ composite substrate at 1350 °C. Substrates prepared by pre-heating green sheets at 900 °C were used as composite substrate for cell fabrication. The cell had $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-x}$ for the cathode.

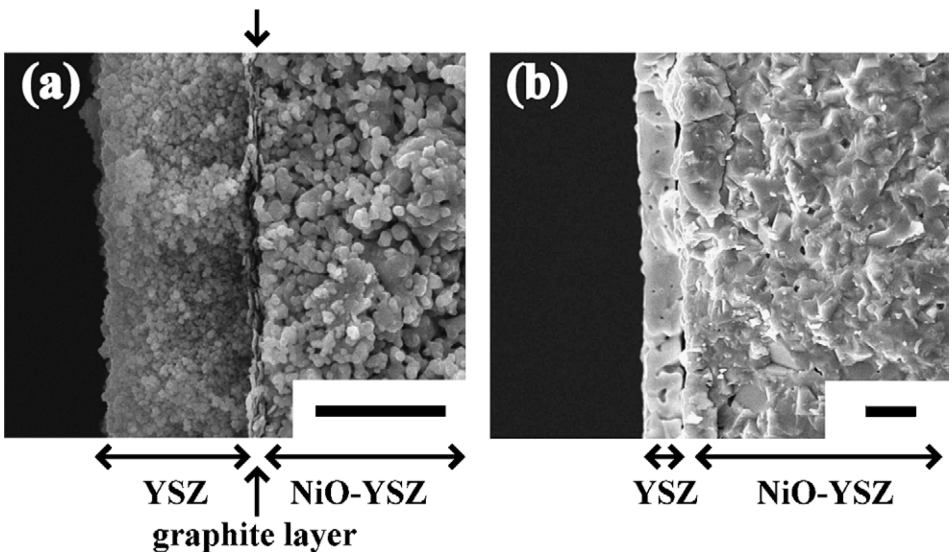

Fig. 4. SEM images of cross-section for YSZ films deposited electrophoretically onto graphite layers on porous NiO–YSZ composite substrates (a) before and (b) after co-firing (bars = 5 μm).

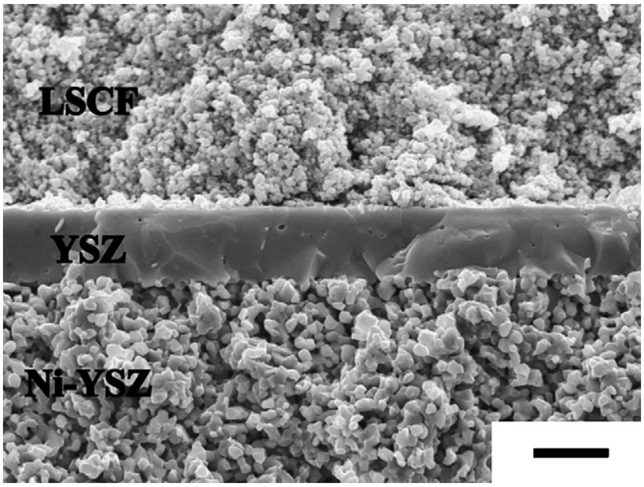

Fig. 6. SEM image of cross-section for anode-supported SOFC after cell performance tests (Bar = 5 μm).

according to method 1 based on the direct-EPD of YSZ powders followed by co-firing at 1350 °C. Fig. 5 shows the cell performance of a single cell constructed on ca. 5 μm thick dense YSZ film. The open-circuit voltages were almost identical to the theoretical values. Maximum output power densities at 500, 600, 700 and 800 °C were greater than 0.06, 0.35, 1.10 and 2.01 W/cm^2, respectively. Those values might be the highest maximum power densities ever reported at those temperatures for SOFCs with YSZ electrolyte. Through achievement of the high cell performance, dense YSZ films with thickness of ca. 5 μm might become applicable to an electrolyte in SOFCs operating at 600 °C. Shown in Fig. 6 is a SEM image of a cross-section for the single cell after cell performance tests. The YSZ film was retained in a dense body, and the substrate was confirmed to be restored into a porous body. Therefore, it is concluded that the EPD, especially the direct-EPD, is an available method to fabricate dense electrolyte thin films for intermediate temperature SOFC.

4. Conclusions

In this work, EPD was used to fabricate YSZ electrolyte films on porous NiO–YSZ composite substrates for anode-supported SOFC. For EPD, thin layers of graphite were pre-coated onto the non-conducting porous substrates. Two electrophoretic fabrication methods were used. One was so-called direct-EPD based on electrophoretic filtration. In direct-EPD, the YSZ powders were deposited on the reverse sides that did not have graphite layers, and were subsequently transformed into dense and continuous films with thickness of ca. 3–15 μm after co-firing with substrates. Densification of YSZ films was affected by sinterability of substrates used. In the other method, the YSZ powders were deposited on the graphite layers on the substrates. The graphite layers were removed during co-firing, and no intermediate compound existed at the interface. Nevertheless, it was difficult to form YSZ films that were strongly adherent to the substrates using this method because an opening remained at the interface after co-firing. A single cell was constructed on ca. 5 μm thick dense YSZ films fabricated on the NiO–YSZ composite substrates by direct-EPD followed by co-firing at 1350 °C. High maximum output power densities over 0.06, 0.35, 1.10 and 2.01 W/cm^2 were attained at 500, 600, 700 and 800 °C, respectively. Those results indicate clearly that EPD is an effective method to form dense YSZ electrolyte thin films on porous NiO–YSZ composite substrates for intermediate temperature SOFC.

Acknowledgements

This work was supported financially by a Grant-in-Aid for Scientific Research (B) (No. 16360331) from the Japan Society for the Promotion of Science (JSPS). This work was also supported in part by a Grant-in-Aid for Scientific Research (B) (No. 17350101) from JSPS and by the Okayama University 21st Century COE Program. The authors are grateful for financial support of the Electrical Technology Research Foundation of Chugoku, Hosokawa Powder Technology Foundation and the Ishikawa Carbon Technology Foundation. The authors thank Dr. T. Fukui and Mr. K. Murata (Hosokawa Powder Technology Research Institute), who fabricated the NiO–YSZ composite substrates used as the anode in this study.

References

1. Will, J., Mitterdorfer, A., Kleinlogel, C., Perednis, D. and Gauckler, L. J., Fabrication of thin electrolytes for second-generation solid oxide fuel cells. *Solid State Ionics*, 2000, **131**, 79–96.
2. Ishihara, T., Sato, K. and Takita, Y., Electrophoretic deposition of Y_2O_3-stabilized ZrO_2 electrolyte films in solid oxide fuel cells. *J. Am. Ceram. Soc.*, 1996, **79**, 913–919.
3. Ishihara, T., Shimose, K., Kudo, T., Nishiguchi, H., Akbay, T. and Takita, Y., Preparation of yttria-stabilized zirconia thin films on strontium-doped $LaMnO_3$ cathode substrates via electrophoretic deposition for solid oxide fuel cells. *J. Am. Ceram. Soc.*, 2000, **83**, 1921–1927.
4. Negishi, H., Sakai, N., Yamaji, K., Horita, T. and Yokokawa, H., Application of electrophoretic deposition technique to solid oxide fuel cells. *J. Electrochem. Soc.*, 2000, **147**, 1682–1687.
5. Zhitomirsky, I. and Petric, A., Electrophoretic deposition of ceramic materials for fuel cell applications. *J. Eur. Ceram. Soc.*, 2000, **20**, 2055–2061.
6. Mathews, T., Manoravi, P., Antony, M. P., Sellar, J. R. and Muddle, B. C., Fabrication of $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$ thin films by electrophoretic deposition and its conductivity measurement. *Solid State Ionics*, 2000, **128**, 111–115.
7. Peng, Z. and Liu, M., Preparation of dense platinum–yttria stabilized zirconia and yttria stabilized zirconia on porous $La_{0.9}Sr_{0.1}MnO_3$ (LSM) substrates. *J. Am. Ceram. Soc.*, 2001, **84**, 283–288.
8. Chen, F. and Liu, M., Preparation of yttria-stabilized zirconia (YSZ) films on $La_{0.85}Sr_{0.15}MnO_3$ (LSM) and LSM–YSZ substrates using an electrophoretic deposition (EPD) process. *J. Eur. Ceram. Soc.*, 2001, **21**, 127–134.
9. Basu, R. N., Randall, C. A. and Mayo, M. J., Fabrication of dense zirconia electrolyte films for tubular solid oxide fuel cells by electrophoretic deposition. *J. Am. Ceram. Soc.*, 2001, **84**, 33–40.
10. Will, J., Hruschka, M. K. M., Gubler, L. and Gauckler, L. J., Electrophoretic deposition of zirconia on porous anodic substrates. *J. Am. Ceram. Soc.*, 2001, **84**, 328–332.
11. Kobayashi, K., Takahashi, I., Shiono, M. and Dokiya, M., Supported $Zr(Sc)O_2$ SOFCs for reduced temperature prepared by electrophoretic deposition. *Solid State Ionics*, 2002, **152–153**, 591–596.
12. Oishi, N., Rudkin, R., Steele, B. C. H., Atkinson, A., Brandon, N. P. and Kilner, J. A., Stainless steel supported thick film IT-SOFCs for operation

at 500–600 °C: Fabrication of ceria film on stainless steel substrate by EPD. In *Proceedings of the Electrochemical Society 2002*, 2002, pp. 230–237.

13. Matsuda, M., Ohara, O., Murata, K., Ohara, S., Fukui, T. and Miyake, M., Electrophoretic fabrication and cell performance of dense Sr- and Mg-doped $LaGaO_3$-based electrolyte films. *Electrochem. Solid-State Lett.*, 2003, **6**, A140–A143.
14. Yamaji, K., Kishimoto, H., Xiong, Y., Horita, T., Sakai, N. and Yokokawa, H., Fabrication of anode supported electrolyte with CeScSZ electrolyte and NiO–CeScSZ anode by EPD technique. In *Proceedings of the International Symposium Solid Oxide Fuel Cells VIII (SOFC VIII)*, 2003, pp. 1011–1018.
15. Sarkar, P., De, D. and Rho, H., Synthesis and microstructural manipulation of ceramics by electrophoretic deposition. *J. Mater. Sci.*, 2004, **39**, 819–823.
16. Zhitomirsky, I. and Petric, A., Electrophoretic deposition of electrolyte materials for solid oxide fuel cells. *J. Mater. Sci.*, 2004, **39**, 825–831.
17. Yamaji, K., Kishimoto, H., Xiong, Y., Horita, T., Sakai, N. and Yokokawa, H., Performance of anode-supported SOFCs fabricated with EPD techniques. *Solid State Ionics*, 2004, **175**, 165–169.
18. Matsuda, M., Ohara, O., Miyake, M., Ohara, S., Murata, K. and Fukui, T., Electrophoretic deposition of a high performance $La(Sr)Ga(Mg)O_3$ electrolyte film for a low temperature solid oxide fuel cell. *Ceramic transactions*, *146*. American Ceramic Society, 2005, pp. 269–275.
19. Matsuda, M., Hosomi, T., Murata, K., Fukui, T. and Miyake, M., Direct EPD of YSZ electrolyte film onto porous NiO–YSZ composite substrate for reduced-temperature operating anode-supported SOFC. *Electrochem. Solid-State Lett.*, 2005, **8**, A8–A11.
20. Sarkar, P. and Nicholson, P. S., Electrophoretic deposition (EPD): mechanisms, kinetics, and application to ceramics. *J. Am. Ceram. Soc.*, 1996, **79**, 1987–2002.
21. Matsuda, M., Miyake, M., Umegaki, T. and Yamashita, K., Electrophoretic coagulation behavior of ferroelectric barium titanate powders in mixed solutions of alcohol and acetylacetone. *J. Mater. Sci.*, 2004, **39**, 4235–4238.