An easy and innovative method based on spray-pyrolysis deposition to obtain high efficiency cathodes for Solid Oxide Fuel Cells

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HIGHLIGHTS

- Electrode preparation method based on spray-pyrolysis deposition on a porous scaffold.
- Polarization resistances as low as 0.07 Ω cm^2 were obtained at 600 °C.
- The electrodes exhibited high conductivity.
- Simple and reproducible method for implementation at industrial scale.

GRAPHICAL ABSTRACT
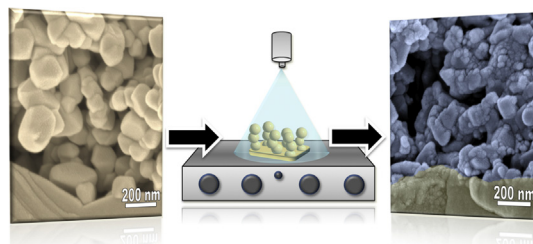
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ABSTRACT

A novel electrode preparation method based on the spray-pyrolysis deposition of metal nitrate solutions onto a porous electrolyte scaffold is proposed. This method has been proved with different cathode materials, usually used in Solid Oxide Fuel Cells, such as $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ and $La_{0.6}Sr_{0.4}Co_{1-x}Fe_xO_{3-\delta}$ (x = 0, 0.2, 0.8 and 1). The electrode microstructure is composed by two layers; the inner layer is a porous electrolyte scaffold homogeneously coated by cathode nanoparticles, providing an increased number of triple phase boundary sites for oxygen reduction, whereas, the top layer is formed by only cathode nanoparticles and acts mainly as a current collector. Polarization resistance values as low as 0.07 and 1.0 Ω cm^2 at 600 and 450 °C, respectively, are obtained at open circuit voltage. This alternative approach has several advantages with respect to the traditional wet infiltration method for large area electrode fabrication, such as higher reproducibility, shorter preparation time in a single thermal deposition step, and easy implementation at industrial scale as a continuous process.

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1. Introduction

Solid Oxide Fuel Cells (SOFCs) are considered as one of the most efficient technologies for large-scale power generation [1,2].

However, the high operating temperatures of these devices difficult their large-scale commercialization. This also results in a premature degradation of the cell components and limits the choice of materials that might be used for their fabrication. Hence, the reduction of the operating temperature to the intermediate temperature range (500–700 °C) is crucial for the development of this technology [3].

The performance of a SOFC at low operating temperatures is limited by the ohmic resistance of the electrolyte and the oxygen

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reduction reactions at the cathode. However, the cathode polarization resistance is the main limiting factor when thin film electrolytes are used [4,5].

SOFC cathodes are usually prepared by conventional solid state reaction and then deposited on the electrolyte by different methods, such as screen-printing and spin-coating, followed by sintering at high temperatures. Alternative synthetic routes have been used to obtain nanostructured cathodes with improved electrochemical properties, including nanoparticles, nanofibers and nanotubes [6–12]. However, the high sintering temperature necessary to ensure an adequate adhesion to the electrolyte leads to an excessive grain growth of the electrodes, reducing the reaction sites, and, consequently, the performance decreases.

One of the most effective strategies to enhance the cathode performance is coating a porous electrolyte skeleton with an active material through a solution infiltration/impregnation process [13–20]. In this method, a porous electrolyte skeleton is deposited on a dense electrolyte, which is fired at high temperatures to ensure good adherence to the electrolyte and structural stability against thermal cycles. Then, a concentrated cation solution, containing the stoichiometric metal salt precursors and complexing agents, is dropwise added into the scaffold layer. After successive infiltration and thermal treatments steps, the scaffold is coated with a layer of the active electrode material. It is well known that this method has several advantages compared to the conventional cathode fabrication: (i) the Triple Phase Boundary (TPB), where the oxygen reduction reaction takes place, is significantly extended, improving greatly the performance; (ii) much less catalyst material is used, reducing fabrication costs; (iii) a good deposited interface and thermal stability between the electrolyte and cathode is obtained; and, iv) the chemical compatibility problems are minimized due to a reduction in the fabrication temperature.

The wet infiltration process has been widely used in small lab-scale research, however, its implementation at large-scale is complicated for several reasons: (i) this method usually requires multiple impregnation-calcination cycles to achieve sufficient conductivity and stability of the electrodes, thus resulting in high time and energy consumptions in the production process; (ii) it is difficult to obtain a homogeneous distribution of the catalyst by manual dropwise addition over large areas, although recently automatic ultrasonic-spray process was used to obtain fine precursor droplets and uniform catalyst distribution in large area cells [21]; and (iii) the electrode area is usually smaller than the electrolyte surface to avoid the mixture of elements between the cathode and anode and/or short circuit of the cell.

Alternative methods to wet infiltration, such as electrodeposition have been used to increase the catalyst content in the electrolyte scaffold, nevertheless, their implementation at industrial scale need to be evaluated [22,23].

In a previous study, $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) cathodes were prepared on large YSZ substrates by a low-cost method based on spray-pyrolysis deposition, achieving high performance at intermediate temperatures [24]. In this work, the spray-pyrolysis deposition is used to coat a porous electrolyte skeleton layer with cathode nanoparticles. This method may be easily scaled up and allows the preparation of electrodes with a more homogeneous deposition of the catalyst over a large area, better reproducibility and shorter preparation times in a single thermal deposition step. This alternative approach has been tested with traditional cathode materials, such as $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ and $La_{0.6}Sr_{0.4}Co_{1-x}Fe_xO_{3-\delta}$ (x = 0, 0.2, 0.8 and 1). The microstructure, electrical properties and potential use of these cathode materials in SOFC are investigated herein.

2. Experimental

2.1. Materials preparation

Pellets of $Ce_{0.8}Gd_{0.2}O_{1.9}$ (CGO) electrolyte were prepared from commercial powders supplied by Rhodia. The powders were pressed into disks of 10 and 1 mm of diameter and thickness, respectively, and then sintered at 1400 °C for 4 h. Substrates of 4×3 cm^2 were also used to test the homogeneity of the catalyst deposition over large areas.

The CGO porous scaffold was obtained from an ink, which was prepared by mixing the electrolyte powders (50 wt%) with a binder material (Decoflux™). The resulting ink was screen-printed onto both faces of the CGO substrates, followed by sintering at 1200 °C for 1 h to ensure adequate adherence.

Precursor solutions for the preparation of the cathodes, $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM) and $La_{0.6}Sr_{0.4}Co_{1-x}Fe_xO_{3-\delta}$ (x = 0, 0.2, 0.8 and 1), were obtained by dissolving stoichiometric amounts of nitrates: $La(NO_3)_3 \cdot 6H_2O$ (99%), $Mn(NO_3)_2 \cdot 6H_2O$ (99%), $Sr(NO_3)_2$ (99.9%), $Fe(NO_3)_3 \cdot 9H_2O$ (98%) and $Co(NO_3)_3 \cdot 6H_2O$ (99%) (Sigma-–Aldrich) in distilled water with a cation concentration of 0.025 M. These samples are hereafter labelled as LSM, LSC, and LSCFx, where x represent the iron content (Table 1).

The solutions were sprayed symmetrically onto both faces of the CGO substrates through a circular mask by using a homemade spray-pyrolysis system equipped with a syringe pump, temperature and motion controllers (Fig. 1). The substrates were heated on an aluminium plate at 200–300 °C with the help of resistance wires. The temperature was measured with a K-type thermocouple placed just below the sample. The hot plate was continuously moved at a constant speed under the spray-nozzle to obtain a more homogeneous deposition of the electrodes. The solutions were atomized by using compressed air as carrier gas, at a pressure of about 2 atm. The flow rate of the solution, deposition time and nozzle to substrate distance were 15 ml/h, 60 min and 20 cm, respectively.

The same cathodes were also prepared on insulating single-crystal sapphire (100) wafers, after depositing the porous CGO scaffold, in order to minimize the influence of the substrate on the electrical properties of the samples.

After the deposition, the samples were annealed in a furnace between 650 and 950 °C for 5 h in air to crystallize the electrodes and to study the phase evolution with the temperature.

2.2. Materials characterization

The structure of the electrodes was analyzed by X-ray powder diffraction (XRD) with a PANalytical X'Pert diffractometer equipped with monochromatic CuK$_{\alpha 1}$ radiation. The phase analysis and identification were performed using the X'Pert HighScore Plus software.

The morphology of the electrodes was observed by Field Emission SEM (FEI, Helios Nanolab 650).

Table 1
Abbreviations used for the different cathodes, amount of deposited cathode with respect to the CGO scaffold (wt%) and conductivity values for the different electrodes at a measured temperature of 600 °C in air atmosphere.

Cathode	Abbreviation	Cathode: CGO	σ (S cm^{-1})	Ea (eV)
$La_{0.8}Sr_{0.2}MnO_{3-\delta}$	LSM	0.25:1	1.57 (5)	0.128 (1)
$La_{0.6}Sr_{0.4}FeO_{3-\delta}$	LSF	0.9:1	4.02 (3)	0.12 (1)
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$	LSCF0.8	0.5:1	5.21 (1)	0.098 (5)
$La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$	LSCF0.2	0.7:1	17.1 (1)	0.071 (2)
$La_{0.6}Sr_{0.4}CoO_{3-\delta}$	LSC	0.9:1	35.8 (1)	0.093 (3)