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Chemical and thermomechanical compatibility between Ni–GDC anode and electrolytes based on ceria

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Abstract

The scope of the present work is to study the thermal and chemical compatibility between a Ni–$Ce_{0.9}Gd_{0.1}O_{1.95}$ cermet, with 39 vol.% Ni, and two electrolytes based on $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC). The cermet was synthesized as a composite NiO–$Ce_{0.9}Gd_{0.1}O_{1.95}$ by a polymeric organic complex solution method and subsequently reduced to Ni–$Ce_{0.9}Gd_{0.1}O_{1.95}$ cermet. The GDC electrolytes were prepared by: (a) chemical precipitation process with nitrates as precursors and $(NH_4)OH$ as precipitant agent and (b) from a commercial submicronic powder modified with 1.0 wt.% Bi_2O_3 for improving the sintering mechanism.

The anode was fixed on the electrolyte by isostatic pressing of powders and the obtained sandwich was cosintered between 1350 and 1400 °C for 2 h to obtain dense electrolytes with high ionic conductivity along with well-developed anode/electrolyte interfaces of solid oxide fuel cells. The cosintered anode/electrolyte interfaces were characterized by using scanning electron microscopy. The study of the possible diffusion of nickel from the anode into the electrolyte was performed by EDAX analysis. The reaction products formed into cosintered materials were determined by X-ray diffraction (XRD). It is found that the anode is compatible with both electrolytes up to 1400 °C without formation of new phases at these temperatures even during prolonged treatments.

Keywords: Sintering; Interfaces; Fuel cells

1. Introduction

Solid oxide fuel cells (SOFCs), which can convert chemical energy directly to electrical power with high efficiency and low pollution, are attracting more and more attention. The conventional SOFCs based on yttria stabilized zirconia (YSZ) electrolyte usually operate at high temperatures such as 900 °C or more to obtain good performance. However, these operating temperatures may cause a series of problems such as electrode sintering, interfacial diffusion and thermal mismatch. These are some of the reasons why low-temperature SOFCs have attracted much attention in more recent years. To reduce the operation temperature, the following two approaches can be considered: one way is to prepare thin layers of YSZ with very low electrical impedance; the other is to replace the YSZ electrolyte by oxygen ion conductors based on other ceramic electrolytes, which have higher ionic conductivity than YSZ.

This paper deals with some features associated to the cells based on the second way, because of the excellent electrical properties of doped ceria electrolytes, especially gadolinia-doped ceria (GDC) $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) electrolyte, which is considered to be one of the most promising materials for SOFCs operating below 700 °C [1–3]. It has an ionic conductivity that is two to three times higher than that of YSZ. Its thermal expansion coefficient ($12.6 \times 10^{-6}\ K^{-1}$) is much closer to that of the Ni-cermet and commercial ferritic stainless steel interconnects, compared with YSZ ($10.5 \times 10^{-6}\ K^{-1}$). Moreover, it has a better chemical compatibility with high performance cobalt-containing cathodes, such as $Sm_{0.5}Sr_{0.5}CoO_3$ [4], $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ [5], and $Ba_{0.5}Sr_{0.5}Co_{0.2}Fe_{0.8}O_3$ [6].

The requirements for anode materials working with ceria electrolytes are: good electrical properties, an appropriate microstructure and a high compatibility with other fuel cell components [7,8]. So, a suitable anode for GDC electrolytes is

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generally suggested to be Ni–GDC cermets. Ni metal is a catalyst for cracking of hydrocarbons and this role is to make the anode a good electronic conductor at the operating conditions of the SOFC device. An issue of significant importance for the successful operation of fuel cells is the chemical compatibility between electrodes and electrolyte materials. It should be ensured that there are no reaction phases on the electrode/electrolyte interfaces, since this could be detrimental for the efficiency of the cell. Furthermore, cation interdiffusion must be precluded because it may negatively modify the properties of both involved materials, i.e. electrode and electrolyte. The scope of the present work is to establish the interphase relations between two ceramic GDC electrolytes and a NiO–GDC composite and to study the chemical compatibility between them by X-ray diffraction (XRD) in powder mixtures, and by scanning electron microscopy (SEM/EDX) in semicells prepared as double-layer pellets. Taking into account that the most usual procedure for obtaining the semicell anode/electrolyte is the previous formation of the pair with the NiO–GDC precursor and posterior "in situ" reduction of the NiO, the work wishes to establish the compatibility relations between both GDC electrolyte and the NiO–GDC composite, and between GDC electrolyte and the Ni–GDC cermet.

2. Experimental procedure

2.1. Powder preparation and characterization

NiO–$Ce_{0.9}Gd_{0.1}O_{1.95}$ (50/50 wt.%) composite powder was prepared by the polymeric organic complex solution method from nitrate precursors [$Ni(NO_3)_2\cdot 6H_2O$, $Ce(NO_3)_3\cdot 6H_2O$ and $Gd(NO_3)_3\cdot 6H_2O$ (99.9% Alfa Aesar)] and a water soluble alcohol (ethylene glycol). 50 wt.% NiO was chosen for attaining 39 vol.% Ni in the final cermet, which is an adequate amount for percolation, such as was proven by Yang et al. [9]. After thermal treatment at 800 °C for 1 h in air a powder with two well-crystallised phases, fluorite and NiO, was achieved. The composite powder was denoted as NiO–GDC. XRD analysis was performed to calculate the lattice parameters of both cubic phases, NiO and GDC, doped and undoped with Bi_2O_3 using Si as internal standard. For the electrolytes based on ceria, two types of processing methods were carried out: one, a chemical route (coprecipitation technique) and another, by adding Bi_2O_3 as a sintering aid to commercial GCD powder (Rhodia GmbH, FRG). For the $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) powders prepared by the coprecipitation process the corresponding nitrates of Gd and Ce were used as starting precursors and $(NH_4)OH$ as precipitant agent. The obtained precipitated powders were calcined at 600 °C for 2 h. For the second route, a final amount of 1.0 wt.% bismuth oxide was added as bismuth nitrate dissolved in ethanol to the submicronic commercial $Ce_{0.9}Gd_{0.1}O_{1.95}$ powder. After drying at 120 °C for 2 h, the two powders were calcined at 700 °C for 2 h. These electrolyte powders were denoted GDC and GDC–Bi, respectively.

2.2. Chemical compatibility characterization

To investigate the chemical compatibility of NiO–GDC with GDC and GDC–Bi, equal amounts of the as-synthesized NiO–GDC were thoroughly ground with GDC or GDC–Bi to form a homogeneous powder mixture, and subsequently isostatically pressed at 200 MPa to form pellets of 15 mm in diameter. These pellets were heat treated between 1350 and 1450 °C for 4 h and aged at 1000 °C for 100 h in air; finally X-ray diffraction (XRD) (Siemens D-5000, Cu Kα radiation) was performed on the grounded powders after thermal treatments. Lattice parameters were calculated after the heat treatment to observe possible modifications of the phases by formation of new, different solid solutions.

2.3. Thermal expansion coefficient characterization

Linear thermal expansion was measured on NiO–GDC, GDC and GDC–Bi by using a dilatometer (Netzsch 407/E, Geratebau, Bayern, Germany) in the temperature range from 25 to 1000 °C in air. Essays were performed at a heating and cooling rate of 5 °C/min. The thermal expansion coefficient α is obtained from data that were taken on the cooling curve in all the cases.

2.4. Microstructural characterization

NiO–GDC/GDC and NiO–GDC/GDC–Bi sandwiches were prepared by means of the same isostatic pressing conditions of the powder pellets. Sintering was done during 2 h at 1400 °C and 1350 °C, respectively and subsequently the sintered pellets were reduced in H_2 (10%)–N_2 (90%) at 700 °C for 2 h. After the reduction cycles, dimensional changes were measured on the obtained cermet. Volume changes were not appreciated with regard to the composite. The selected sintering temperatures were based on the densification results previously obtained for both types of electrolytes, as described in detail elsewhere [10,11]. SEM on polished and fractured surfaces was employed for determining the microstructure of the transversal sections of the pair samples. Possible chemical reaction and interdiffusion between the anode and the electrolytes were analysed via energy dispersive X-ray spectroscopy (EDAX).

3. Results and discussion

Table 1 shows the lattice parameters of the phases corresponding to the NiO–GDC composite, and to the GDC

Table 1
Lattice parameters of the NiO and GDC phases before and after the heat treatments

Compounds	Lattice parameter, a (±0.0001 nm)
Green compacts	
NiO	0.4176
GDC	0.5415
GDC–Bi	0.5417
After 1450 °C + 1000 °C treatments, before reduction	
NiO	0.4177
GDC	0.5416
GDC–Bi	0.5417

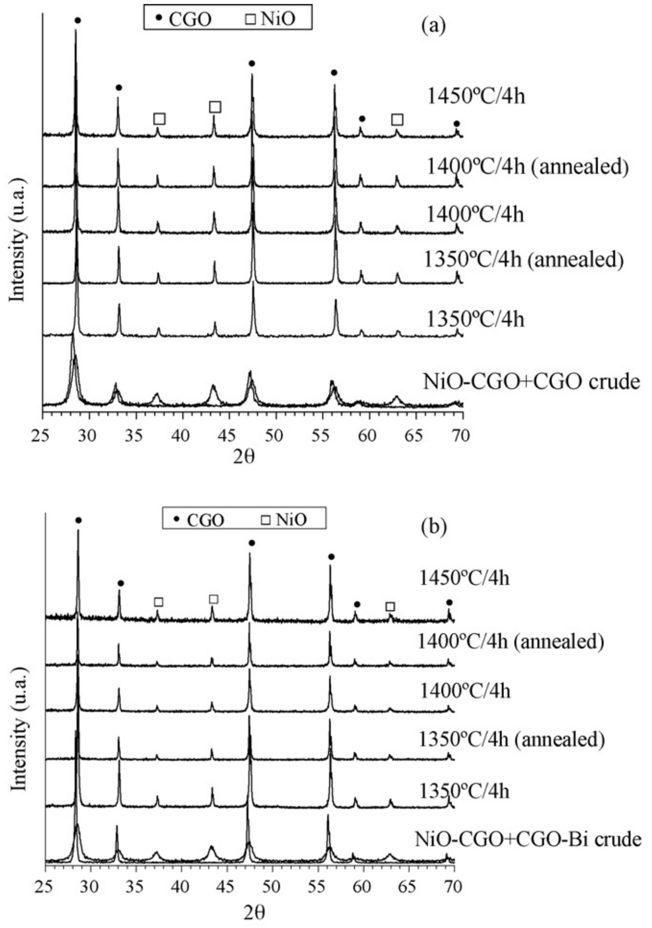

Fig. 1. XRD patterns of mixed powder: (a) NiO–GDC + GDC and (b) NiO–GDC + GDC–Bi, fired between 1350 and 1450 °C for 4 h and after that annealed in air at 1000 °C for 100 h.

electrolyte. Obviously the lattice parameter of both GDC compounds that of electrolyte and composite is the same. Bi-doped electrolyte showed a slightly higher lattice parameter owing to Bi cation incorporation [12]. Fig. 1a displays the XRD patterns of the pair NiO–GDC/GDC, obtained after the different heat treatments, along with the corresponding initial phases (GDC and NiO). It is found that these initial phases have not suffered any transformation, even in the most severe conditions, i.e. high sintering temperature 1450 °C for 4 h and long operating time, 1000 °C for 100 h in air, such as is seen in Table 1, in which are shown the corresponding lattice parameters after such a heat treatment. Furthermore, XRD patterns revealed no peaks of secondary phases, i.e. there is no obvious peaks from phases other than NiO and GDC until the detection limit of the XRD technique. In the same way, Fig. 1b illustrates the chemical compatibility of NiO–GDC with GDC–Bi, giving similar results, that is, there is a chemical compatibility between NiO–GDC and GDC–Bi up to 1450 °C. Such as was shown in Ref. [9], the GDC–Bi is stable up to 1450 °C, and maintains its ionic conductivity.

Fig. 2 displays the thermal expansion behaviour of NiO–GDC together with those of GDC–Bi, which is the same as that of the pure GDC, and consequently not shown for the shake of clearness in the figure. The curves show two clear features. Firstly, the thermal expansion rates of the composite NiO–GDC are significantly greater than those of the electrolyte based on ceria. Secondly, both expansion curves are linear, and the coefficients of thermal expansion (CTE) calculated from the thermal expansion curves are similar to previously reported values [13–16].

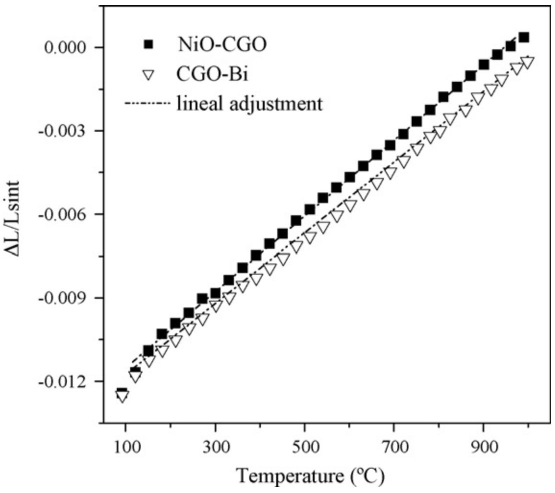

Fig. 2. Thermal expansion vs. temperature plot of NiO–CGO and CGO–Bi.

Table 2 compares these results with literature data. Although the CTE of GDC and GDC–Bi obtained in the present study ($\alpha = 12.6\ \mathrm{K}^{-1}$) are larger than those reported in similar systems by Corbel et al. [13] and Hayashi et al. [14], 11.9 and 12.2 K^{-1}, respectively, they are in good agreement with those reported by Bance et al. [15] at high temperatures, 12.5–12.8 K^{-1}. Observed thermal expansion behaviour of GDC is not dependent on the content of bismuth oxide. In the case of NiO–GDC composite, the experimental CTE value obtained is in agreement with that reported by Ishihara et al. [16] for a similar composite and furthermore is similar to the calculated theoretical value ($\alpha = 13.59 \times 10^{-6}\ \mathrm{K}^{-1}$) from the following equation:

$$\alpha_{\mathrm{AB}} = \frac{\%\mathrm{vol}_{\mathrm{A}}\alpha_{\mathrm{A}} + \%\mathrm{vol}_{\mathrm{B}}\alpha_{\mathrm{B}}}{100} \qquad (1)$$

where $\%\mathrm{vol}_{\mathrm{i}}$ is the volume percentage and α is the coefficient of thermal expansion ($\alpha_{\mathrm{A}} = \alpha_{\mathrm{NiO}} = 14.5\ \mathrm{K}^{-1}$ [9] and $\alpha_{\mathrm{B}} = \alpha_{\mathrm{CGO}} = 12.6\ \mathrm{K}^{-1}$ [measured]).

Fig. 3 shows cross-sectional SEM views corresponding to interfaces electrode/electrolyte cosintered at 1350 °C for 2 h, (a) NiO–GDC composite/GDC–Bi electrolyte, and (b) Ni–

Table 2
Coefficients of thermal expansion of electrolytes (GDC–Bi and GDC) and composite (NiO–CGO)

Experimental results		Literature	
Composition	α ($\times 10^6\ \mathrm{K}^{-1}$)	Composition	α ($\times 10^6\ \mathrm{K}^{-1}$)
GDC–1% Bi_2O_3	12.6	NiO–CGO	13.2
CGO	12.7	CGO	12.6
NiO50–CGO50	13.5	CGO	12

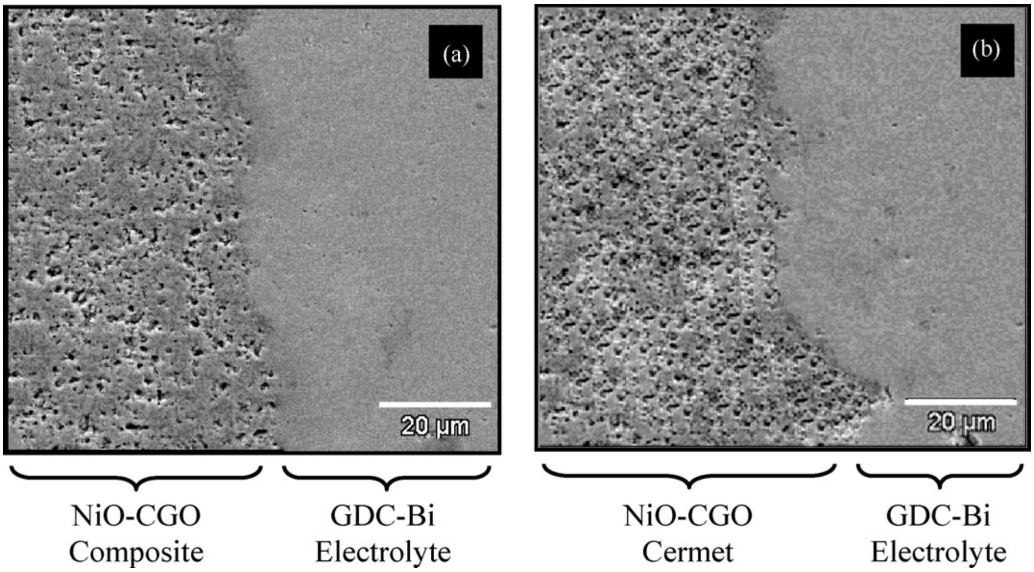

Fig. 3. SEM micrographs of the polished surface of interface between: (a) NiO–GDC and GDC–Bi cosintered at 1350 °C for 2 h and (b) Ni–GDC and GDC–Bi, after H_2 reduction at 700 °C for 2 h.

GDC cermet/GDC–Bi electrolyte. In both cases, the GDC layer is strongly attached to the Ni–GDC phase and showed a well-defined interface. Also it can be seen that the reducing process at 700 °C, made for obtaining the Ni metallic phase does not alters the interface. It can be observed that for the whole cosintering process no delaminations and other type of structural defects were formed within the laminate structure. This fact confirms the correct selection of both electrolyte and

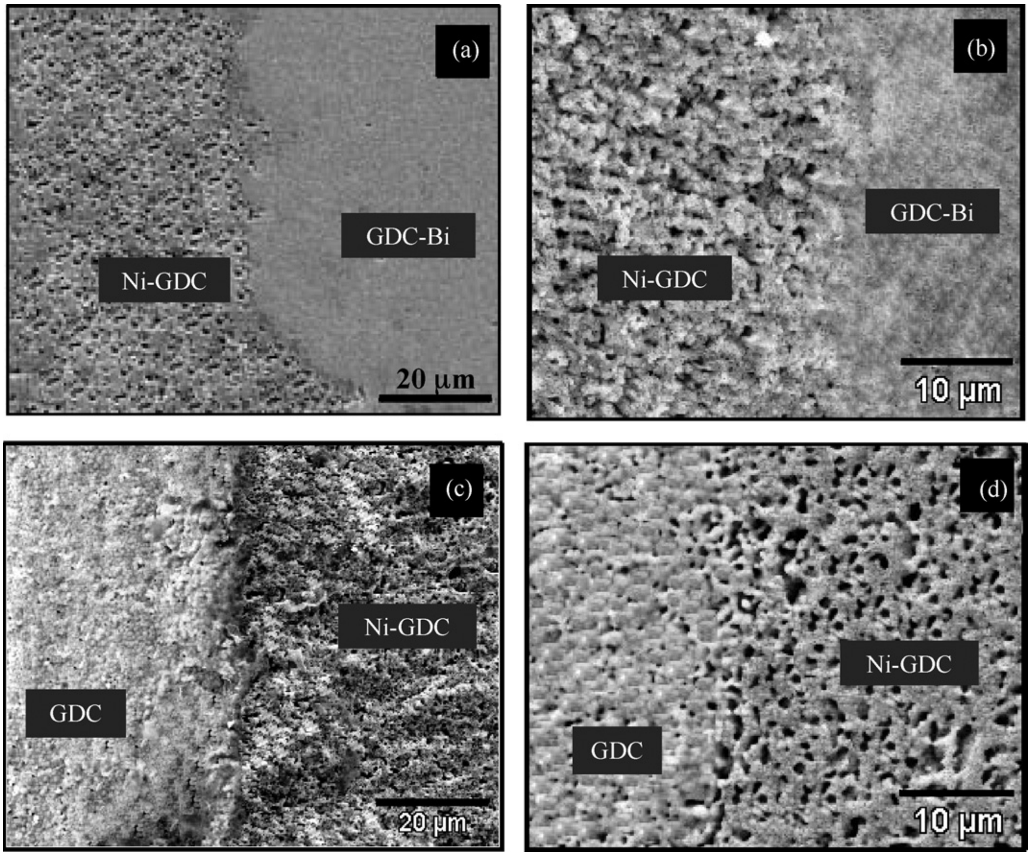

Fig. 4. SEM micrographs of the interface between Ni–GDC and GDC–Bi cosintered at 1350 °C for 2 h (a) fracture surface, (b) polished surface and Ni–GDC and GDC cosintered at 1400 °C for 2 h, (c) fracture surface and (d) polished surface.

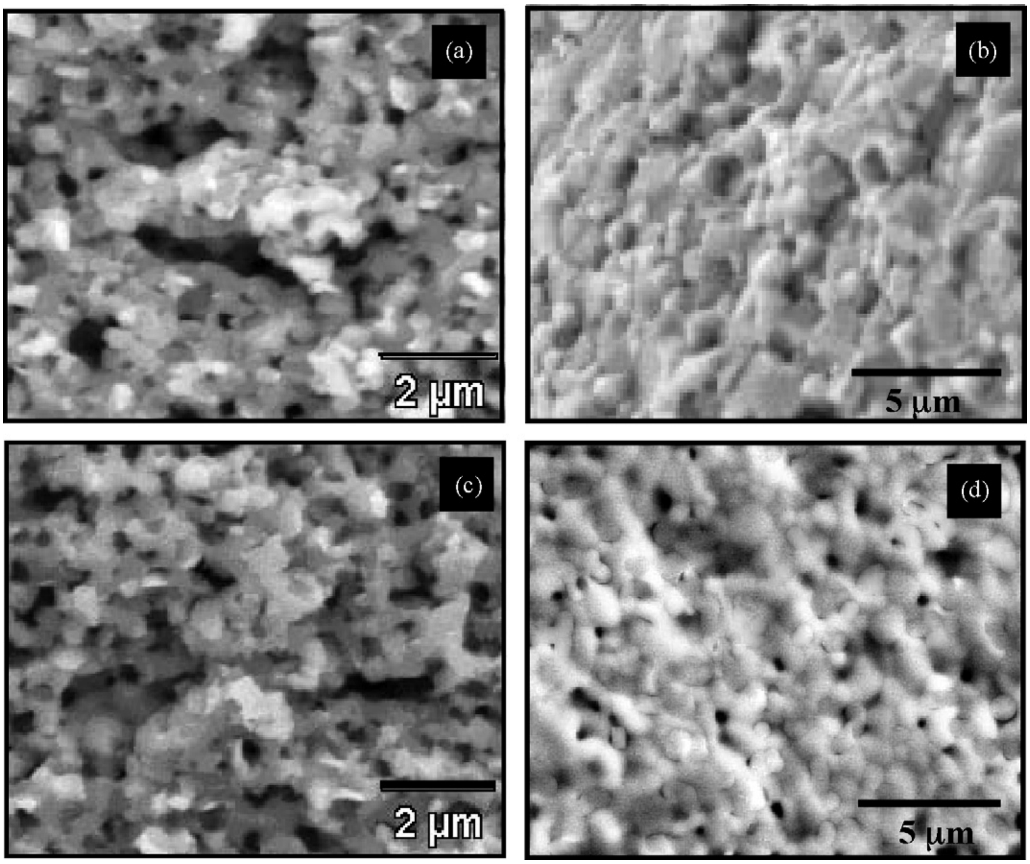

Fig. 5. SEM micrographs corresponding to fracture surface (a and c) Ni–GDC porous cermet cosintered at 1350 and 1400 °C for 2 h, respectively, (b) fracture surface GDC–Bi electrolyte and (d) fracture surface GDC electrolyte.

anode materials due to their similar CTE. Furthermore, according with X-ray analysis (Table 1 and Fig. 1b) there is no presence of any new secondary phases, that is, interfacial reactions did not take place between NiO composite and GDC-based electrolytes neither during heat treatment at high temperatures nor during the NiO reduction process to metallic Ni. The behaviour of the NiO–GDC/GDC pair is very similar, and, therefore, is not represented in this figure.

According to the ceramic data corresponding to the electrolytes, in both cases it has been possible to obtain good densification, adequate to ensure a good operation of the cell. Nevertheless, in the case of the electrolyte without Bi_2O_3 (GDC) the final density is lower (95%) compared to GDC–Bi, 97% (Fig. 4). On the other hand, their respective microstructures are very similar; both are homogeneous with a submicronic average grain size of approximately 0.8 μm. In Fig. 4, microstructures of the interphases have been taken only after the reducing process of the composites to cermets. They show microstructures of electrolyte (GDC and GDC–Bi) and anode (Ni–GDC) at 1400 and 1350 °C, respectively. As a first observation, it can be seen that there are not cracking or separation in the interface caused by the possible volume change during the reduction of NiO to Ni. Fig. 5a–b shows the Ni–GDC cermets fracture surfaces at higher magnification to see more detailed microstructure of the anode and electrolyte. It can be seen that there is a uniform distribution of porous/spherical Ni particles surrounded by GDC particles. This distribution is desirable for anodic reactions and electronic conduction. Anode microstructures show high interconnected porosity (∼25% total porosity) and good connections between particles, especially between Ni–Ni grains, that is, continuity is maintained in metallic phase, which is essential to improve the triple phase boundary (TPB) area where reaction between hydrogen, Ni and GDC takes place. Table 3 resumes the measured values of the total and open porosity in the composites NiO–GDC and in the cermets Ni–GDC.

Table 3
Total and open porosity of the NiO–electrolyte and Ni-electrolyte before and after reduction cycle

Composition	NiO50–CGO50
% volume of Ni on cermet	39.03
Before reduction (composite)	
Total porosity (% on composite)	7.6
After reduction (cermet)	
Total porosity (% on cermet)	25.1
Open porosity (% on cermet)	21.5

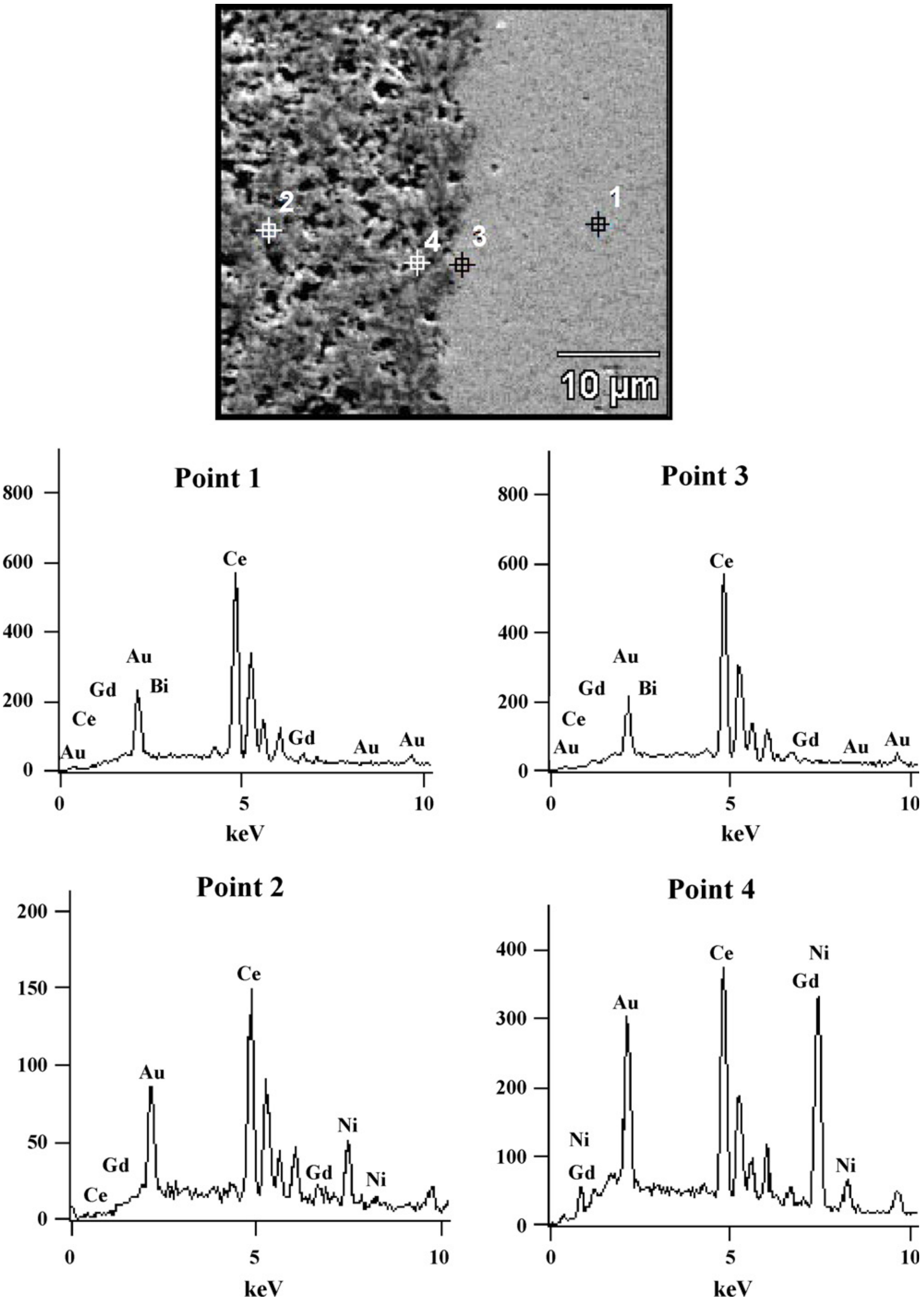

Fig. 6. EDAX analysis of nickel distribution across the interface of Ni–GDC/GDC–Bi cosintered at 1350 °C for 2 h (upper figures). EDAX analysis of Ni, Ce, Gd, etc. at the marked positions (lower figures).

The diffusion of nickel from the NiO–GDC composite into the GDC or GDC–Bi electrolyte was studied by EDAX analysis. Nickel distribution across the interface was similar in both pairs, that is, a different cosintering temperature does not affect significantly nickel diffusion. As shown in Fig. 6, corresponding to the Ni–GDC/GDC–Bi interface cosintered at 1350 °C for 2 h, nickel diffusion was not detected at the electrolyte surface, even in the adjacent to the anode. It is observed that in the electrolyte near of the interface (point 3) there is no nickel present, whereas in the anode region near to the interface (point 4) nickel and cerium gadolinium oxide phases are present, in accordance with the expected anode composition. Fig. 7 shows similar characteristics for the Ni–GDC/GDC anode electrolyte pair.

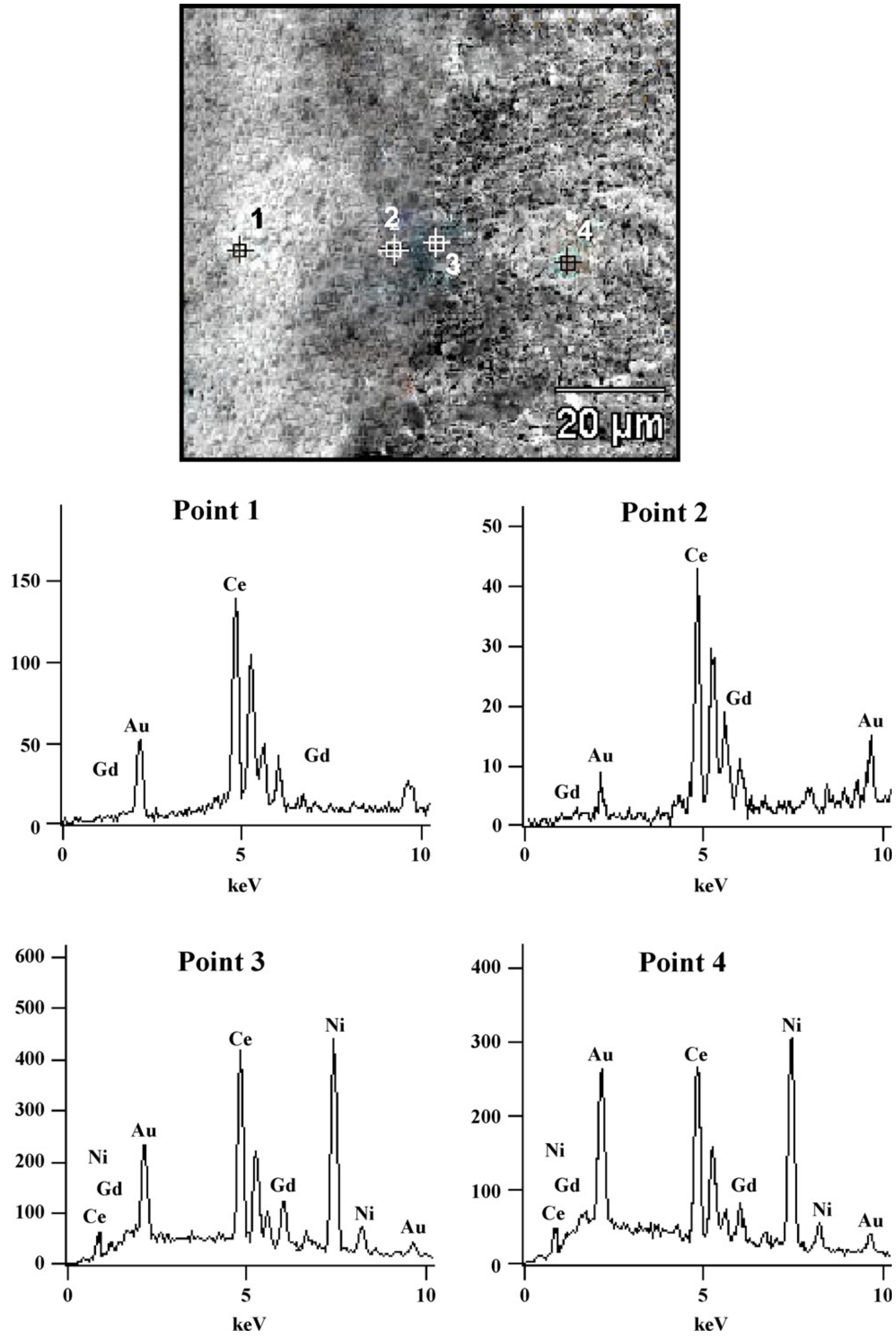

Fig. 7. EDAX analysis of nickel distribution across the interface of Ni–GDC/GDC cosintered at 1400 °C for 2 h (upper figures). EDAX analysis of Ni, Ce, Gd, etc. at the marked positions (lower figures).

4. Conclusions

According to the results described above, the 50 wt.% NiO/$Ce_{0.9}Gd_{0.1}O_{1.95}$ composite anode seems to be compatible with gadolinia-doped ceria electrolyte, with and without Bi_2O_3, at temperatures up to 1400 °C and for long times. Neither phase degraded at all the temperatures and times studied. CTE values obtained for NiO–GDC cermet are similar to the most commonly used electrolytes based on ceria. Therefore, the CTE values of NiO–GDC make it useful for use as the anode material for advanced IT-SOFCs. There is no presence of Ni migration from the cermet anode to the ceramic electrolyte. Therefore, it is possible to cosinter single cells of NiO–GDC/doped ceria electrolytes without the appearance of new phases in the boundary between electrode and electrolyte.

Acknowledgements

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References

[1] S.C. Singhal, Advances in solid oxide fuel cell technology, Solid State Ionics 135 (2000) 305–313.

[2] B.C.H. Steele, Appraisal of $Ce_{1-y}Gd_yO_{2-y/2}$ electrolytes for IT-SOFC operation at 500 °C, Solid State Ionics 129 (2000) 95–110.

[3] M. Mogensen, N.M. Sammes, G.A. Tompsett, Physical, chemical and electrochemical properties of pure and doped ceria, Solid State Ionics 129 (2000) 63–94.

[4] C.R. Xia, W. Rauch, F.L. Chen, M.L. Liu, $Sm_{0.5}Sr_{0.5}CoO_3$ cathodes for low-temperature SOFCs, Solid State Ionics 149 (2002) 11–19.

[5] W.G. Wang, M. Mogensen, High-performance lanthanum–ferrite-based cathode for SOFC, Solid State Ionics 176 (2005) 457–462.

[6] Z.P. Shao, S.M. Haile, A high-performance cathode for the next generation of solid-oxide fuel cells, Nature 431 (2004) 170–173.

[7] N.Q. Minh, Ceramic fuel-cells, Journal of the American Ceramic Society 76 (1993) 563–588.

[8] N.Q. Minh, High-temperature fuel-cells. 2. The solid oxide cell, Chemtech 21 (1991) 120–126.

[9] N.T. Yang, X.X. Meng, X.Y. Tan, Z.M. Li, Anode of intermediate temperature solid oxide fuel cells, Journal of Inorganic Materials 21 (2) (2006) 409–414.

[10] V. Gil, C. Moure, P. Durán, J. Tartaj, Low-temperature densification and grain growth of Bi_2O_3-doped ceria gadolinia ceramics, Solid State Ionics 178 (2007) 359–365.

[11] V. Gil, J. Tartaj, C. Moure, Low temperature synthesis and sintering behaviour of Gd-doped ceria nanosize powders: comparison between two synthesis procedures, in press.

[12] V. Gil, J. Tartaj, C. Moure, P. Durán, Sintering, microstructural development, and electrical properties of gadolinia-doped ceria electrolyte with bismuth oxide as a sintering aid, Journal of the European Ceramic Society 26 (2006) 3161–3171.

[13] G. Corbel, S. Mestiri, P. Lacorre, Physicochemical compatibility of CGO fluorite, LSM and LSCF perovskite electrode materials with $La_2MO_2O_9$ fast oxide-ion conductor, Solid State Sciences 7 (2005) 1216–1224.

[14] H. Hayashi, M. Kanoh, C.J. Quan, H. Inaba, S.R. Wang, M. Dokiya, H. Tagawa, Thermal expansion of Gd-doped ceria and reduced ceria, Solid State Ionics 132 (2000) 227–233.

[15] P. Bance, N.P. Brandon, B. Girvan, P. Holbeche, S. O'Çdea, B.C.H. Steele, Spinning-out a fuel cell company from a UK University—2 years of progress at Ceres Power, Journal of Power Sources 131 (2004) 86–90.

[16] T. Ishihara, T. Shibayama, H. Nishiguchi, Y. Takita, Nickel–Gd-doped CeO_2 cermet anode for intermediate temperature operating solid oxide fuel cells using $LaGaO_3$-based perovskite electrolyte, Solid State Ionics 132 (2000) 209–216.