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Scalable synthetic method for SOFC compounds

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ABSTRACT

Although economically competitive SOFC systems seems to be ready for commercialization, a broad inventory of key starting materials and fabrication processes are needed to enhance systems and reduce costs. These necessities are raised by the demands for large scale SOFC industrial production. Taking into account these reasons, we have synthesized the mean components of a fuel cell, on a large scale, by the glycine nitrate combustion method.

The synthesized different components of SOFC have been the interconnector protective coating ($MnCo_{1.9}Fe_{0.1}O_4$), contact layer ($LaNi_{0.6}Fe_{0.4}O_3$), cathode ($La_{0.6}Sr_{0.4}FeO_3$), interlayer ($Sm_{0.2}Ce_{0.8}O_{1.9}$), electrolyte $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ and anode $(Ni_{0.3}O\text{-}(ZrO_2)_{0.92}(Y_2O_3)_{0.08})$ material, obtaining reproducible pure samples and amounts up to 12 g for each batch, being able to increase easily this amount to lots of hundred of grams.

The obtained materials have been characterized by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-ray fluorescence (XRF), X-ray diffraction (XRD), dilatometry, scanning electron microscopy (SEM), particle size distribution and conductivity measurements.

1. Introduction

New kind of necessities arises from the development of technologies used in synthesis of SOFC materials. These necessities are originated from the demands for appropriate industrial production procedure of SOFC materials, and the respective final products. Therefore, Combustion Synthesis (CS) is an important method for advanced SOFC component fabrication, because is economical and energy efficient method [1].

CS methods can be classified into three categories, on the basis of the physical nature of reaction mixture itself: (i) flame synthesis or gas phase combustion, (ii) heterogeneous condensed phase combustion synthesis and (iii) solution combustion synthesis (SCS) [2]. Focusing in the SCS route, it consists of using an oxidizer (generally metal nitrates) and a suitable organic fuel (urea, citric acid, glycine, etc.) [3,4]. In this sense, SCS represents an exothermic method, which can provide enough energy to evaporate volatile impurities as well as, for the complete calcination of the products, producing, by a single step, pure nanostructured and homogeneous oxide powders with appropriate microstructural properties [5,6].

The major parameters such as fuel mixture and fuel/oxidizer ratio can play a significant role on phase formation of different compounds [7]. The choice of organic fuel (usually glycine, urea, sucrose, citric acid or alanine) is important because different fuels have different properties such as decomposition temperature, heat of combustion and reducing valency [8]. In general, a good fuel should react non violently, producing non toxic gases, an reacting as a complexant for metal cations [9]. As consequence, glycine was selected as the fuel since it is more cost-effective, has demonstrate that can be conveniently employed to prepare ceramic powders and its combustion heat (-3.24 kcal g^{-1}) is greater than that of urea (-2.98 kcal g^{-1}) or citric acid (-2.76 kcal g^{-1}), being more stronger complexing agent and forming stable gels in nitrate solution [9–12]. The advantages of the glycine nitrate combustion process are relatively low cost, fast heating rates, short reaction times, high composition homogeneity and high energy efficiency [13].

The commonly used materials for fuel cell devices are porous cermets of metallic $NiO\text{-}(ZrO_2)_{0.92}$ $(Y_2O_3)_{0.08}$ (NiO-YSZ) as an anode and dense $(ZrO_2)_{0.92}$ $(Y_2O_3)_{0.08}$ (YSZ) layers as electrolyte [14–16]. According to other authors and to our previous studies, $La_{0.6}Sr_{0.4}FeO_3$ (LSF40) has demonstrated to be a practical cathode using $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) as barrier between cathode and electrolyte,

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avoiding poorly conducting secondary phases which increases contact resistance of the system [17–20]. Earlier studies have concluded that the use of $LaNi_{0.6}Fe_{0.4}O_3$ (LNF60) cathode contact layers improves electrons transfer through the contact interface from interconnect to active cathode layer [21,22]. Also, $MnCo_{1.9}Fe_{0.1}O_4$ (MCF10) can be used as an interconnect protective coating to avoid the Cr poisoning to the cathode [23,24].

The present work presents the adaptation of an existing lab-scale cell components production method to an industrially ready and easily scalable method using glycine-nitrate combustion synthesis. After the synthesis optimization, up to 12 g of sample have been obtained in each batch. The synthesized components were: anodes, electrolytes, interlayers, cathodes, contact layers and interconnect protective coatings. Therefore, results of a complete characterization study have been reported including compositional identification of phases, crystal structure, electrical and ionic conductivity, thermal expansion and morphological structure, showing a good reproducibility in all the cases.

2. Experimental

2.1. Powder preparation

All the SOFC component powders were prepared by a glycine nitrate process (GNP). Stoichiometric amounts of the corresponding metal nitrates, which were chosen because their low price under 2.90 € per gram, were dissolved in deionized water (see Table 1), to yield 36 g of the final oxide powders.

For all compositions glycine was then added into the nitrate aqueous solution while stirring. In all the cases a glycine nitrate molar ratio of 1 was used. The effect of different glycine nitrate ratio was previously analyzed for these kind of compounds in the research group [5]. The resulting viscous liquid was auto-ignited by heating up to approximately 455 °C. The obtained powders were calcined between 600 and 800 °C for 5 h to remove carbon residues. In the case of LSF40, LNF60 and MCF10, the resulting powders were pelletized and calcined in air at 950 °C for 8 h, which after several test, demonstrated to be the most economical treatment conditions to obtain pure samples.

2.2. Characterization techniques

Compositional analysis was performed for all the prepared samples to confirm that the expected elemental composition was achieved. The metal contents of Mn, Co, Fe, Sr, Ni and La, were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Horiba Yobin Yvon Activa spectrophotometer. Because their difficulty to dissolve, the analysis of Sm, Ce, Zr and Y contents were carried out with X-ray fluorescence (XRF) on a Fischercope X-ray XDAL.

Room-temperature X-ray diffraction (XRD) data were recorded using an integration time of 10s/0.026° step in the $5 < 2\sigma < 70°$ range with a Philips X'Pert-PRO X-ray diffractometer equipped with a secondary beam graphite monochromated and Cu-Kα radiation.

The morphologies of the powder samples were observed using a scanning electron microscope (JEOL JSM-7000F). Secondary electron images were taken at 20 kV and $1 \cdot 10^{-11}$ A, using a working distance of 8 mm. Particle size distribution of the powders was carried out using a Mastersizer particle size analyzer (Malvern Instruments). All the measurements were done using isopropanol as dispersion medium and using ultrasounds to break up the agglomerates that are formed.

To measure bulk conductivity and thermal expansion coefficient (TEC), pellets of the powders were sintered between 1050 and 1350 °C, and then, cut in 1 × 3 × 7 mm bars. The bulk density of each sample was calculated by measuring the mass and the dimensions of the bars. The samples had a density of around 75% of the theoretical (X-ray) density.

DC conductivity measurements were performed in air by the four-point DC method using a VSP potentiostat controlled by PC using Lab Windows/CVI field point system.

Electrical contacts were made using Pt wires and Pt paste placed over whole end faces ensuring a homogeneous current flow. Voltage contacts were made as small as possible to avoid any disturbance of the contacts on the current flow. Measurements were performed from 450 to 950 °C. The conductivity (σ) was determined from a set of V-I values by taking $\sigma = 1/\rho = L/A \times dI/dV$, where L is the distance between voltage contacts and A is the sample cross section. Finally, TEC measurements were carried out from room temperature to 950 °C in air with a heating rate of 5 °C/min by using a Unitherm Model 1161 dilatometer system (Anter Corporation PA 15235).

3. Results and discussion

3.1. Elemental composition

In order to be able to study the reproducibility of large-scale synthesis of used compounds, three different synthesis have been perform for each compound, labeling as batch the 12 g of product gained in each synthesis. The nominal composition of the samples and the results from the ICP-AES analysis are shown in Table 2.

Within the experimental errors for all the samples, the experimental compositional values match the nominal composition.

Because the difficulties to dissolve SDC, NiO-YSZ and YSZ samples, the compositional measurements of these samples has been performed by XRF technique. The results are shown in the Table 3.

The results obtained by XRF analysis (Table 3) were close to the nominal values for all the studied samples. In all the cases, the difference between the relative amounts of the elements in different batches was not significant. Thus, the synthesis procedure shows an adequate chemical reproducibility.

3.2. Structural study

The purity of the samples was studied by X-ray diffraction. All the materials (LSF40, LNF60, MCF10, SDC, NiO-YSZ and YSZ) prepared through the glycine nitrate (GN) combustion route present the desired final phases. For the LNF60 compound, the appearance of extra shoulders in the experimental profile indicates a possible phase segregation to give two perovskite phases with different Ni/Fe ratio. In the NiO-YSZ case, the diffractogram presents peaks relative to the phases of NiO and YSZ (cubic structure), which evidences that the materials did

Table 1
Summary of used starting materials.

Compound	Starting materials[a]
$La_{0.6}Sr_{0.4}FeO_3$ (LSF40)	$La(NO_3)_3{\cdot}6H_2O$ (> 99%), $Sr(NO_3)_2$ (> 99%) and $Fe(NO_3)_2{\cdot}9H_2O$ (> 98%)
$LaNi_{0.6}Fe_{0.4}O_3$ (LNF60)	$La(NO_3)_3{\cdot}6H_2O$ (> 99%), $Ni(NO_3)_2{\cdot}6H_2O$ (> 98.5%) and $Fe(NO_3)_2{\cdot}9H_2O$ (> 98%)
$MnCo_{1.9}Fe_{0.1}O_4$ (MCF10)	$Mn(NO_3)_2{\cdot}xH_2O$ (> 98%), $Co(NO_3)_2{\cdot}6H_2O$ (> 98%) and $Fe(NO_3)_3{\cdot}9H_2O$ (> 98%)
$Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC)	$Sm(NO_3)_3{\cdot}6H_2O$ (> 99.9%) and $Ce(NO_3)_3{\cdot}6H_2O$ (> 99%)
$Ni_{0.3}O\text{-}(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ (NiO-YSZ)	$Y(NO_3)_3{\cdot}6H_2O$ (> 99.9%), $ZrO(NO_3)_2{\cdot}xH_2O$ (> 99%) and $Ni(NO_3)_2{\cdot}6H_2O$ (> 98.5%)
$(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$ (YSZ)	$Y(NO_3)_3{\cdot}6H_2O$ (> 99.9%) and $ZrO(NO_3)_2{\cdot}xH_2O$ (> 99%)

[a] All the starting materials used were from Sigma-Aldrich.