Obtaining and characterization of La$_{0.8}$Sr$_{0.2}$CrO$_3$ perovskite by the combustion method

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Abstract: This research is focused on the synthesis and characterization of a perovskite oxide based on La$_{0.8}$Sr$_{0.2}$CrO$_3$ system by the combustion method. The material was obtained in order to contribute to analyse the effect of synthesis route in the obtaining of advanced anodic materials for solid oxide fuel cells (SOFC). The obtaining of solid was achieved starting from corresponding nitrate dissolutions, which were polymerized by temperature effect in presence of citric acid. The solid precursor as a foam citrate was characterized by infrared (FTIR) and ultraviolet (UV) spectroscopy, confirming the effectiveness in synthesis process. The solid was calcined in oxygen atmosphere at 800°C and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive of X-ray spectroscopy (EDX) and solid state impedance spectroscopy (IS). Results confirm the obtaining of an orthorhombic solid with space group $Pnma$ (62) and cell parameters $a=5.4590Å$, $b=7.7310Å$ and $c=5.5050Å$. At morphological level the solid showed a heterogeneous distribution with an optimal correspondence with proposed and obtained stoichiometry. The electrical characterization, confirm a semiconductor behaviour with a value of 2.14eV Band-gap according with previous works.

1. Introduction

Since its discovery 70 years ago, the solid oxide fuel cells (SOFC) have taken great importance in the clean production of energy, because these devices can produce electricity from a continuous feed of hydrogen and oxygen, without generation of greenhouse gases with a high efficiency or limitations established by the Carnot cycle [1,2]. In this regard, the high temperature solid oxide fuel cells (HT-SOFC), allow to use different raw materials to provide the hydrogen fuel at anodic level, however in many cases, the purity of feed gases need to be improved to avoid problems related with the carbon deposition in anodic component, represented by the current state of art of Ni-YSZ cermet. Therefore, the need arises to find more efficient ceramic systems that do not allow the formation of secondary phases and carbonaceous deposits [3-6]. Among the most promising materials to replace the conventional cermet anodes, are included some mixed oxides derived from a perovskite structure particularly concentrated in lanthanum and strontium chromites, which exhibit good levels of conductivity in air and fuel hydrogen rich atmospheres, additionally are resistant to graphite deposition [7], due to chromium cation that promote the catalytic oxidation of light hydrocarbons like methane and propane in the reforming process with steam [8].

Under above considerations in order to find new and simple methods to obtain innovative materials at low cost in design of SOFC anodes, this paper focused on the implementation of a synthesis route, which enables the obtaining of homogeneous ceramic materials as opposed to conventional methods of solid stet reaction [9-16]. For this purpose we developed a comparative
study highlighting the main advantages of this methodology in terms of the main techniques of chemical, structural and electrical characterization.

2. Experimental
The ceramic oxide was synthesized starting from corresponding nitrates La(NO$_3$)$_3$·6H$_2$O, Sr(NO$_3$)$_2$, Cr(NO$_3$)$_3$·9H$_2$O in 1.0mol L$^{-1}$. The dissolutions of nitrates were dosed in stoichiometric form in a glass vessel with magnetic stirring at 80°C. The addition of citric acid was performed in a 1:1 relation with respect to total metal cations concentration. The obtaining of a dense sol was achieved after thermal treatment for 3 hours after that, the temperature was increased at 250°C to form a viscous material that which is then entered into spontaneous combustion, providing a solid carbonaceous precursor. The precursor was characterized by infrared (FTIR) and ultraviolet (UV) spectroscopy in a Perkin-Elmer FTIR-1000 computer and HP 8453 UV-Vis respectively, in order to confirm the presence of citrate species. The solid was calcined at 800°C under oxygen flow (50mL min$^{-1}$) for 2 hours to eliminate remnant carbon from previous stage.

The obtained oxide was macerated and characterized by X-ray diffraction (XRD), to identify the nature of the crystalline phase and purity. The analysis were performed on a PANalytical X’Pert PRO MPD-, equipped with X’Celerator detector in Bragg Brentano configuration, using the Cu K$_\alpha$ radiation ($\lambda$=1.54186Å) between 20 and 80°. The X-ray data were analysed using the X’Pert HighScore software and the crystallite size was evaluated by the Debye-Sherrer equation. The SEM analysis was performed in a LEO 440 microscope (Leica-Zeis), equipped with an electron gun and microprobe analysis for EDX. The solid state electrical impedance analysis (IS), was performed on an AUTOLAB potentiostat-galvanostat using modified cell at room temperature and a La$_{0.8}$Sr$_{0.2}$CrO$_3$ blank to validate the obtained material. The blank and the oxide was compressed in a uniaxial system at 5.0MPa pressure and sintered at 900°C for 1 hour in similar way to avoid measurements errors.

3. Results and discussion
The UV analysis of precursor, showed two major electronic transitions located at 340 and 470nm (Figure 1), in the range of 200 to 700nm, where the citrate ligand provides a strong signal of electronic transition ($\pi\rightarrow\pi^*$), while the n-$\pi^*$ transitions are considerably minor. Such transitions are characteristic and are related with the presence of unsaturated compounds with metal heteroatoms in correspondence with Pino et al. [17]. From UV results was possible to identify the value of Band-gap around 2.14eV for the obtained material, which is consistent with studies of Strehlow et al. [18].

Figure 1. UV spectrum of metalorganic precursor La$_{0.8}$Sr$_{0.2}$CrO$_3$ between 300 and 600nm.
The FTIR results shown in Figure 2 and analysed comparatively with the SDBS database, allow obtaining the relationship between the transmittance signals with the main vibration bands. The presence of these signals is justified by the thermal decomposition process of the gels at 250°C and the signs located below 1000 cm\(^{-1}\) are related with the vibrational movements associated with the different metal cations La\(^{3+}\), Sr\(^{2+}\) and Cr\(^{3+}\) with hydroxyl groups and oxygen atoms, which confirm the bond between citrate ligands and the metal cations as has been previously confirmed for similar perovskite compositions [16].

The XRD analysis of the calcined oxide using the X’Pert High Score software (Figure 3), permit to classify the oxide with the La\(_{0.85}\)Sr\(_{0.15}\)CrO\(_3\) reference compound, with a ICSD 051197 code, space group \(Pnma\) (62), orthorhombic system and cell parameters \(a=5.4590\) Å, \(b=7.7310\) Å and \(c=5.5050\) Å, with a preferential crystal orientation along \((1\ 2\ 1)\) facet as shown in Figure 4. The crystallite size evaluated with the highest diffraction signals permit to identify nanometric sizes of sample around 4.4nm.

The Rietveld refinement analysis, allowed to identify that the signals located about 24 and 31° 2\(\theta\) are associated with the presence of strontium chromate (SrCrO\(_4\)), as secondary phase of system. The above explained by the formation of oxygen vacancies, allow the mobility of ions at high temperatures and the formation of intermediate low concentration species, as has been shown previously [19]. According to Waernhus et al. [20] the SrCrO\(_4\) has a high resistivity and is catalytically inactive, because the strontium cation consent the stabilization of the perovskite structure by a load balancing, therefore deficiencies at site A of the structure, promote such substitutions causing that B site elements form different kinds of binary oxides.

Results of scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) shown in Figure 5, allow to corroborate the obtaining of a heterogeneous distribution of particles with a high coherence between proposed and obtained compositions, articulate with the synthesis process [21]. In Table 1, is shown the difference between proposed and obtained composition, which does not exceed a difference by more than 0.10% (w/w), confirming the effectiveness in the control of used stoichiometry.
Figure 5. X-ray energy dispersive spectrum and scanning electron microscopy of La$_{0.8}$Sr$_{0.2}$CrO$_3$ oxide.

Table 1. Composition results (%w/w) of La$_{0.8}$Sr$_{0.2}$CrO$_3$ sample obtained by EDX technique.

| Percentage values by weight (%) | La   | Sr   | Cr   | O    | Total |
|--------------------------------|------|------|------|------|-------|
| Experimental                   | 48.63| 7.722| 22.65| 21.00| 100   |
| Theoretical                    | 48.60| 7.664| 22.75| 20.99| 100   |
| Difference                     | 0.03 | 0.058| 0.10 | 0.01 |       |

Figure 6, shown the solid state impedance spectrum, where the two curves shown the impedance versus frequency and phase versus frequency change. The incidence of chromium in the structure relates to the development of charge carriers, permit to understanding the interactions between electrons and atoms in the solid material, so, the obtained resistivity value (6131 ohm), is result of SrCrO$_4$ in the La$_{0.8}$Sr$_{0.2}$CrO$_3$ oxide, requiring its elimination through thermal treatments as claimed by Gómez et al. [22,23]. According to these results, the solid state impedance spectroscopy was a useful tool to validate the contamination of main crystalline phase, since the Bode impedance plot for blank did not show the same behaviour.

Figure 6. Bode impedance plot of (a) blank and (b) La$_{0.8}$Sr$_{0.2}$CrO$_3$ samples.
4. Conclusion
The UV and FTIR analysis, corroborate the obtaining of citrate species corresponding with synthesis method, which favour the consolidation of a crystalline phase with morphology and surface characteristics to be explored in design of SOFC anodes. The XRD analyses confirmed that a highly crystalline material was obtained, with \textit{Pnma} (62) space group, orthorhombic structure and crystallite sizes around 4.4 nm with preferential orientation along (1 2 1) facet. The SEM and EDX analysis, allow corroborate several morphological and surface characteristics of relevance for electrocatalytic activity. The impedance analysis, validate a resistive behaviour of sample due to secondary phases of SrCrO$_4$ in contrast with the blank measurements, leading to the conclusion that the main crystal phase needs to be consolidated to promote integration of the remaining oxides to the main structure. Nevertheless, the synthesis method allows to obtain material with morphological and surface properties of relevance for the design of SOFC anodes.

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