Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 37 (2011) 273–277
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Yttria-stabilized zirconia closed end tubes prepared by electrophoretic deposition

E. Caproni [a], D. Gouvêa [b], R. Muccillo [a,*]

[a] Center of Science and Technology of Materials, Energy and Nuclear Research Institute, Travessa R 400, Cidade Universitária, S. Paulo, SP 05508-900, Brazil
[b] Department of Metallurgical Engineering and Materials, Polytechnique School, University of S. Paulo, Av. Prof. Mello Morais 1463, SP 05508-030, Brazil

Received 23 June 2010; received in revised form 10 July 2010; accepted 27 August 2010
Available online 29 September 2010

Abstract

The electrophoretic deposition technique was used for the preparation of ZrO_2:8 mol% Y_2O_3 (yttria-stabilized zirconia, 8YSZ) closed end tubes for application in high temperature oxygen sensing devices. The 8YSZ ceramic suspensions with different average particle sizes were investigated looking for the best conditions for electrophoretic deposition of thin wall closed end ceramic tubes. High deposition rate of the ceramic particles onto graphite were obtained with isopropanol as solvent and 4-hydroxybenzoic acid as dispersant, with good surface quality of the deposited layer. The green tubes were dried and sintered at 1500 °C, and their properties were analyzed by X-ray diffraction for determination of the structural phases, scanning probe microscopy for observation of grain morphology, and impedance spectroscopy for evaluation of the oxide ion electrical resistivity. Pt/YSZ tube/Pt electrochemical cells were assembled for exposure to oxygen in the 60–650 ppm range using an electrochemical YSZ oxygen pump and sensor system. The signal response of the electrophoretic deposited sensor was similar to the response of the sensor of the oxygen pump. Several thin wall 4 mm diameter × 30 mm length closed end tubes may be obtained in a single operation, showing the ability of this technique for processing large quantities of tubular solid electrolytes with electrical properties suitable for use in high temperature devices.

Keywords: Electrophoretic deposition; Yttria-stabilized zirconia; Oxygen sensor

1. Introduction

The electrophoretic deposition (EPD) is a suitable technique for manufacturing ceramic pieces with complex geometry shapes [1]. The deposition is achieved by applying a dc electric field on a metallic substrate immersed into a suspension containing the ceramic particles. The control of the shape is possible through electrode design and knowing the shrinkage behavior of the ceramic piece upon sintering. The mechanism of EPD has two main steps [1–3]: firstly, a dc electric field is applied to a suspension of the ceramic particles forcing the charged particles to move towards an oppositely charged electrode; secondly, the particles are deposited onto the electrode producing a relatively dense and homogeneous compact or film. The EPD technique can be applied to any solid available in the form of a fine powder (<30 μm average particle size) or a colloidal suspension [1–3]. Electrophoretic depositions have been carried out using aqueous [4–6] and non-aqueous solvents [7–11]; the former may be susceptible to electrolysis, usually at low electric fields.

A fundamental requirement for a successful application of the EPD technique is the production of a stable suspension of particles in a suitable solvent and with a high zeta potential, i.e., with charged particles. The incorporation of charge on the surface of the particles is achieved by ion adsorption or by creating an electric double layer. The electric double layer provides the stabilization of the particles in the suspension and allows the motion of the particles under an electric field [12]. Not only zeta potential measurements are required, but other evaluations like average particle size and transmittance help to optimize the search to define a suitable suspension for EPD [13].

Zirconia stabilized with 8 mol% yttria (8YSZ) is a ceramic material largely used as solid electrolyte in oxygen sensors

* Corresponding author. Tel.: +55 11 31339203; fax: +55 11 31339276.
E-mail addresses: muccillo@usp.br, ceramica@ipen.br (R. Muccillo).

0272-8842/$36.00
doi:10.1016/j.ceramint.2010.08.042

[14,15] and in solid oxide fuel cells [16] due to its high oxide ion conductivity at temperatures higher than approximately 400 °C, the onset of the electrolytic domain. The electromotive force E due to the exposure of 8YSZ to oxygen follows the Nernst equation $E = (RT/4F)\ \ln\ (p_{O2}/p_{O2ref})$, where R is the ideal gas constant, T the absolute temperature, F the Faraday constant, p_{O2} the partial pressure of oxygen in the medium, and p_{O2ref} the partial pressure of oxygen of a reference (usually air) [17]. Electrophoretic deposition has been used for forming YSZ solid electrolyte films [18] and pieces [4], taking into account many advantages of the technique: simple apparatus, short forming time, little restriction of the shape of the substrate and suitability for mass production. Electrophoretic deposition of YSZ has also been done successfully on non-conducting porous substrates [9]. More recently, conditions were successfully established for electrophoretic deposition of individual zirconia and yttria particles, followed by cubic phase formation during sintering [19].

The deposition of ceramic particles into an electrode by the EPD technique is simple, but to avoid crack formation to produce afterwards homogeneous and dense sintered pieces is not an easy task. Two problems are faced when YSZ submicron particles are added to non-aqueous solvents: first, a fast sedimentation because fine particles have a strong tendency to agglomerate in contact with the solvent, requiring dispersants; second, cracking during drying, which could be prevented by adding organic binders [8] or using particles with different sizes [20].

Many other methods, screen printing being considered a simple and cost-effective one, have been reported for preparing thin films of ceramic oxides, mainly for YSZ deposition on anode substrates of solid oxide fuel cells [21–23].

In this work, ceramic suspensions were prepared with ZrO_2:8 mol% Y_2O_3 with different particle sizes for monitoring the reactivity of the ceramic powder dispersed in alcoholic solvent medium with the addition of dispersant. The main idea was to establish suitable conditions for preparing stable suspensions for obtaining simultaneously several closed end tubes without cracks after burning out the substrate (graphite rod), drying the green ceramic tube and sintering to high density to obtain ceramic pieces impervious to oxygen. The microstructural and the electrical characterizations of the ceramic pieces were also carried out.

2. Experimental

The 8YSZ was a commercial powder from Tosoh, USA (TZ-8Y granules of specific surface area 16 ± 3 m^2/g). Part of the 8YSZ powders was calcined at 850 °C for 1 h for producing the larger size granules. The average granule size was evaluated by laser scattering (Cilas granulometer). The results are shown in Fig. 1. The average particle sizes, estimated by the width of the 50% amplitude of the frequency distribution, were 0.75 μm and 19.5 μm for the original and the calcined powders, respectively.

Several combinations of these powders were dispersed in isopropanol (1 vol.% of solids) under ultrasound for 30 min to break up agglomerates as well as for homogenization. The stability of the suspension was monitored by evaluating the electrophoretic mobility (ESA 9800 Matec Applied Sciences) as a function of dispersant concentration (4-hydroxybenzoic acid). The dispersant/solvent volume ratio was 5 g/100 mL. The best combination, namely, the one that after electrophoretic deposition did not present cracks during drying was a mixture of 70 wt.% 8YSZ particles of 0.75 μm average size and 30 wt.% 8YSZ particles of 19.5 μm average size.

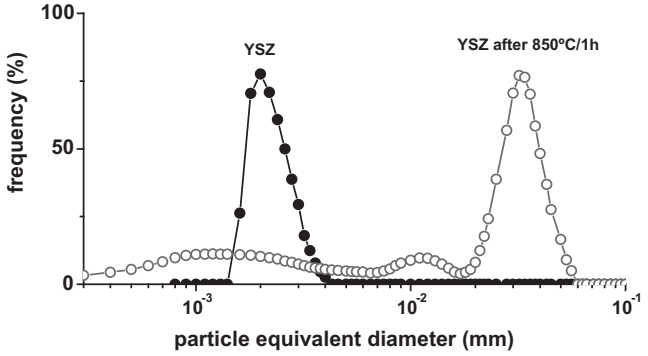

Fig. 1. Particle size distribution of zirconia:8 mol% yttria powders before and after calcination at 800 °C/1 h.

The electrophoretic deposition of the ceramic particles was carried out under 80 V (Hewlett Packard power supply model 6116A) applied for 2 min to the cathode (Alfa Aesar graphite rod, 3.03 mm diameter, 99.9995%), positioned at the center of the anode (a stainless steel container anode filled with the alcoholic suspension of the ceramic particles). The deposition process was repeated dipping 16 (4 × 4 matrix) graphite rods simultaneously. Fig. 2 shows the 16 pieces after removal from the container (top), after drying (bottom left) and after high temperature annealing for the burn out of the graphite rods and the densification of the ceramic tube.

The suspension was prepared by dispersing 10 vol.% of the ceramic powder in isopropanol and adding 3 wt.% dispersant under ultrasound for 30 min. The tubes were dried in KCl environment and fired at 900 °C for 2 h for burning out the graphite, and sintered at 1500 °C for 0.5 h to promote densification. The sintered tubes were cross-sectioned and 2 mm thickness rings were analyzed. The apparent density was evaluated by the Archimedes method, the structural phases by X-ray diffraction (Bruker-AXS model D8 Advance, CuKα radiation, 40 kV–40 mA), and the electrical conductivity by impedance spectroscopy at 400 °C (Hewlett Packard 4192A impedance analyzer, 100 mV signal, 5 Hz to 13 MHz frequency range, 16 frequencies per decade) in ceramic rings with silver electrodes applied into the parallel surfaces.

The polished and thermally etched flat surface of the rings was observed in a scanning probe microscope (Jeol JSPM-5200, contact mode, dynamic force topography images, 25 μm × 25 μm scanning area at a time). Polishing was done with diamond paste down to 1 μm and thermal etching at 1400 °C for 20 min.

For the analysis of the specimen response to oxygen, the closed end tube specimens, with the external and internal areas

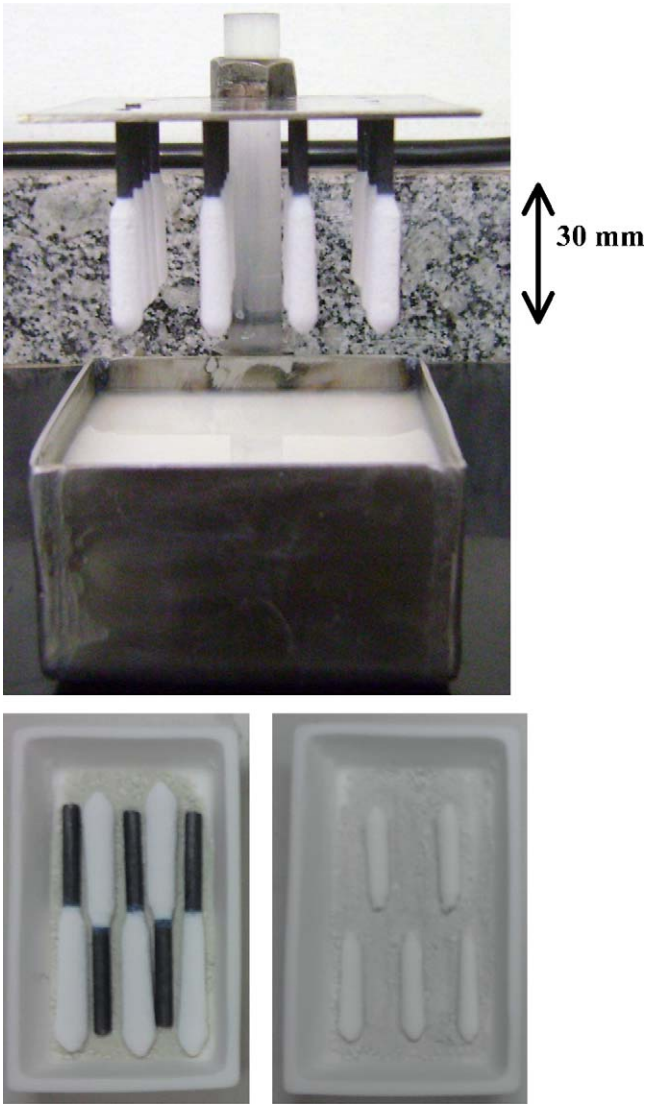

Fig. 2. Top: picture of 16 8YSZ one end closed tubes deposited by electrophoresis onto graphite rod electrodes, taken just after emerging from the 8YSZ dispersion solution. Bottom: left—8YSZ deposited by electrophoretic deposition, after drying; right: after sintering.

coated with platinum (Demetron 308A), were assembled inside a tubular furnace set at the desired temperature, and connected to a p_{O2} station [24] consisting of a YSZ oxygen pump and a YSZ oxygen sensor operating in the 6–800 ppm range. Argon was used as carrier gas for the oxygen produced at the oxygen pump. Platinum terminal leads were used to connect the electrode surfaces of the tubular 8YSZ specimen to an ICEL MD-6510 digital voltmeter datalogger.

3. Results and discussion

Fig. 3 shows the dependence of the electrophoretic mobility of the 8YSZ ceramic granules in isopropanol on the content of 4-hydroxybenzoic acid dispersant. The measured value for the 8YSZ granules at pH 6.9 in isopropanol without dispersant is 0.265×10^{-8} m^2/V s. This spontaneous charging of the mobile species and the pH value for suspension may be explained by

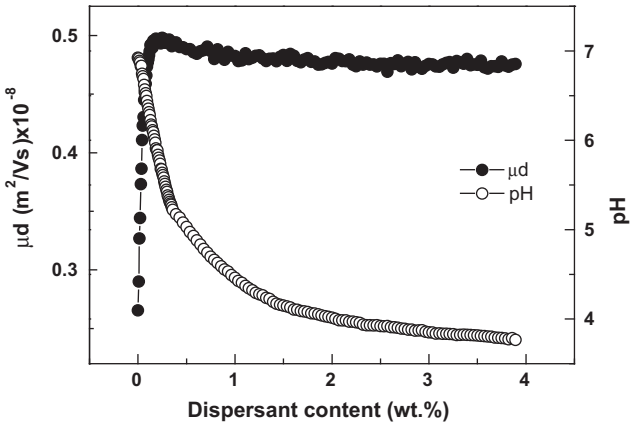

Fig. 3. Electrophoretic mobility of 8YSZ particles as a function of dispersant (4-hydroxybenzoic acid) content in isopropanol suspensions.

the low amount of H_2O in the solvent [25]. Even a small amount of water in alcohol is known to produce H^+ and OH^- species by electrolytic dissociation [10]. Fig. 3 shows that H^+ ions are adsorbed at the surface of the ceramic powder. The electrophoretic mobility depends on the H^+ adsorption in the alcoholic medium, the H^+ ions behaving as the main responsible for the electric potential. The concentration of ions and their behavior at the granule surfaces depend on the alcoholic medium used in the suspension.

Stable suspensions of zirconia–yttria ceramic granules were prepared by adding the ceramic powder to isopropanol. The reaction between the surface of the powder granules and the alcoholic medium produces electrical charges at the surfaces leading to an electrostatic repulsion required for the stabilization of the dispersion.

The specific adsorption at the solid/solvent interface of the dispersing agent increases the dynamic mobility of the granules, improving the repulsion with an even better dispersion of the suspension. This happens up to ~0.25 wt.% of polyelectrolyte content. For higher contents, the mobility remains constant and all dispersing agent contributes to the increase of the ionic force of the solution [26,27].

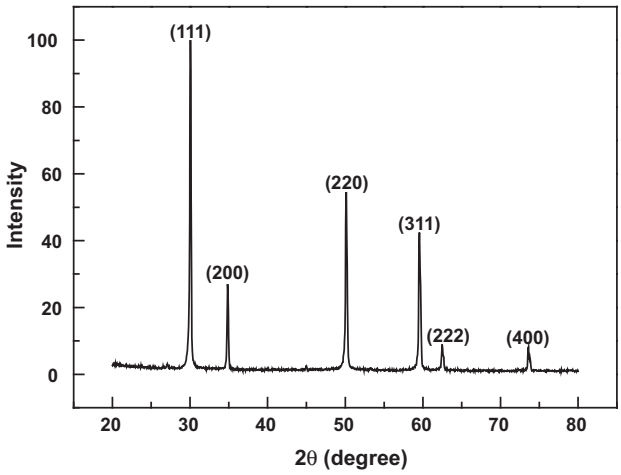

Fig. 4. X-ray diffraction pattern of 8 mol% yttria-stabilized zirconia solid electrolyte obtained by EPD.

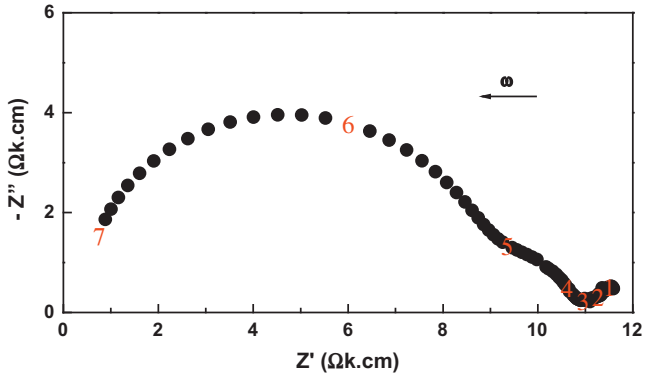

Fig. 5. Impedance spectroscopy diagram, measured at 400 °C, of the sintered 8 mol% yttria-stabilized zirconia electrolyte obtained by EPD. The numbers stand for the logarithm of the frequency (Hz).

Taking into account the electrophoretic mobility results, ceramic suspensions were prepared for testing the deposition of the YSZ granules onto graphite cylindrical electrodes.

Fig. 4 shows results of X-ray diffraction measurements of a sectioned surface of the 8 mol% yttria-stabilized zirconia tubes shown in Fig. 2. The pattern is of a cubic phase with the main diffraction line at $2\theta = 30.05^{\circ}$ (111, 100%). The apparent density is higher than 92% of the theoretical density, evaluated by the Archimedes technique. The achieved densification shows that the sintered material is impervious to oxygen molecules and therefore may be used as solid electrolyte in oxygen sensors.

The impedance spectroscopy diagram of the sample used for X-ray diffraction measurement is shown in Fig. 5. The measurement was carried out at 400 °C, a temperature where oxide ion conductivity takes place, in the electrolytic domain. Two semicircles may be deconvoluted from the diagram, one at high frequencies, related to intragranular properties, and another at low frequencies, related to grain boundary properties [28]. The total electrical resistivity, ~11 kΩ cm, was determined at the intersection of the impedance diagram with the real axis in the low frequency region. This value is of the same order of magnitude of the electrical resistivity of 8YSZ sensors at the same temperature.

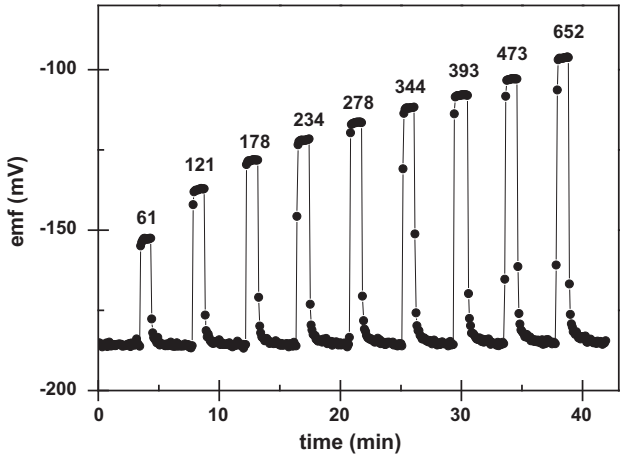

Fig. 6. Electromotive force signal response of the electrophoretic deposited YSZ solid electrolyte tubes for oxygen level inputs in the 60–650 ppm range at 850 °C.

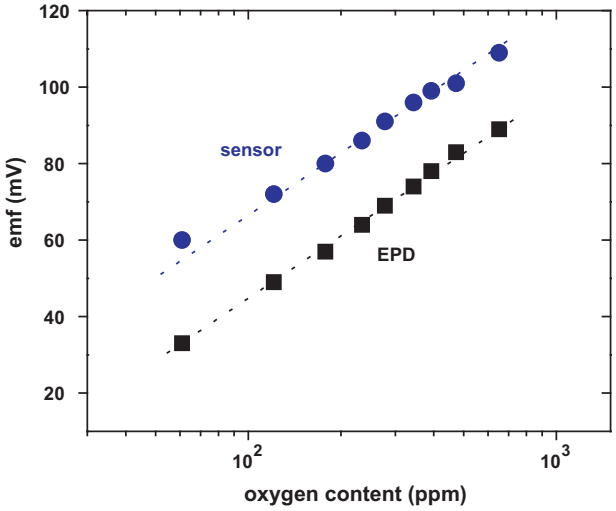

Fig. 7. Dependence of the electromotive force signal of the electrophoretic deposited YSZ solid electrolyte tube on the logarithm of the oxygen content.

Measurements of the electromotive force of a p_{O2}/Pt/tubular YSZ/Pt/air setup with the 8YSZ solid electrolyte obtained by EPD were performed for different levels of oxygen reaching the outer surface of the tubular electrolyte. The oxygen content in the 60–650 ppm range was provided by the oxygen pump/oxygen sensor setup described in the experimental part. Fig. 6 shows the EMF signals at 850 °C for several oxygen level inputs monitored by the oxygen sensor. The electromotive force generated across the solid electrolyte is proportional to the logarithm of the concentration of mobile species (oxygen ion vacancies) according to the Nernst equation. Fig. 7 shows this dependence for the EPD tubular sensor and for the sensor of the

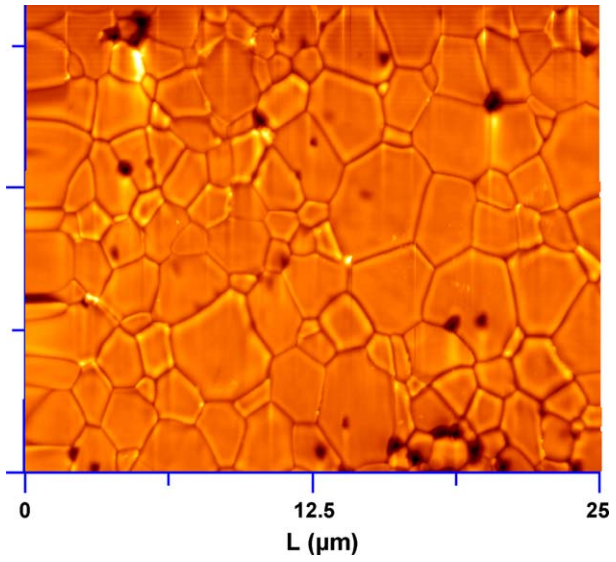

Fig. 8. Dynamic force microscopy topographic image of a polished and etched surface of a section of the sintered 8YSZ tube prepared by electrophoretic deposition.

p_{O2} station. No corrections were done for the difference in sensing areas; both follow the Nernst equation.

Fig. 8 shows a typical scanning probe microscopy image of the polished and thermally etched (1400 °C/20 min) surface of the section of the sintered tubular 8YSZ ceramic prepared by EPD. The ceramic is dense without relevant intergranular pores and the grain size distribution is in the 1–5 μm range.

4. Conclusions

Dispersions of zirconia–yttria particles in isopropanol were investigated for finding the best conditions for electrophoretic deposition. A bimodal distribution of granule sizes consisting of 70 wt.% particles of 0.75 μm average size and 30 wt.% particles of 19.5 μm average size was adequate for avoiding cracks upon drying before sintering. The addition of 4-hydroxybenzoic acid as dispersant increased the electrophoretic mobility of the ceramic granules, increasing the suspension stability, and therefore providing suitable conditions for deposition of the ceramic granules on sacrificial carbon electrode substrates. Small (4 mm diameter × 3 cm) closed end tubes were successfully obtained by the EPD technique, showing the ability of that technique for processing large quantities of tubular solid electrolytes with suitable electrical resistivity to be used in lambda sensors.

Acknowledgements

This work was supported by FAPESP (Procs. 05/53241-9 and 06/61025-7) and CNPq (Proc. 306496/88) grants and scholarships.

References

[1] A.R. Boccaccini, J.A. Roether, B.J.C. Thomas, M.S.P. Shaffer, E. Chavez, E. Stoll, E.J. Minay, The electrophoretic deposition of inorganic nanoscaled materials, J. Ceram. Soc. Jpn. 114 (2006) 1–14.
[2] O.O. Van der Biest, L.J. Vandeperre, Electrophoretic deposition of materials, Ann. Rev. Mater. Sci. 29 (1999) 327–352.
[3] I. Corni, M.P. Ryan, A.R. Boccaccini, Electrophoretic deposition: from traditional ceramics to nanotechnology, J. Eur. Ceram. Soc. 28 (7) (2008) 1353–1367.
[4] L. Besra, T. Uchikoshi, T.S. Suzuki, Y. Sakka, Bubble-free aqueous electrophoretic deposition (EPD) by pulse-potential application, J. Am. Ceram. Soc. 91 (10) (2008) 3154–3159.
[5] J.S. Cherng, J.R. Sau, C.C. Chung, Aqueous electrophoretic deposition of YSZ electrolyte layers for solid oxide fuel cells, J. Solid State Electrochem. 12 (7–8) (2008) 925–933.
[6] R. Fischer, E. Fischer, G. De Portu, E. Roncari, Preparation of ceramic micro-laminate bt electrophoresis in aqueous system, J. Mater. Sci. Lett. 14 (1) (1995) 25–27.
[7] S.T. Aruna, K.S. Rajam, A study on the electrophoretic deposition of 8YSZ coating using mixture of acetone and ethanol solvents, Mater. Chem. Phys. 111 (1) (2008) 131–136.
[8] I. Zhitomirsky, A. Petric, Electrophoretic deposition of electrolyte materials for solid oxide fuel cells, J. Mater. Sci. 39 (3) (2004) 825–831.
[9] L. Besra, C. Compson, M.L. Liu, Electrophoretic deposition of YSZ particles on non-conducting porous NiO–YSZ substrates for solid oxide fuel cell applications, J. Am. Ceram. Soc. 89 (10) (2006) 3003–3009.
[10] H. Negishi, K. Yamaji, N. Sakai, T. Horita, H. Yanagishita, H. Yokokawa, Electrophoretic deposition of YSZ powders for solid oxide fuel cells, J. Mater. Sci. 39 (3) (2004) 833–838.
[11] Y.H. Lee, C.W. Kuo, C.J. Shih, I.M. Hung, K.Z. Fung, S.B. Wen, M.C. Wang, Characterization on the electrophoretic deposition of the 8 mol% yttria-stabilized zirconia nanocrystallites prepared by a sol–gel process, Mater. Sci. Eng. A 445 (2007) 347–354.
[12] F. Harbach, H. Nienburg, Homogeneous functional ceramic components through electrophoretic deposition from stable colloidal suspensions—I. Basic concepts and application to zirconia, J. Eur. Ceram. Soc. 18 (6) (1998) 675–683.
[13] M.F. De Riccardis, D. Carbone, A. Rizzo, A novel method for preparing and characterizing alcoholic EPD suspensions, J. Colloid Interface Sci. 307 (1) (2007) 109–115.
[14] R. Ramamoorthy, P.K. Dutta, S.A. Akbar, Oxygen sensors: materials, methods, designs and applications, J. Mater. Sci. 38 (21) (2003) 4271–4282.
[15] A.M. Azad, S.A. Akbar, S.G. Mhaisalkar, L.D. Birkefeld, K.S. Goto, Solid-state gas sensors—a review, J. Electrochem. Soc. 139 (12) (1992) 3690–3704.
[16] S.P.S. Badwal, K. Foger, Solid oxide electrolyte fuel cell review, Ceram. Int. 22 (3) (1996) 257–265.
[17] K.P. Jagannathan, S.K. Tiku, H.S. Ray, A. Ghosh, E.C. Subbarao, in: E.C. Subbarao (Ed.), Technological Applications of Solid Electrolytes, Solid Electrolytes and Their Applications, Plenum Press, New York, London, 1980, p. 204.
[18] L. Jia, Z. Lu, X.Q. Huang, Z.G. Liu, Z. Zhi, X.Q. Sha, G. Li, W. Su, Preparation of YSZ film by gravity-electrophoretic deposition and its application in SOFC, Ceram. Int. 33 (4) (2007) 631–635.
[19] R.H.R. Castro, P.K. Kodama, D. Gouvêa, R. Muccillo, Electrophoretic deposition of ZrO_2–Y_2O_3: a bi-component study concerning self-assemblies, J. Mater. Sci. 44 (7) (2009) 1851–1857.
[20] S. Hayashi, C. Sato, Z. Nakagawa, Effect of different electrode materials on electrophoretic depositional behavior of yttria-stabilized zirconia powder, J. Mater. Sci. 41 (24) (2006) 8068–8073.
[21] X. Ge, X. Huang, Y. Zhang, Z. Lu, J. Xu, K. Chen, D. Dong, Z. Liu, J. Miao, W. Su, Screen-printed thin YSZ films used as electrolytes for solid oxide fuel cells, J. Power Sources 159 (2006) 1048–4050.
[22] L. Zhao, X. Huang, R. Zhu, Z. Lu, W. Sun, Y. Zhang, X. Ge, Z. Liu, W. Su, Optimization on technical parameters for fabrication of SDC film by screen printing used as electrolyte in IT-SOFC, J. Phys. Chem. Solids 69 (2008) 2019–2024.
[23] W. Sun, X. Huang, Z. Lu, L. Zhao, B. Wei, S. Li, K. Chen, N. Ai, W. Su, J. Phys. Chem. Solids 70 (2009) 164–168.
[24] M.C. Steil, F.C. Fonseca, Y.V. França, J.F.Q. Rey, E.N.S. Muccillo, R. Muccillo, An experimental setup for electrical measurements as a function of temperature and partial pressure of oxygen, Cerâmica 48 (307) (2002) 146–152.
[25] R.H.R. Castro, P.J.B. Marcos, E.K. Sakamoto, D. Gouvêa, Surface reactivity and electrophoretic deposition of ZrO_2–MgO mechanical mixture, J. Mater. Sci. 42 (16) (2007) 6946–6950.
[26] I.R. Oliveira, A.R. Studart, R.G. Pileggi, V.C. Pandolfelli, Dispersão e Empacotamento de Partículas—Princípios e Aplicações em Processamento Cerâmico, Fazendo Arte Editorial, S. Paulo, Brazil, 2000.
[27] Y. Hirata, A. Nishimoto, Y. Ishihara, Effects of addition of polyacrylic ammonium on colloidal processing of α—alumina, J. Ceram. Soc. Jpn. 100 (1992) 972–978.
[28] J. Bauerle, Study of solid electrolyte polarization by a complex admittance method, J. Phys. Chem. Solids 30 (12) (1969) 2657–2670.