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Thick Film Cermet of ZrO_2–Y_2O_3–TiO_2/Ni: Anodic Polarization Study

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Abstract

Thick films of $[(ZrO_2)_{0{\cdot}92}(Y_2O_3)_{0{\cdot}08}]_{0{\cdot}9}(TiO_2)_{0{\cdot}1}/$*Ni (35 vol%) have been deposited onto yttria stabilized zirconia (YSZ) substrates. The cermets were prepared by mixing a YSZ commercial powder,* TiO_2*, NiO and a controlled amount of carbon. Thixotropic slips with a solids content of 60 wt% were obtained. After sintering at 1300°C in air, without introduction any reducing atmosphere, the thick film cermets show good adherence and chemical and mechanical compatibility with YSZ electrolyte. The hydrogen oxidation on the cermets, using a three-electrode cell, has been studied. The polarization resistance is consisted of two separated contributions, one might be associated to the typical proton charge transfer, and the second one, might be originated from the adsorption reaction of electroactive species. The anodic polarization curve exhibited a maximum of current density for an overpotential close to that of the Ni–NiO system, which could be associated to the oxidation of hydrogen on NiO. © 1998 Published by Elsevier Science Limited. All rights reserved*

Keywords: films, composites, ZrO_2, inclusions, anodic polarization.

1 Introduction

The attempts to find, develop or manufacture a material, which incorporates most of the desirable properties of both ceramics and metals, have been widely encouraged,[1] specially for structural high-temperature high stress-resistant applications. The interest in cermets has become much broader with respect to applications, but their high cost, brittleness, nonuniformity, etc., makes difficult to use these materials in engines or other structural applications.

Fortunate, the appearance nowadays of other technologies as ceramic-metal joining,[2] reaction bonding of aluminum oxide (RBAO),[3,4] solid oxide fuel cells (SOFCs) and gas separator membranes, the attempts to combine ceramics and metals make this aim a practical and reliable idea.

On the other hand, nickel is widely known for its excellent response as metal electrocatalyst, particularly in hydrogen oxidation, the combination of both metallic Ni and yttria stabilized zirconia ceramic in different proportions yields a cermet material which is currently use as anode in electrochemical devices (i.e. in SOFCs).

The anodes for solid oxide fuel cells (SOFCs) have been studied by many researchers in order to improve overvoltage characteristics and long-term reliability.[5–8] These properties are strongly dependent on the anode material and its morphology. This cermet is usually prepared by a powder mixing process followed by firing in a controlled atmosphere. NiO is reduced to metallic Ni by heating the samples in a reducing atmosphere at high temperature[5–8] or by an electrochemical vapor deposition process (EVD).[9] The cermet Ni–YSZ electrical conductivity depends strongly on Ni content. Dees *et al.*[5] and Kawada *et al.*[7] have reported that to enhance the electronic conductivity, the cermet should have a Ni concentration higher than 30 vol%. Below this Ni content, which corresponds to the percolation limit, the cermet conductivity is similar to that of zirconia matrix.

Zirconia-mixed conductors are good candidates to replace the state of the art in SOFC cermet anodes. Ceria- and titania-doped YSZ mixed conductors could be good candidate materials as fuel electrode matrix.[10–21] It is expected that mixed conductivity will originate an increase in the surface area available for the electrochemical reaction, reducing polarization losses.[22] These mixed conductors based on stabilized zirconia are usually

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obtained if a significant amount of Ce^{4+} or Ti^{4+} cations are introduced in solid solution. The data reported in the literature suggest that the titania-doped YSZ materials exhibit a higher electronic conductivity than those of ceria-doped YSZ, for the same dopant concentration, and under the same working conditions.[10,11] For this reason, in this work, titania has been chosen as dopant. Swider and Worrell[23] prepared thin films of yttria (12 mol%) stabilized zirconia–titania (8 mol%) using metal–organic deposition (MOD) whereby metal–organic solutions of Zr-, Y-, and Ti-2-ethylhexanoates. This method implies to use of quite expensive precursors. Colomer *et al.*[24] developed a new processing method to prepare $[(ZrO_2)_{0.92}(Y_2O_3)_{0.08}]_{0.9}(TiO_2)_{0.1}$/Ni 35 vol% thick film cermets. In addition, there is no information on reviewed literature about the electrochemical behavior of titania-doped YSZ as matrix for cermet-anode.

The electrochemical response, anodic and cathodic polarizations, have been studied by several authors.[5–8,25–29] At present, it has still not been established the exact nature of the anodic reaction kinetic, further, there are a lot of discrepancies due to the experimental problems. Recently, Mogensen *et al.*[30] reported a critical overview of the SOFC literature and they established a main recommendation to overcome the large number of these discrepancies. One possible alternative is to prepare a cermet near the Ni percolation limit (~30–35 vol%) with a total Ni particle dispersion avoiding inhomogeneous current conduction paths, Ni particle sintering, etc. In this way, it is obtained a correct overpotential versus low density current polarization curves and the overpotential values are not affected by the high current effects.

By using a new cermet synthesis method, Colomer *et al.*[24] obtained a cermet with a thickness as low as (~5 μm) and high Ni particle dispersion, and then no nickel-particle percolation was observed. In these conditions, an actual anodic polarization response might appear at low current density. Therefore, the objective of the present work is to develop a three-electrode assembly, which consists of a 5 μm thick film cermet with composition $[(ZrO_2)_{0.92}(Y_2O_3)_{0.08}]_{0.9}(TiO_2)_{0.1}$/Ni (35 vol%) deposited onto YSZ substrate and platinum as counter and reference electrodes, in order to measure the anodic polarization under low current density regime.

2 Experimental

The matrix cermet powder $[(ZrO_2)_{0.92}(Y_2O_3)_{0.08}]_{0.9}(TiO_2)_{0.1}$/Ni (35 vol%) was processed via ceramic solid state reactions, from YSZ (Tosoh Corporation, Tokyo Japan) and TiO_2 (Merck Darmstadt, Germany). The detailed experimental is described elsewhere.[24] Carbon black (Raven Industries, Latrobe, PA) was added not only as reducing agent but also as controlling and porosity nucleating agent. The slurry, for aerographic deposition method, was prepared by mixing the cermet powder with α-terpineol dispersant and solvent (8250, Dupont, Wilmington, DE). Then, it was ball milled for 2 h and after this, a binder (ethyl-cellulose) and a plasticizer 2-(2-ethoxy-ethoxy) ethanol were added.

Aerographic method was used to deposit the slurry as a cermet-anode layer onto sintered YSZ electrolyte substrate with high uniform surface quality. The dried cermet was sintered in two steps, firstly it was heat-treated at 500°C for 10 min and subsequently fired at 1300°C for 30 min. After sintering, the adherence of the deposited layers was assayed by the tape-test. Crystal evolution was recorded by X-ray diffraction (XRD) (Model D-5000 diffractometer, Siemens). Cermet porosity was determined by mercury porosimetry (Model Autopore II 9220, Micromeritics.) The residual carbon content in the sintered cermet was analyzed by Leco WR-112 analyzer. The microstructure of the as-sintered samples and transverse cross sections were examined by scanning electron microscopy and energy-dispersive X-ray analysis (SEM–EDX), Model DSM 950, Karl Zeiss.

In order to measure its conductivity, a pellet cermet was sintered in a controlled atmosphere furnace (10^{-18} atm). Samples were electroded with platinum paste and the electrical conductivity measurements were performed in a controlled atmosphere furnace using a YSZ sensor and a YSZ electrochemical pump.[31,32] The temperature range was 900–1100°C and a fixed frequency of 10 kHz was used.

Anodic polarization measurements were carried out at 900°C in a potentiostatic mode using the three-electrode configuration shown in Fig. 1 The solid electrolyte is a dense YSZ (8 mol% yttria) rod, 20 mm in diameter and 2 mm in thickness. The working electrode (WE) is a cermet square of 7 mm side deposited onto YSZ substrate. The counter (CE) and reference electrodes (RE) were painted out onto the opposite side of the working electrode (WE) using platinum paste, and subsequently heat-treated at 900°C. A platinum grid current collector was pressed onto the cermet to assure a homogeneous distribution of the current lines. By means of an Autolab Impedance Analyzer equipped with a PG stat 20 Potentiostat (ECOCHIMIE), a set of voltages versus H_2 (0, 50, 100, 150, 200, 300, 400 and 500 mV) were applied. The resulting current was recorded after reaching the steady-state condition.

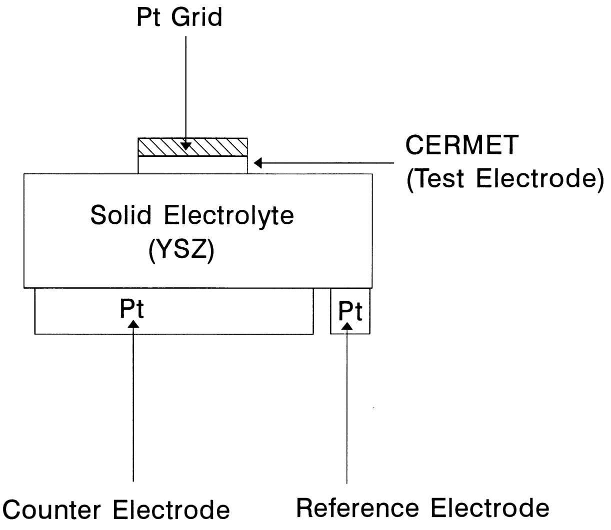

Fig. 1. Schematic diagram of the cell configuration used for polarization measurements.

Impedance spectrum was also drawn under polarization in the frequency range 10^{-2}–5×10^{4} Hz using an amplitude of 30 mV. All experiments were carried out under one single atmosphere of H_2/N_2 10/90 gas mixture saturated with water vapor at 25°C, i.e. $pO_2 = 10^{-18}$ atm.

The overpotential, η, was calculated from the applied voltage V_{app} and from the resulting current, I, using the following expression:

$$\eta_{\text{air}} = V_{\text{app/air}} - R_0 I \tag{1}$$

where R_0 is the electrolyte resistance, I is the current and $V_{\text{app/air}}$ is given by:

$$V_{\text{app/air}} = V_{\text{app/H}_2} + \frac{RT}{4F}\ln\frac{10^{-18}}{0{\cdot}21} \tag{2}$$

In this work, $[(ZrO_2)_{0\cdot92}(Y_2O_3)_{0\cdot08}](TiO_2)_{0\cdot1}$/Ni (35 vol%) will be labeled YSZ–TiO_2/Ni.

3 Results and Discussion

3.1 XRD, microstructural characterization and electrical conductivity

XRD patterns of the thick-film cermet were made before and after sintering. YSZ–TiO_2 solid solution and metallic nickel diffraction peaks were observed for the sintered cermet, neither NiO nor Carbon peaks were detected. Furthermore by Leco test the residual carbon was also negligible.

The deposited layers adhered well to the YSZ substrate after sintering. In fact, the layers were not removed from the substrate using the tape-test. Figure 2 shows the cermet microstructure obtained after sintering. The white, grey and dark areas represent the nickel, titania doped zirconia and the pores, respectively. Good homogeneity and uniform distribution of Ni in the matrix can be observed. Cross section of thick film cermet illustrates (Fig. 3) a clean and uniform interface morphology between the cermet (anode) and the YSZ (electrolyte). The layer thickness was ~5 μm. The average porosity value was about 52% and the average pore diameter was 2·5 μm. The porosity achieved can be attributed to an intergranular porosity, such a porosity ranging between 10 and 0·1 μm, which corresponds to macropore formation. The porosity value is an appropriated one for anode morphology, and adequate optimization for anodic polarization measurements. No Ni-particles percolation was observed.

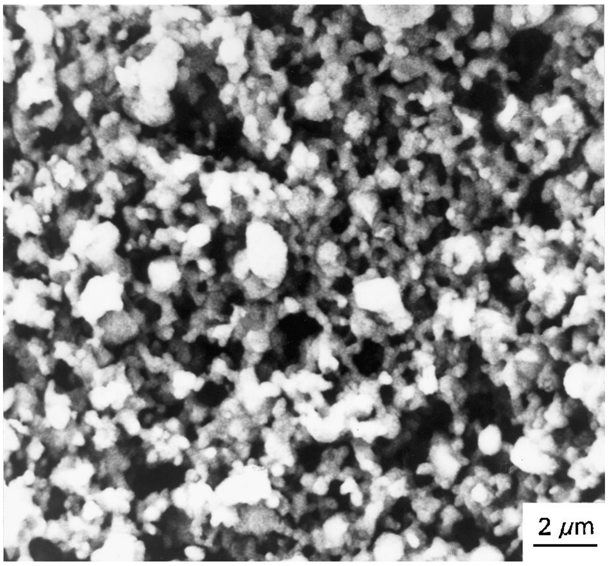

Fig. 2. SEM micrograph of the cermet electrode after anneal at 1300°C.

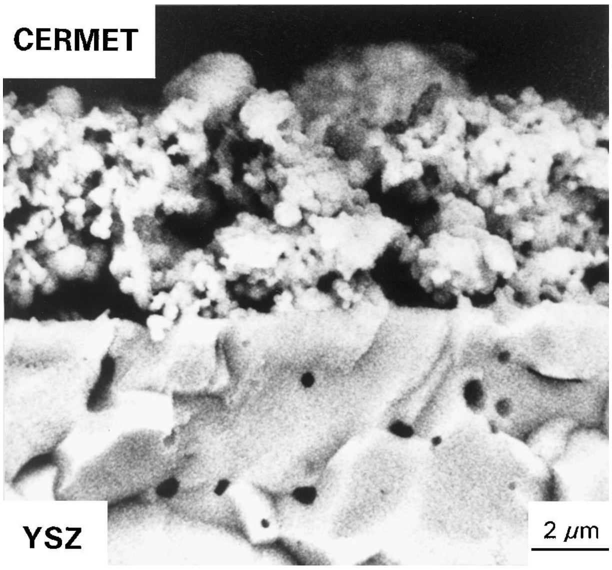

Fig. 3. SEM micrograph of cross section of thick film cermet sintered at 1300°C.

3.2 EIC measurements

The impedance diagrams obtained under polarization conditions are shown in Fig. 4 Beside the high frequency ohmic resistance (R_0), two capacitive loops, always overlapped, can be seen. Thus, all the spectra were fitted to two depressed semicircle arcs in series with a pure resistance using the non linear square fit method and the equivalent circuit shown in Fig. 5. It is commonly assumed in the literature that the high frequency arc is related to concentration processes involving either adsorption or diffusion of electroactive species.[26] Bellow $\eta = -876\,\text{mV air}^{-1}$, the charge transfer resistance (Rct) remained almost constant. This is in agreement with the classical Butler–Volmer theory that, in fact, predicts a constant value of the charge transfer reaction resistance at a low polarization level. Above $\eta = -823\,\text{mV air}^{-1}$, Rct increased twice and this fact suggests a modification in the charge transfer mechanism which takes place when Ni starts to oxidize. Simultaneously, the concentration impedance decreased due to the promotion of adsorption/desorption of electroactive species. Under higher anodic polarization a huge increase of the impedance is observed suggesting a strong inhibition of hydrogen oxidation due to a total oxidation of Ni particles to NiO.

3.3 Anodic polarization measurements

The anodic polarization measurements were carried out keeping constant the pH_2/pH_2O ratio equal to 14. The maximum overpotential (η) applied was $-577\,\text{mV air}^{-1}$, in order to avoid a possible damage caused by the modification of cermet microstructure during Ni oxidation. The anodic curve was reproducible after several cycling which means that the cermet was not degraded. Figure 6 shows a typical curve of the

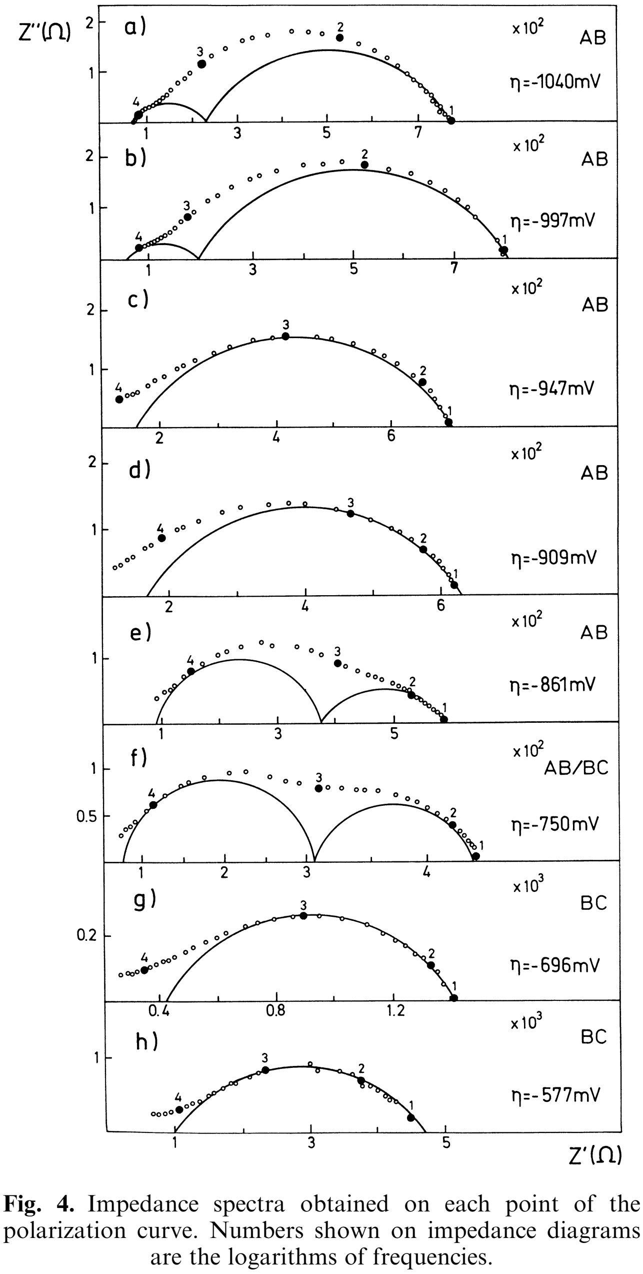

Fig. 4. Impedance spectra obtained on each point of the polarization curve. Numbers shown on impedance diagrams are the logarithms of frequencies.

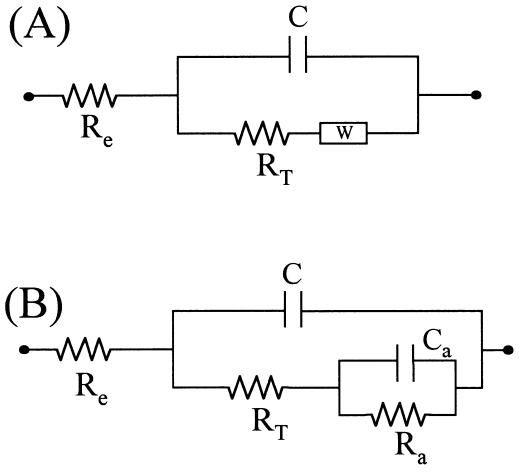

Fig. 5. Fitted equivalent circuits associated to the impedance spectra obtained.

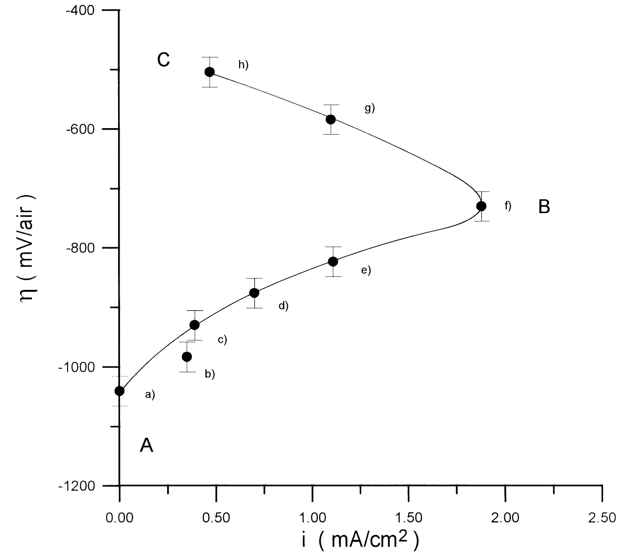

Fig. 6. Polarization curve for a YSZ–TiO_2lNi cermet at 900°C in hydrogen atmosphere ($PO_2 = 10^{-18}$ atm).

anodic oxidation of hydrogen on the Ni/YSZ or mixed conductor particles/YSZ interfaces. The curve is divided into two domains of polarization AB and BC in the same way than that reported by Guindet *et al.*[28]

The $\eta - i$ curve exhibits a current density peak, at a potential value close to the Ni/NiO system.[33] The AB domain can be attributed to the oxidation of hydrogen on nickel or on mixed conductor particle. In this domain, the variation of the overvoltage, η, versus current density, i, is described by the following Tafel-type law.

$$i = i_0 \exp\left(\frac{2F}{RT}\eta\right) \qquad (3)$$

with i_0 1·28 $mAcm^{-2}$ and the reaction order is close to 0·5.

The same behavior has been obtained by Kawada *et al.*[7,25] for hydrogen oxidation on a Ni/YSZ cermet at 1000°C with a pH_2/pH_2O ratio equal to 32·3 and by Guindet *et al.*[27] for hydrogen oxidation on a pure nickel ball as working electrode at 960°C, with pH_2/pH_2O ratios equal to 3·6, 7·15 and 14·3.

The first one domain (AB) reaches the current density peak at -730 mV air^{-1}, this overpotential corresponds to the Ni oxidation potential.[33] Same result was reported by Guindet *et al.*[28] being the working electrode a pure nickel ball approximately 3 mm in diameter.

In the BC domain, the current density is a decreasing function of the anodic overvoltage. This behavior is similar to those observed for the passivation processes and may be explained by the progressive oxidation of the nickel of the cermet leading to an increase in its overall resistance. These results agree well with those of the Guindet *et al.*[28]

4 Conclusions

A thick film cermet of $[(ZrO_2)_{0\cdot92}(Y_2O_3)_{0\cdot08}]_{0\cdot9}(TiO_2)_{0\cdot1}$/Ni (35 vol%) with a good adherence to the substrate was obtained. Sintering was carried out without introducing any reducing atmosphere, which will allow the co-sintering of all components in one unique stage.

In the working conditions, by using a low current density regime, two processes are detected in the H_2 oxidation at Ni//YSZ and YSZ–TiO_2//YSZ interfaces: a typical charge transference and a surface adsorption of electroactive species rather than diffusion one. At overpotential values higher than -730 mV air^{-1} the Ni oxidation takes place. Above this η a passivation effect was observed.

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References

1. Tinklepaugh J. R. and Crandall, W. B., *Cermets*, Reinhold Publishing Corporation, New York, 1960.
2. Suganuma, K., Miyamoto, Y. and Koizumi, M., Joining of ceramics and metals. *Ann. Rev. Mater Sci.*, 1988, **18**, 47–73.
3. Claussen N, Travitzky N. A. and Wu, S., Tailoring of reaction-bonded Al_2O_3 (RBAO) ceramics. *Ceram. Eng. Proc.*, 1990, **11**, 806–820.
4. Wu, S., Gesing, A., Travitzky, N. A. and Claussen, N., Fabrication and properties of Al-infiltrated RBAO-based composites. *Journal of the European Ceramic Society*, 1991, **7**, 277–281.
5. Dees, D. W., Claar, T. D., Easier, T. E., Fee, D. C. and Mrazek, F. C., Conductivity of porous Ni/ZrO_2–Y_2O_3 cermets. *J. Electrochem. Soc.*, 1987, **134**, 2141–2146.
6. Middleton, P. H., Seiersten, M. E. and Steele, B. H. C., Morphology and electrochemistry of porous nickel/zirconia cermets. In *Proceedings of the 1st International Symposium on Solid Oxide Fuel Cells*, Vol. 89–11, ed. S. C. Singhal. The Electrochemical Society, Pennington, NJ, 1989, pp. 90–95.
7. Kawada, T., Sakai, N., Yokokawa, H., Dokiya, M., Mori, M. and Iwata, T., Structure and polarization characteristics of Solid Oxide Fuel cell anodes. *Solid State Ionics*, 1990, **40–41**, 402–406.
8. Perego, C., Zanibelli, L., Catrullo, M. and Piro, G., Temperature programmed reduction (TPR) characterization of NiO/YSZ for solid oxide fuel cell. In *Proceeding of 3rd International Symposium on Solid Oxide Fuel Cells* Vol. 93–94, ed. S. C. Singhal and H. I. Iwahara. The Electrochemical Society, Pennington, NJ, 1993, pp. 454–463.
9. Isenberg, A. O. and Zymboly, G. E., High performance cermet electrodes. US Patent No. 4 582, 766, 1986.
10. Liou, S. S. and Worrell, W. L., Electrical properties of novel mixed-conducting oxides. *J. Appl. Physics A*, 1989, **49**, 25–31.
11. Càles, B. and Baumard, J. F., Mixed conduction and defect structure of ZrO_2–$CeO_2Y_2O_3$ solid solutions. *J. Electrochem. Soc.*, 1983, **131**, 2407–2413.
12. Ananthapadmanabhan, P. V., Venkatramani, N., Rohatgi, V. K., Momin, A. C. and Venkateswarlu, K. S., Structure and ionic conductivity of solid solutions in the system $0{\cdot}9[(ZrO_2)_{1-x}\text{-}(CeO_2)_x]_{0\cdot1}(Y_2O_3)$. *Journal of the European Ceramic Society*, 1990, **6**, 111–117.
13. Abrantes, J. C. C., Labrincha, J. A., Marques, F. M. B. and Frade, J. R., Electrical conductivity in the system CeO_2–Dy_2O_3–ZrO_2. In *Ceramics Today–Tomorrow's Ceramics*, Part C, ed. P. Vincenzini. Elsevier Science, Amsterdam, 1991, pp. 2265–2274.
14. Marques, R. M. C., Frade, J. R. and Marques, F. M. B., Transport properties of zirconia based solid solutions with mixed valence dopants. *Bol. Soc. Esp. Ceram. Vidr.*, 1991, **30**, 464–468.
15. Naito, H. and Arashi, H., Electrical properties of ZrO_2=–TiO_2–Y_2O_3 system. *Solid State Ionics*, 1992, **53–56**, 436–441.
16. Colomer, M. T., Jurado, J. R., Marques, R. M. C., Marques, F. M. B., Evaluation of titania doped YSZ for SOFC anodes. In *Proceeding of 3rd International Symposium on Solid Oxide Fuel Cells*, Vol. 93–94, ed. S. C.

Singhal and H. I. Iwahara. The Electrochemical Society, Pennington, NJ, 1993, pp. 523–532.

17. Lindegaard, T., Clausen, C. and Mogensen, M., Electrical and electrochemical properties of $Zr_{0.77}Y_{0.13}Ti_{0.1}O_{1.93}$. In *Proceeding of 14th Riso International Symposium on Materials Science*, ed. F. W. Poulsen, J. J. Bentzen, T. Jacobsen, E. Skou and M. J. L. Ostergard. Riso National Laboratory, Roskilde, Denmark, 1993, pp. 311–318.
18. Marques, R. M. C., Marques, F. M. B. and Frade, J. R., Characterization of mixed conductors by dc techniques. Part II- Experimental results. *Solid State Ionics*, 1994, **73**, 27–34.
19. Colomer, M. T., Jurado, J. R., Marques, R. M. C. and Marques, F. M. B., Role of grain boundaries on the electrical properties of titania doped ytrria stabilized zirconia. *Mater. Res. Bull.*, 1995, **30**, 515–522.
20. Swider, K. E. and Worrell, W. L., Electronic conduction mechanism in yttria-stabilized zirconia-titania under reducing atmospheres. *J. Electrochem. Soc.*, 1996, **143**, 3706–3711.
21. Colomer, M. T., Durán, P., Caballero, A. and Jurado, J. R., Microstructure, electrical properties and phase equilibria relationships in the ZrO_2–Y_2O_3–TiO_2 System: the subsolidus isothermal section at 155°C. *Mat. Sci. and Engin*, 1997, **A229**, 114–122.
22. Schouler, E. J. L., Relation between solid oxide electrolyte surface properties and electrode reaction kinetics. *Solid State Ionics*, 1983, **9-10**, 945–952.
23. Swider, K. E. and Worrell, W. L., Metal-organic deposition of thin-film yttria-stabilized zirconia–titania. *J. Mater. Res.*, 1996, **11**, 381–386.
24. Colomer, M. T., Nieto, E. and Jurado, J. R., Developing a thick film cermet. *Am. Ceram. Soc. Bull.*, 1996, **75**, 85–88.
25. Kawada, T., Sahai, N., Yokokawa, H., Dokiya, M., Mori, M. and Iwara, T., Characteristics of slurry-coated nickel zirconia cermet anodes for Solid Oxide Fuel Cells. *J. Electrochem. Soc.*, 1990, **137**, 3042–3047..
26. Mogensen, M. and Lindegaard, T., The kinetics of hydrogen oxidation on a Ni–YSZ SOFC electrode at 1000°C. In *Proceedings of 3rd International Symposium on SOFCs*, Vol. 93–94, ed. S. C. Singhal and H. Iwahara. The Electrochemical Society, Pennington, NJ, 1993, 484–493.
27. Norby, T., Velle, O. J., Leth-Olsen, H., Tunold, R., Reaction resistance in relation to three phase boundary length of Ni/YSZ electrodes. In *Proceedings of 3rd International Symposium on SOFCs*, Vol. 93–94, ed. S. C. Singhal and H. Iwahara. The Electrochemical Society, Pennington, NJ, 1993, pp. 473–478.
28. Guindet, J., Roux, C. and Hammou, A., Hydrogen oxidation at the Ni/Zirconia electrode. In *Proceedings of 2nd International Symposium on Solid Oxide Fuel Cells*, ed. F. Gross, P. Zegers, S. C. Singhal and O. Yamamoto. Commission of the European Communities, Luxembourg, 1991, pp. 553–559.
29. Misuzaki, M., Yamamura, T., Mori, N., Tagawa, H, Hirano, K., Ehara, S., Takagi, T., Hishinuma, M., Sasaki, H., Sogi, T., Nakamura, Y. and Hashimoto, K., Kinetic studies on Ni/YSZ anode reaction of SOFC in H_2–H_2O atmospheres by the use of nickel pattern electrodes. In *Proceedings of the 17th Riso International Symposium on Materials Science. High Temeperature Electrochemistry. Ceramics and Metals*. ed. F. W. Poulsen, N. Bonanos, S. Linderoth, M, Mogensen and B. Zachau-Christiansen. Riso Nat. Lab., Roskilde, Denmark, 1996, pp. 363–368.
30. Mogensen, M., Sunde, S. and Primdahl, S., SOFC anode kinetics. In *Proceedings of the 17th Riso International Symposium on Materials Science High Temperature Electrochemistry, Ceramics and Metals*, ed. F. W. Poulsen, N. Bonanos, S. Linderoth, M. Mogensen and B. Zachau-Christiansen. Riso Nat. Lab., Roskilde, Denmark, 1996, 14 pp. 77–100.
31. Marques, F. M. B. and Wirtz, G. P., Electrical properties of ceria-doped yttria. *J. Am. Ceram. Soc.*, 1991, **74**, 598–605.
32. Marques, F. M. B. and Wirtz, G. P., Oxygen fugacity control in nonflowing atmospheres: I, experimental observations in CO/CO_2 and O_2/N_2 mixtures. *J. Am. Ceram. Soc.*, 1992, **75**, 369–374.
33. Elliot, J. F. and Gleiser, M., Thermochemical properties of selected elements, In *Thermochemistry for Steelmaking*, Chapter 2, Addison–Wesley Reading, MA, 1960, pp. 13–122.