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Correlation between yttria stabilized zirconia particle size and morphological properties of NiO–YSZ films prepared by spray coating process

A.C. Nascimento, R.M.F. Basaglia, F.T.A. Cunha, C.G. Fonseca, M.C. Brant, T. Matencio, R.Z. Domingues *

Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais, Av. Antônio Carlos, 6627, CEP: 31270-901 Belo Horizonte, MG Brazil

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Abstract

A systematic approach was taken to investigate the morphology of NiO–yttria stabilized zirconia (YSZ) films deposited by a spray coating process. The final morphological aspects of anode films were influenced by the particle size of YSZ powders and the milling time of the slurries used for film deposition. YSZ powders with average particle size of 17 and 52 nm were obtained from powders calcined at 800 and 1000 °C, respectively. The results obtained by rheological studies pointed out that slurries prepared from YSZ powders calcinated at 1000 °C and milling time of 20 h had more stability. All slurries presented thixotropic and pseudoplastic behaviors.

Keywords: Solid oxide fuel cell (SOFC); Anode; Microstructure; NiO/YSZ

1. Introduction

Solid oxide fuel cells (SOFCs), are electrochemical devices that can convert the chemical energy of a fuel into electrical energy without pollution [1–3]. Due to their higher operating temperatures (700–1000 °C) these devices can use several kinds of fuels such as hydrogen, natural gas, and ethanol [4], and also can be used with high efficiency in cogeneration systems [5,6]. However, the performance of SOFCs depends on both the electrodes and electrolyte materials and their processing, besides another factors. Single cells are constructed with layered electrodes and include functional and current collector layers on both cathodic and anodic ends [7–9]. The functional layer is responsible for electrochemical reactions and thus must provide the active sites where the triple contact between electronic and ionic conductors and the gaseous phase (the triple phase boundary) takes place [10,11]. Ni–yttria stabilized zirconia (Ni/YSZ) is the most widely used anode material for SOFC in which YSZ is used as the electrolyte [12,13]. The utilization of this composite instead of pure Ni improves the electrolyte/anode contact area by minimizing the differences of thermal dilatation coefficients of metallic and ceramic materials and by increasing the number of sites where the electrochemical reaction can occur [14]. The anode composite has the desired requirements for an SOFC anode: YSZ acts as a matrix to Ni grains and inhibits Ni coalescence and aggregation [15,16], and Ni has high electrical conductivity and is an excellent catalyst for hydrogen oxidation [17–19]. The electrochemical performance of an anode is described elsewhere as being very dependent on its microstructure [20,21], thickness, porosity [22] and composition [23].

For anode films deposited by a spray [17,24] or tape casting processes [2], a slurry is usually prepared in two steps. Initially, ceramic powders of a given particle size are pre-homogenized together with the dispersant in a suitable solvent in a ball milling for a certain time, and then further organic additives such as binders and plasticizers, are added in adequate quantities. The resulting slurry is milled again for an additional time [25,26].

The film performance is, besides other factors, determined by its homogeneity [27], adherence and porosity. These

* Corresponding author. Tel.: +55 31 3409 5770; fax: +55 31 3409 5700.
E-mail address: rosanazd@ufmg.br (R.Z. Domingues).

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parameters are influenced by the conditions of slurries preparation and also by the powders' characteristics. Particle sizes before and after milling, the powder amount used during the slurry preparation, specific surface area [28] and milling time [29] are the more important parameters. They are responsible for the rheological behavior which is an efficient tool to predict the sinterability and microstructure of films.

Mechanical and electrochemical performances of the deposited films are enhanced if higher homogeneous and stable suspensions are used [25]. The rheological parameters are valuable data to provide control parameters of slurry quality. The present work evaluates how the parameters such as time of milling and the calcination temperature of YSZ powders influence on the slurry rheological properties and microstructure of anode NiO/YSZ films deposited by a spray coating process.

2. Experimental

2.1. Starting materials

YSZ (8 mol% yttria) powders were prepared by a co-precipitation method [30,31] using zirconium (IV) butoxide (Fluka) and yttrium oxide (Sigma) as starting materials. After this first step, the powder was separated into two aliquots which were calcined at 800 and 1000 °C (YSZ800 and YSZ1000), in order to obtain YSZ powders with different particle sizes.

YSZ/NiO composites were prepared by an impregnation method [32,33] using the previously prepared YSZ800 and YSZ1000 powders and nickel (II) nitrate hexahydrate (Sigma–Aldrich). The two composites obtained were named as NiOYZS800 and NiOYSZ1000. The nominal weight ratio of NiO/YSZ was 56/44. After impregnation, the composites were dried at 280 °C for 4 h and calcinated at 800 °C for 8 h.

Slurries of NiO/YSZ powders were prepared using reagent grade organic additives. Ethylene glycol was used as a solvent and plasticizer, Triton X-100 [polyoxyethylene (10) isooctylphenyl ether] the tensioactive, menhaden fish oil (MFO) the dispersant, and poly(methyl methacrylate) (PMMA) was used as binder. Four samples of each compound, NiOYZS800 and NiOYSZ1000, were prepared using the identical composition and were submitted to milling times of 5, 10, 20 and 40 h in a ball mill that contained zirconia balls.

The slurries were deposited by spray coating [24] on commercial YSZ pellets (TZ8Y, Tosoh Corp., Japan) [34] using a Lince model MP5 spray. The sinterization of films was performed in air at 1150 °C for 6 h. Table 1 gives the symbols used to denote the films obtained from slurries prepared with different milling times.

The thickness of the layer deposited was about 10 μm for all films. Fig. 1 shows the interface between anode and YSZ substrate for sample L2.

2.2. Powder and slurry characterizations

The crystallographic characterizations of YSZ and their NiO/YSZ compounds were performed by X-ray diffraction (XRD) in a Rigaku diffractometer (GeigerflexModel, semi-automatic) equipped with Cu K_α radiation. The YSZ and NiO crystallite size were determined by means of the Scherrer equation [35], $D = 0.9\lambda/\beta\cos\theta$, where D is the crystallite size, λ is the wavelength of the radiation (1.5418 Å for Cu K_α radiation), β is corrected peak width at half-maximum intensity, and θ is the peak position.

Table 1
Symbols used to characterize the films as a function of milling time.

Starting powder	Milling time (h)	Films
NiO/YSZ800	5	F1
	10	F2
	20	F3
	40	F4
NiO/YSZ1000	5	L1
	10	L2
	20	L3
	40	L4

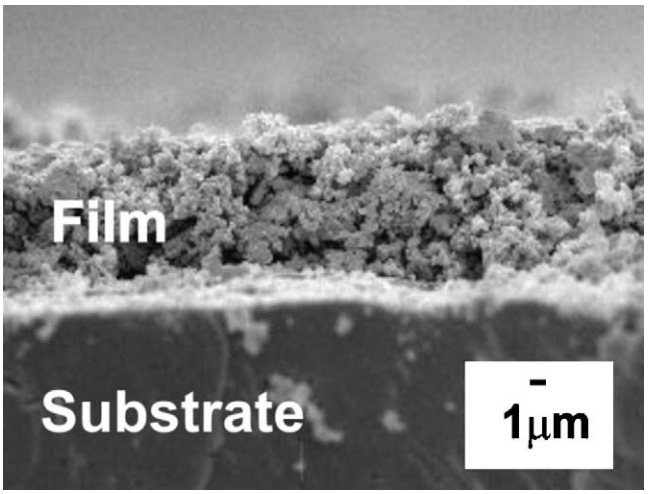

Fig. 1. SEM of the L2 anode film deposited on a YSZ substrate.

The specific surface area, A, of YSZ powders calcinated at 800 and 1000 °C was determined by the multipoint Brunauer–Emmett–Teller (BET) nitrogen absorption method using a Quantachrome NOVA 1200 apparatus.

YSZ average particle sizes (d) were estimated by means of the equation: $d = 6/\rho A$ [36], where 6 is a constant, A is the specific area calculated from BET data, and ρ is the theoretical density of the material calculated by the equation $\rho = ZM/N_A V$ [36], with Z representing the number of formula units in the unit cell, M representing the formula weight, N_A representing the Avogadro's number and V representing the unit cell volume (V was calculated using the lattice parameters determined from XRD data).

The rheological behavior of different slurries was determined at 25 °C with a Haake rheometer model using triplicate samples of 1 mL suspensions. Initially, samples were sheared with shear rate of 5 s^{-1} for 10 s. Viscosity versus shear rates upward and downward curves were then obtained in the shear range of 5–200 s^{-1} for 600 s. Microstructural analyses of anode films were performed by Scanning Electron Microscopy (SEM)