



Assessment of NiO-CGO composites as cermet precursors

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ABSTRACT

NiO-Ce_{0.9}Gd_{0.1}O_{1.95} (NiO-CGO) composite powders produced by a one-step chemical route were assessed as precursors of fuel cell anode cermets. Porous NiO-CGO composites were prepared by uniaxial pressing followed by firing at 1400 °C for 4 h. Ni-CGO cermets were subsequently obtained by reduction in 10 vol% H₂ + 90 vol% N₂ at 750 °C. Similar materials obtained by conventional mechanical mixing of commercial powders were also prepared and tested. The structure and particle size of the calcined material were investigated by X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM). The electrical properties of all materials were duly studied by impedance spectroscopy (NiO-CGO) (in air and several N₂ + O₂ gas mixtures) or dc conductivity (Ni-CGO). The total and relative magnitude of impedance arcs observed in the low temperature impedance spectra can be used to obtain significant insight on microstructural characteristics, due to a variable role of NiO when shifting from a well percolated electronic conducting pathway to a dispersed ion-blocking phase. The confirmed superior conductivity of one-step materials was interpreted as a consequence of the presence of a network of well-connected and homogeneously distributed NiO/(Ni) grains, as shown by SEM.

1. Introduction

Research on solid oxide fuel cell (SOFC) functional materials and corresponding microstructural optimization steadily increased over the past three decades [1–12], being strongly important towards the future commercialization of SOFCs as efficient and environmentally friendly energy conversion devices. Fuel cell electrodes should have high electrical conductivity, chemical stability towards the electrolyte and gaseous environment, thermal expansion coefficient matching that of the electrolyte, suitable porosity (around 20–40%) to facilitate gas phase transport, and also high electrocatalytic activity to boost reaction kinetics. In general, these aspects are determined by the composition and microstructure of the electrode. The latter is mainly established by the nature of the starting powders and the manufacturing technique [8,13–15]. The development of cost-effective novel synthesis routes able to produce powders with tuned electrode microstructures and tools to assess the efficacy of processing steps is crucial to improve electrode performance for low-intermediate operating temperatures.

The microstructural design of nickel/Gd-doped ceria (Ni-CGO) or nickel/yttria stabilized zirconia (Ni-YSZ) cermets is one of the most studied issues to improve the electrochemical performance of anode-supported SOFCs. Nanocomposite powders obtained by chemical or mechanical processes are used along with improved manufacturing

techniques and electrode firing conditions [16–18]. From a microstructural point of view, it is well known that enhanced performance of Ni-based cermets correlates with increasing triple phase boundary length (TPBs), where electrolyte, electrode and gas phase are in mutual contact [19–22]. Efforts to improve the electrochemical performance of Ni-CGO cermets include the synthesis of NiO-CGO nanocomposite powders with uniform chemical distribution and small particle size of both phases [16,23].

A newly developed one-step synthesis of NiO-CGO nanocomposite powders provided promising Ni-CGO cermet anodes [24,25]. Since the final properties of anodes are strongly dependent on the precursor composite, it is also of great interest to investigate their microstructure and electrical properties prior to NiO reduction.

The electrochemical performance of composites based on an oxide-ion conductor (e.g., yttria stabilized zirconia) and including a dispersed ion-blocking phase (e.g., alumina) were widely investigated by impedance spectroscopy [26–28]. This technique was consistently able to highlight the relationship between microstructure and electrical properties. However, to our knowledge there was no attempt to inspect NiO-CGO composites in a similar manner. Accordingly, in the present work, the electrical properties of NiO-CGO composites prepared following distinct routes were studied with special attention to the percolation of the electronic pathway. This study was complemented with the

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electrical characterization (total dc conductivity) of a derived Ni-CGO cermet.

2. Experimental procedure

NiO-Ce_{0.9}Gd_{0.1}O_{1.95} (NiO-CGO, 50 wt% NiO, unless otherwise specified) composite powders were prepared by a one-step sol-gel based method in which NiO and CGO resins are obtained from polymeric precursors and then thermally treated to directly produce the NiO-CGO precursor powder [24]. The as-prepared in situ nanocomposite was calcined at 700 °C for 0.5 h and ball milled with zirconia balls at 50 rpm for 1 h to break agglomerates. Commercial NiO (J. T. Baker) and CGO (Ce_{0.9}Gd_{0.1}O_{1.95}, Praxair) powders were also mechanically mixed (planetary mill at 300 rpm for 4 h) to produce a conventional NiO-CGO composite. For the sake of simplicity in the following text the two types of powders and corresponding composites will be named as OS (one-step) or MM (mechanically mixed).

Powders of all composites were uniaxially pressed into rectangular compacts (15 mm × 5 mm × 5 mm) under 65 MPa, followed by firing at 1400 °C for 4 h in air. OS samples were additionally reduced at 750 °C for 3 h in a 10 vol% H₂ + 90 vol% N₂ atmosphere. The open porosity before and after NiO reduction was calculated from measured densities (Archimedes method). Pure CGO samples sintered at 1500 °C for 4 h were also prepared to be used as reference for the electrical properties of selected composites.

X-ray diffraction (XRD) was used to assess phase purity. Diffraction patterns were collected using a Shimadzu XRD-7000 diffractometer (CuK_α radiation, 40 kV and 25 mA) in the angular range of 20 ≤ 2θ ≤ 80° (0.02°/step, 2 s/step). The MAUD (Materials Analyzing Using Diffraction) software package was used to assess the structural and microstructural parameters of composites powders. This software, based on the Rietveld method and Fourier analysis, applies the RITA/RISTA routine [29,30]. Crystallite sizes were estimated using the standard (Delft) line broadening model (adopting a Voigt function [31,32]).

The powder particle size and selected area electron diffraction (SAED) patterns were obtained by Transmission Electron Microscopy (TEM, Hitachi H9000). Microstructural characterization of polished and thermally etched (25 °C below the firing temperature) samples was carried out by Scanning Electron Microscopy (SEM, Hitachi TM 3000).

The electrical properties of NiO-CGO composites were mostly studied by impedance spectroscopy in air. A few experiments were also conducted at 700 °C in N₂ + O₂ gas mixtures, using a closed chamber furnace including one YSZ (yttria stabilized zirconia) oxygen sensor to monitor the oxygen partial pressure in the immediate vicinity of the sample. Impedance spectra were acquired from 100 to 700 °C using a Hewlett Packard 4284A LCR meter in a two-probe configuration (frequencies ranging from 20 Hz to 1 MHz with a test signal amplitude of 0.5 V). The electrical conductivity of Ni-CGO cermets derived from NiO-CGO composites was measured using the bar-shaped samples by a dc four-probe method at 450–750 °C in a 10 vol% H₂ + 90 vol% N₂ atmosphere. All electrical measurements used platinum paste and leads for electrical contacts, properly spaced in the four-probe measurements.

3. Results and discussion

3.1. Structural and microstructural analysis of composites

The OS NiO-CGO (after calcining at 700 °C for 0.5 h) powder XRD pattern, Rietveld fitting, TEM micrograph and SAED pattern are all shown in Fig. 1. The MM composite powder XRD pattern is also shown in Fig. 1. Both XRD patterns (Fig. 1a) could be indexed to the expected cubic space groups for CGO (space group Fm-3m, JCPDS file 75-0161) and NiO (Fm-3m, file 47-1049), and showed no secondary phases. The CGO and NiO phase content were around 49 and 51 wt%, respectively, in both composites, indicating a good control of the synthesis method.

The lattice parameters were 4.179 (NiO) and 5.418 (CGO) Å, 4.178 (NiO) and 5.415 (CGO) Å for the MM and OS composites, respectively. These values are close and in good agreement with literature data for the two phases [33,34]. The crystallite sizes were 28.0 and 25.0 nm (NiO) and 108.7 and 16.0 nm (CGO) for the MM and OS powders, respectively. The characteristics of presently obtained powders matched closely those previously reported, obtained in distinct circumstances, ranging between 10 and 18 (CGO) and 20–26 (NiO) nm [24,25,35,36], confirming the reliability of the synthesis method.

Fig. 1b shows indiscernible NiO and CGO phases with particle size below 50 nm in OS composite powders. While reduction of particle size by mechanical milling is energy consuming and highly demanding with respect to milling conditions, preventing an easy downsizing of particle size, one-step synthesis was hereby confirmed as a rather effective alternative. The SAED pattern confirmed the electron diffraction from the network planes of NiO (green/dark grey) and CGO (orange/light grey) phases. Typical interplanar spacings of diffraction rings 1 and 4, assigned to the main X-ray diffraction peaks of CGO and NiO are 0.314 and 0.220 nm, respectively.

The microstructures of OS and MM NiO-CGO composites, obtained before NiO reduction, are shown in Fig. 2a and b, respectively, as backscattered electron SEM images. Light and dark grey phases correspond to CGO (light) and NiO (dark). The OS composites exhibit a homogenous dispersion of NiO and CGO grains (with NiO larger than CGO). On the contrary, NiO particles in MM composites seem coarser, suggesting defective phase percolation.

The homogeneous microstructure of a typical Ni-CGO cermet derived from an OS powder fired at 1400 °C is also shown in Fig. 2c. Pores in the Ni-CGO cermet are mainly due to the oxygen loss associated with the reduction of NiO to Ni, resulting directly from the lower density of NiO (6.808 g/cm³, JCPDS 47-1049) when compared to Ni (8.911 g/cm³, JCPDS 04-0850). Submicrometric Ni and CGO phases are intimately dispersed throughout the OS based cermet, contributing to optimize the interfacial surface area.

Based on these results and usual targets for Ni-CGO composites, the OS composites fired at 1400 °C, with 6 vol% porosity in air and 26 vol% porosity in hydrogen, seemed a promising material. In fact, with cermet porosity levels > 25 vol%, gas phase mass transfer limitations are expected to be small [37] but percolation of the conducting phases might be partly lost, a situation mostly critical in the case of the metal. Fine tuning of the sintering conditions was an obvious tool to adjust these characteristics. In fact, exploited alternative processing conditions, here ignored for the sake of brevity, originated characteristics deviating significantly from the above target. Pore formers can also be used to adjust the porosity (total and pore size distribution), preventing gas phase diffusion limitations, but this approach was outside the scope of this work.

3.2. Electrical properties

Fig. 3 shows typical impedance spectra obtained in air at 200 °C for NiO-CGO composites fired at 1400 °C, normalized with respect to the appropriate cell dimensions, with Z' and Z'' being the real and imaginary parts of the impedance, respectively. The spectra of composite samples consist of one or two arcs in the studied frequency and temperature ranges. These arcs will be hereby identified as HF (high frequency) and IF (intermediate frequency) arcs.

The 50 wt% NiO MM composite exhibits a total impedance much higher than observed for the corresponding OS composite (Fig. 3b versus a). For materials with the same chemical and phase composition the difference in magnitude of total impedance and even in the magnitudes of IF and HF arcs should be related to the specific microstructural features of each sample, namely phase percolation.

In these composites both solid phases should offer parallel pathways for charge transport, with CGO providing an ionic pathway and NiO (a p-type semiconductor) providing an electronic pathway. Therefore, the

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