



Short communication

Redox behaviour of Gd-doped ceria–nickel oxide composites

V. Gil*, A. Larrea, R.I. Merino, V.M. Orera

Instituto de Ciencia de Materiales de Aragón, C.S.I.C.-Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain

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ABSTRACT

Reduction kinetics of NiO–gadolinium-doped ceria (GDC) composites was studied. NiO–GDC ceramic rods were fabricated by cold isostatic pressing of powders of nanometer size obtained by chemical synthesis. The rods were sintered in air at the maximum contraction temperature, 1350 °C, and treated in reducing atmosphere at different temperatures and reduction times. Progress of the reduction process was followed by the gravimetric method. By adjusting the data obtained from weight loss during the isothermal reduction at temperatures between 500 and 700 °C to standard diffusion models for a cylinder, it was possible to obtain effective diffusion coefficients for the material. The process activation energy was 0.9 ± 0.2 eV indicating that, in the whole temperature range studied, the reduction kinetics is controlled by the diffusion of O^{2-} throughout the ceramic matrix of GDC. SEM studies in reduced, partially reduced and completely reduced samples reveal a submicrometric microstructure with a uniform distribution of Ni phase surrounded by pores within ceramic GDC matrix. This microstructure is suitable for IT-SOFC anodes.

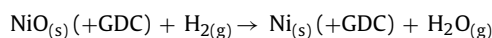
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1. Introduction

In the last few decades, ceria materials doped with rare earths (Y^{3+} , Gd^{3+} , Sm^{3+} , etc.), especially gadolinia-doped ceria (GDC), have been proposed as electrolyte materials for intermediate temperature (500–700 °C) solid oxide fuel cell (IT-SOFC) [1]. Ceria-based materials are also being considered for the SOFC fuel electrodes because of the mixed ionic and electronic conductivity of reduced ceria [2]. Ceria-based anodes have some important advantages over conventional Ni-based anodes. For example, their ability to endure repetitive oxidation and reduction and the ability to avoid carbon deposition from hydrocarbon fuels. However, below 700 °C the electronic conductivity of doped ceria is not high enough to guarantee the cell current collection. A possible alternative would be to use ceria as the ceramic part in nickel porous cermet anodes (Ni–GDC). Beneficial effects of this strategy have been reported and interpreted as being probably due to the broadening of the three-phase boundary (TPB), that is, the zone where the electrochemical reaction takes place [3]. In addition, choice of GDC instead of for example Yttria stabilized Zirconia (YSZ) would result in better matching of the thermal expansion coefficients between the cermet Ni–GDC and the GDC electrolyte.

It is important to consider that the electrochemical performance of cermets depends largely on their microstructure. Cermet microstructure is a critical issue in the case of anode supported cells

where the cermet is the structural component thus having thicknesses of several hundred microns [4]. The best electrochemical response of the anode material is for a uniform distribution of small Ni particles in the also uniform porous ceramic matrix. The chemical synthesis of the NiO–GDC powders, used in the present work, allows us to obtain nanometric powders with a uniform and homogeneous distribution of both phases. Using these powders we have been able to fabricate very homogeneous and fine grained NiO–GDC ceramics. Ni–GDC porous cermets are obtained by thermal treatment of NiO–GDC composites in reducing atmosphere (commonly by “in situ” reduction during the first cell start-up). During this process, the nickel oxide is converted into metallic nickel according to this reaction:



Since the precursor oxide is confined inside a GDC matrix, the reduction in volume is converted into pores. Finally, in the cermet the GDC constitutes a three-dimensional matrix where Ni particles and pores are confined and the volume fraction of the phases is crucial in order to obtain good mobility of both the reacting species and the electrons. The microstructure is also important in order to inhibit Ni grain coalescence during the sintering process and at working temperatures.

Additionally, the study of the reaction mechanisms that take place during the reduction of NiO is very important since it allows us to define the best processing conditions to obtain a uniform distribution of fine metallic particles and pores within the cermet.

In recent years, the kinetics of the reduction of NiO to metallic Ni have been extensively studied in the conventional YSZ-based

* Corresponding author. Tel.: +34 976 761333; fax: +34 976 761229.
E-mail address: vgil@unizar.es (V. Gil).

ceramic cermets [5,6] and in textured cermets obtained from directionally solidified eutectic YSZ/NiO and CoO materials [7]. However, except for the pioneering work of Wandekar et al. [8] where some structural, electrical and redox properties of NiO–GDC composites are reported, there are no previous studies on the redox kinetic process of these materials.

In this work, we study the redox kinetics of gadolinium-doped ceria and nickel oxide composites prepared from nanopowders obtained by a chemical process. The redox study was carried out in the 500–700 °C temperature range.

2. Experimental details

Ceramic NiO–Ce_{0.9}Gd_{0.1}O_{1.95} composites (NiO–GDC 50 wt.%) have been prepared from nanopowders synthesized by a chemical process based on a modified Pechini method. The chemical synthesis and the composition selected are detailed in a previous work [9].

Rods, 1 mm in radius and 20 mm in length, were prepared from these precursor powders by cold isostatic pressing at 200 MPa and further sintering in air at 1350 °C for 2 h. The selected sintering temperature was based on the densification behaviour studied previously [10].

The reduction kinetics has been studied by monitoring the weight losses as a function of the processing time during isothermal and isochronal experiments at different temperatures and times (500–700 °C, 15–1000 min). Cylindrical samples of GDC/NiO ceramics of approximately the same size (0.45 ± 0.01 g) were thermally treated in reducing atmosphere, 5 vol.% H₂ (95 vol.% N₂) in a tubular furnace for a given time and then fast quenched to room temperature. The weight loss was monitored by a digital balance (Mettler AE50) with a relative precision of 10⁻⁴.

The microstructural characterization of the samples (before, partially and totally reduced) has been carried out by Scanning Electron Microscopy (SEM, JEOL 6400). Presence of Ce³⁺ ions was monitored by measuring its electronic Raman signal in a Dilor XY spectrometer with a CCD detector [11].

In order to determine the properties of the ceramic matrix, the metal phase was leached out by immersion of the reduced rods into HNO₃ solution (2.2 M) at 80 °C for 24 h. The chemical composition of the isolated GDC skeleton was studied by Energy Dispersive Spectroscopy (EDS) microanalysis using a INCA-300 system (Oxford Instruments) fitted to a JEOL 6400 SEM.

3. Results and discussion

3.1. Microstructural characterization

Fig. 1(a) shows a back-scattered electron SEM image of a polished surface corresponding to the sample NiO–GDC before reduction. The brighter grains correspond to the GDC phase while the NiO grains appear dark and also with submicronic grain size. The black regions correspond to pores in the sample. After sintering at 1350 °C, the composite with 97% of theoretical density, presents a homogeneous microstructure in terms of grain size and shape and it is formed by equiaxial grains, having a size between 0.5 and 1 μm.

Fig. 1(b) is a back-scattered electron SEM image on polished surface of a fully reduced sample (700 °C for 120 min, ~98% reduced). The microstructure presents Ni grains (light grey), which are submicronic in size, embedded into a GDC matrix (bright). After reduction the porosity (black areas) increases, which is consistent with the NiO volume reduction that should occur upon reduction and this reaches its maximum when the reduction process is completed (~30 vol.% porosity). Comparing the samples before and after reduction, we observed that the external dimensions of the sample

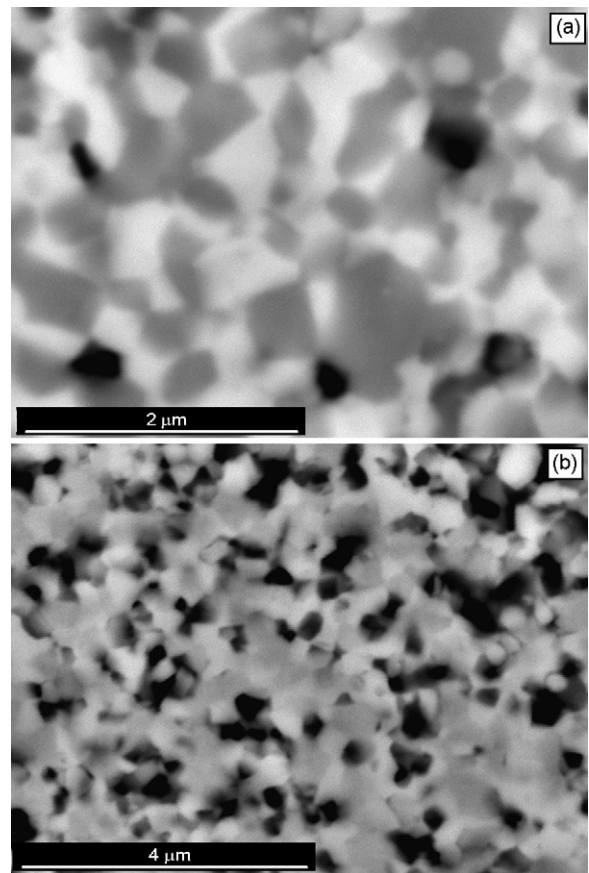


Fig. 1. SEM microstructure of a polished surface of (a) NiO–GDC composite before reduction process and (b) Ni–GDC cermet after fully reduced at 700 °C for 180 min. NiO grains (dark grey), Ni grains (light grey), GDC grains (bright) and pores (black areas).

are not modified by the reduction process. Reduced samples are also free of defects which indicate that GDC matrix forms the rigid structure of the cermet.

In order to determine whether the NiO is dissolved into the GDC structure or not, analysis was performed on emptied GDC ceramics by Energy Dispersive Spectroscopy. In all cases, the spectra revealed signals coming only from Ce and Gd. The absence of signals corresponding to Ni indicates that there is no presence of these atoms in the GDC solid solution, or to be more precise, that the concentration of them is lower than the detection limit of the equipment (about 0.5% of total cations). As an example, Fig. 2 shows the EDS analysis obtained for the fully reduced rods at the highest temperature (700 °C).

Finally, the total absence of Ce³⁺ in the reduced rods was confirmed by the Raman technique. In all the Raman spectra we only observed a broad band at ~465 cm⁻¹. This band is characteristic of the fluorite CeO₂ structure, which has only one Raman active triply degenerate F_{2g} mode [12].

3.2. Reduction kinetics

The reduction kinetics has been studied by the thermogravimetric method in isochronal and isothermal experiments. The measured mass loss values (M_t) at a given reduction time were normalized with respect to the theoretical maximum amount of mass loss calculated from composite composition M_∞ . A value of 0 corresponds to the initial condition of 0% reduction while a value of 1 corresponds to full reduction. X-ray powder diffraction measurements were used to confirm the complete reduction of NiO

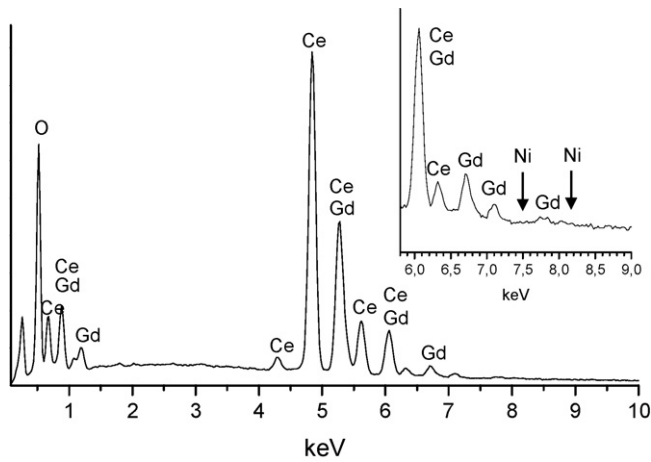


Fig. 2. EDS analysis of isolated GDC matrix obtained from fully reduced rods at 700 °C for 180 min.

into Ni when a stable mass loss was reached. In the isochronal experiments we measured the fraction of reduced mass M_t/M_∞ for a given period of time at different temperatures (500–700 °C). As we observe in Fig. 3, for a given time of treatment the mass loss increases with the increasing of the reduction temperature, i.e. the reduction process in the Ni–GDC cermet is thermally activated in the range 500–700 °C.

Reduction of the NiO–GDC bulk samples was completed at lower temperatures (≥ 700 °C) than in the case of the previously reported NiO–YSZ cermets [5,7], where temperatures ≥ 900 °C were needed for the same reduction time. Since at low temperatures the oxygen diffusion through the ceria matrix is much faster than in the YSZ matrix this result favours the process being limited by oxygen diffusion through the ceria matrix. The value reported for the activation energy of pure YSZ ($E_a = 1.04$ eV) [13] is a little higher than that of pure GDC ($E_a = 0.9$ eV) [14].

Fig. 4 shows the experimental results obtained in the isothermal reduction experiments, where the mass change vs. time is represented. In agreement with the isochronal experiments it can be seen that reduction is a thermally activated mechanism.

Then we compared the experimental results with theoretical predictions. For long enough cylinders we can use the solution to

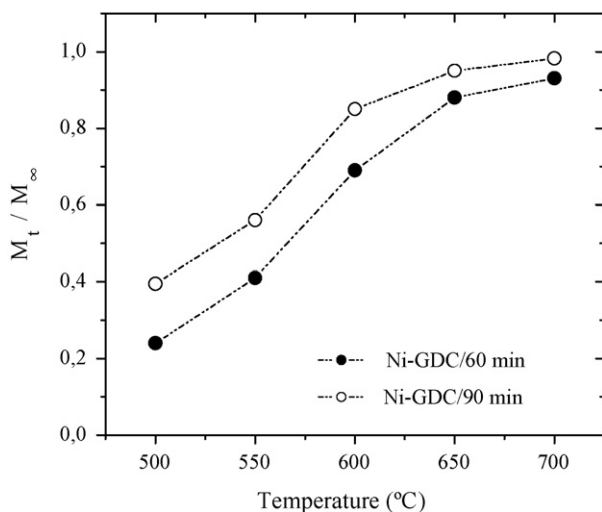


Fig. 3. Mass loss fraction vs. temperature after 60 and 90 min of reduction experiments for NiO–GDC composites.

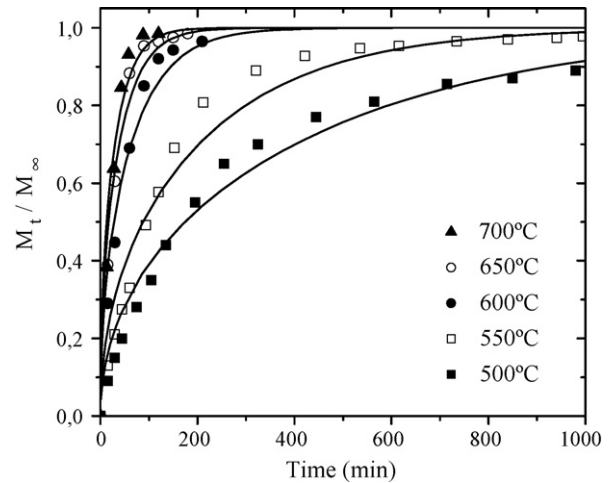


Fig. 4. Mass loss fraction vs. time for isothermal reduction experiments of NiO–GDC rods. The points correspond to gravimetric determinations and the curves to fitting to Eq. (1) using the effective diffusion parameter D as the fitting parameter.

the diffusion differential equation for an infinite cylinder [15].

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} \exp(-D \alpha_n^2 t) \quad (1)$$

where a is the radius of the cylinder and α_n are the positive roots of the Bessel function $J_0(x)$. D is the effective diffusion coefficient which in our case is the fitting parameter.

Although the experimental data are well described by this equation (Fig. 4), a slight mismatch exists, probably because of the approximation to the infinite cylinder of the experimental rods.

For short times it is possible to obtain an approximated solution for the differential equation to the diffusion in an infinite cylinder, taking only the first term in Eq. (1) giving.

$$\frac{M_t}{M_\infty} = \frac{4}{\sqrt{\pi}} \left(\frac{Dt}{a^2} \right)^{1/2} \quad (2)$$

Fig. 5 shows the mass change vs. the square root of time. The linear dependence with $t^{1/2}$ of the experimental reduced mass fraction for short periods of times confirms that the reduction process is limited by diffusion.

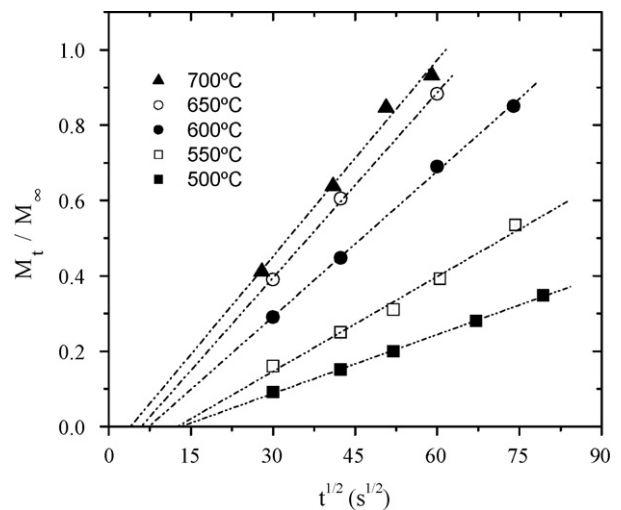


Fig. 5. Mass loss fraction vs. time for isothermal reduction experiments of NiO–GDC rods. The points correspond to gravimetric determinations and the curves to fitting to Eq. (2) using the effective diffusion parameter D as the fitting parameter.

Table 1

Diffusion coefficients, D , for Ni–GDC cermet obtained by fitting of Eq. (1). Comparison with D for Ni–YSZ cermet reported in literature and the obtained with Eq. (3) for pure GDC.

Temperature (°C)	D_{eff} [Ni–GDC] ($\text{cm}^2 \text{s}^{-1}$)	D_{eff} [Ni–YSZ] ($\text{cm}^2 \text{s}^{-1}$) [7]	D [GDC] ($\text{cm}^2 \text{s}^{-1}$)
700	$10.2 \pm 0.2 \times 10^{-7}$	9.1×10^{-8}	9.6×10^{-8}
650	$7.7 \pm 0.9 \times 10^{-7}$	5.0×10^{-8}	–
600	$4.7 \pm 0.6 \times 10^{-7}$	1.8×10^{-8}	2.6×10^{-8}
550	$1.8 \pm 0.2 \times 10^{-7}$	–	–
500	$7.0 \pm 0.5 \times 10^{-8}$	–	8.1×10^{-9}

It is important to notice that since a value of 0 of the normalized mass loss corresponds to an initial condition of 0% reduction, a plot of the mass change vs. the square root of time should be linear and cross the origin. Nevertheless, in Fig. 3 there appears to be an induction period, more noticeable at low reducing temperatures. This effect could be due to experimental limitations. The cold sample is contained in a quartz tube that is introduced into the hot furnace (it is like a “reversed quenching”) producing an instant heating. Then there will be a finite amount of time required to reach the desirable reduction temperature again in the furnace chamber, quartz tube and sample. Therefore, the readings taken during the first 1–2 min of the experiment may contain errors.

Table 1 compiles the effective diffusion coefficient values, D , for Ni–GDC cermet obtained by fitting Eq. (1) to the experimental points in Fig. 4. Diffusion coefficients of Ni–YSZ samples are included for comparison [7]. In the whole range of temperature studied the values of the effective diffusion coefficients are one order of magnitude higher in the Ni–GDC sample. This is probably due to the better oxygen ionic conduction at low temperatures in GDC matrix than in YSZ and favours O^{2-} ion diffusion through the GDC matrix being the limiting process for the composite reduction.

Alternatively, the diffusion coefficient D ($\text{cm}^2 \text{s}^{-1}$) can be estimated from ionic conductivity data for pure GDC using the Nernst–Einstein equation:

$$D = \frac{\sigma_i kT}{C_i (Ze)^2} \quad (3)$$

where σ_i is the ionic conductivity, k is the Boltzmann constant, T the temperature, C_i the concentration of ionic carriers (N cm^{-3}) and Z their charge.

For comparison, Table 1 includes the values of the oxygen self-diffusion data calculated using Eq. (3) and the ionic conductivity values reported in the literature [14]. The comparison corroborates that the diffusive species controlling the reduction in the Ni–GDC cermet is very probably the oxygen ion. The oxygen dif-

fusion through the Ni–GDC cermet obtained is faster than in bulk GDC, as a consequence of the microstructures. Whereas D measures the oxygen diffusivity in dense GDC, in the porous Ni–GDC cermet the oxygen diffusion will be a combination of diffusion through the GDC phase and through the pores.

Since the process is thermally activated, an Arrhenius plot was used to calculate the activation energy, E_a :

$$D(T) = D_0 \exp\left(\frac{-E_a}{kT}\right) \quad (4)$$

Fig. 6 represents the effective diffusion coefficients that control the thermally activated reduction process, vs. $1/T$. Activation energies of 0.88 ± 0.08 and 0.875 ± 0.06 eV for D -values obtained from either Eq. (1) or the short times approach given by Eq. (2), respectively, were obtained. Both activation energy values are similar and between the estimated error values, which validates the method used. In addition these activation energy values are in perfect agreement with the value reported in the literature for oxygen ion diffusion in GDC with a similar composition ($E_a = 0.9$ eV) [14]. This coincidence also supports the fact that O^{2-} diffusion through the GDC matrix is the limiting process for the reduction of the NiO–GDC composite.

4. Conclusions

We have produced dense and defect-free NiO–GDC rods which upon reduction experienced no volume changes and presented homogeneous and uniform fine grained microstructures.

The reduction behaviour of NiO–GDC ceramic rods was studied at temperatures between 500 and 700 °C. For NiO–GDC composites and in the whole temperature range studied, the redox process is controlled by the oxygen diffusion, presumably through the GDC ceramic matrix, as the process presents activation energy similar to the oxygen ion conductivity of pure GDC ceramics.

The NiO within NiO–GDC composites was found to be reduced completely to Ni at temperatures lower than 700 °C in a relatively short period of time (180 min). No changes in geometry and microstructure (apart from full Ni reduction) were detected.

It is confirmed that in reducing atmosphere and at temperatures lower than 700 °C the reduction of Ce^{4+} to Ce^{3+} does not take place in this composite.

Furthermore it is possible to state that Ni^{2+} is not dissolved into the GDC lattice, or at least, up to the sintering temperatures used of 1350 °C.

Acknowledgements

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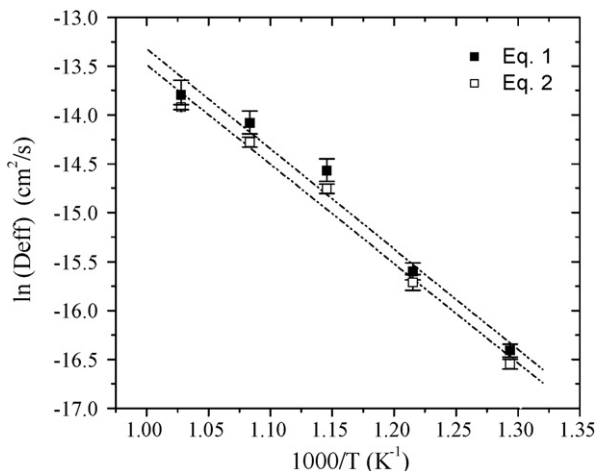


Fig. 6. Arrhenius plot for the reduction process. Effective diffusion coefficients, $D(T)$, vs. $1/T$, obtained from Eqs. (1) and (2).

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