PREPARATION AND CHARACTERIZATION OF PEROVSKITE OXIDES BY POLYMERIZATION-COMBUSTION

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ABSTRACT

This paper describes the preparation of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ perovskite oxide, using a polymerization-combustion route, to obtain materials for potential applications like electrodes in solid oxide fuel cells (SOFC). For such purpose, initially the solid precursor was characterized by FT-IR spectroscopy and thermal analysis (TGA-DTA), showing the obtention of polymeric citrate precursors. The thermal analysis (TGA-DTA), X-ray diffraction (XRD) and scanning electronic microscopy (SEM), provides information about the formation of a perovskite phase, while the texture, relief and roughness found are characteristic of the method of synthesis used. The size of crystallites, calculated using the Scherrer calculator software and transmission electron microscopy (TEM), confirmed the presence of nanometric crystallites (< 41.0 nm), whereas the chemical composition and crystallographic structure, indicating a high correlation with respect to proposed system, which was confirmed by X-ray fluorescence (XRF), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). Finally the electrical characterization by impedance spectroscopy (IS), determined the capacitance and resistance of the system in order to provide information related to the concentration of charge carriers and the diffusion rate of ions in the material a high conductivity values, related to semiconductor behavior for potential applications.

Keywords: anodes, citrate, coordination compounds, perovskite.

INTRODUCTION

The lanthanum and strontium chromite $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ system, is a ceramic material used as anode component in solid oxide fuel cells, due to its good conductivity in air and fuel-rich atmospheres, high stability and compatibility with other cell components [1]; additionally, it has to proved be a efficient catalyst in the combustion of light hydrocarbons like methane and propane, among others [2, 3-6]. However, the associated problems with low surface areas, loss of composition by volatilization of chromium and strontium species due to the effect of prolonged times of calcination [7], has enabled the development of alternative synthesis methods at low temperatures, which facilitate the obtention of materials that preserving and improving most of its textural, morphological and electrical properties [8, 9]. In this context, this paper describes the preparation of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ system, through polymerization-combustion process that promotes the obtention of coordination compounds in aqueous medium, under controlled conditions of pH and temperature, which when exposed to temperatures above 250 °C and oxidizing atmospheres to propitiate a spontaneous combustion process for obtention of solid oxides, this fact, decrease the synthesis temperature and prevents the potential volatilization of species, facilitating the modulation in the final concentration of ceramic as well as the preservation of a series of surface and textural properties of high interest in the field of SOFC components.

EXPERIMENTAL

For synthesis of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ oxide, we used the corresponding metal nitrates of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 99.9%, $\text{Sr}(\text{NO}_3)_2$ 99.8%, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 99.98% and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 99.98% Merck 1.00 M. Similarly, citric acid monohydrate 2.00 M (99.99% from Merck) was used. The solutions of cations were measured in a glass reactor equipped with magnetic stirring (150 rpm.), temperature control and reflux at 80 °C for 4 hours. The order of addition of the precursors was: Sr, La, Cr and Fe, established by its corresponding hydrolysis constants, so that the total amount of cations in the reaction mixture was 0.01 mol. Once added each one of the cations, we proceeded to add the solution of citric acid in a molar ratio 1.5:1 to propitiate the development of the respective coordination compounds. Thus, the final concentration of cations in solution was 0.150 M for the lanthanum, 0.050 M for strontium, 0.160 M for iron, 0.040 M for chromium and 0.600 M for citric acid. The mixture was kept under reflux for 4 hours and then to recover the solvent by heating to 120 °C, to obtain a viscous liquid which was treated at 250 °C to form a precursor solid foam, which, was treated in a platinum crucible at 700 °C for 30 minutes, using a ramp of 50 °C hour⁻¹ in air atmosphere to remove carbon residues remaining on the stage of self-combustion at 300 °C [10].

The obtained foam precursor was analyzed using a Perkin-Elmer FTIR-1000 spectrophotometer, to confirm the presence of citrate species. The results were analyzed comparing the absorbance spectrums obtained and reported in OMNIC32® software and SDBS (Spectral database for organic compounds) databases.

The relationship between weight change and heat exchange in function of temperature (TGA-DTA) was carried out simultaneously on a Mettler Toledo TG-APMS TGA/SDTA851e/LF/1600 equipment under conditions of air flow 50 mL min⁻¹, in a platinum crucible with a heating rate of 5 °C min⁻¹ between 25-1000 °C, to evaluate the optimum temperature for the consolidation of the crystalline phase.

The chemical composition and crystallographic structure of solid was determined by X-ray diffraction, on a PANalytical X'Pert PRO MPD diffractometer, equipped with Ultra fast X'celerator detector and Bragg-Brentano configuration, using Cu K_α radiation ($\lambda = 1.54186$ Å) between 10 and 90 ° with steps of 0.02 ° and irradiations of 40.80 seconds per step. The measures were developed with a voltage of 40 kV and a current of 20 mA. The refinement, indexing and the simulation of the structures was done with Cellref3.0® and Rietveld® software, allowed to establish the chemical composition and crystallographic structure. The crystallite size estimation was done using the highest diffraction signals, using the Debye-Scherrer equation, taking the value of half peak width set by a Lorentzian function and using a constant of 0.89 as reference.

Analysis by scanning electron microscopy (SEM) was carried out in a LEO 440 microscope (Leica-Zeiss), equipped with an electron gun and a spectrometer that measures the energy dispersive X-ray. The images were obtained with a focus distance of 10-25 mm, an accelerating voltage of 20 kV and a current of 100-200 pA, measurement time of 100 seconds and counting rate 1.2 kcps. The samples were placed on a sticker attached to a graphite holder and aluminum objects shaded with platinum to obtain a better contrast in images.

The transmission electron microscopy analysis was performed on a JEOL 2100 microscope equipped with a LaB₆ thermoionic gun operated with accelerating voltage of 200 kV, equipped with a CCD image acquisition system. For the analysis of the samples, they are milled to obtain fine powders, which were sieved to 200 U.S. mesh standard and dispersed in a probe tube with 5.0 mL of acetone, each tube was placed in ultrasound for a period of 30 min, after which an aliquot of 1.0 mL of the upper each tube and again diluted to 5.0 mL with acetone, leaving again on ultrasound for a period of 5 min more,

and finally, each copper grid was added one drop of each tube and allowed to dry at 45 °C for 1 hour.

The composition of the solid was evaluated by X-ray fluorescence in a sequential spectrometer of dispersive X-ray wavelength Bruker S4 Pioneer and energy dispersive X-ray diffraction (EDS), with the purpose of obtain a compositional information of the ceramic.

In order to provides useful information on physicochemical properties of the system, the IS technique allowed the characterization of the electrical properties and the evaluation of information related to microscopic characteristics of the ceramic material by means variable frequency data, which was obtained in a impedance analyzer Agilent 4294A between 40 Hz to 13 MHz with an AC amplitude of 0, 1 volts. For fixed-frequency measurement in the selected range, we used a QuadTech 1920 LCR Analyzer, obtaining Nyquist type impedance plots. For this, it was prepared a pellet of 0.060 g of finely ground solid, using isostatic pressure (vacuum) of 1.0 t, in a Perkin-Elmer® pelletizer for 60 seconds. The pellet thus obtained was polished using SiC abrasive paper 400, in order to provide a uniform surface for electrode fixation process, adjusting the thickness of the pellet at 0.50 mm. The faces of the tablets were coated using a ink platinum (Engelhart Clal product: Ink Platinum 6082), which was deposited by thermal treatment for 1 hour at 900 °C using a heating ramp of 5 °C min⁻¹ for provide an adequate contact area, finally, data from this analysis were corrected by the global geometry of the pellet and the reference cell.

RESULTS AND DISCUSSION

In the initial part of the synthesis process, the preparation and the nature of the precursors of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ oxide is subject to the presence in the reaction medium of different species whose concentrations are a function of pH, ligand concentration and ionic strength, among others. This modeling was performed using the Hydra-Medusa software [11], to evaluate the behavior of each cation in solution with the purpose of obtain a homogeneous reaction medium. Once regulated the best synthesis conditions, the resulting solution was subjected to different thermal treatments, to obtain the solid foam precursor, which served to carry out subsequent characterization analysis.

The infrared characterization of the $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ precursor, allowed us to determine by comparison between the obtained absorbance and reported spectra in OMNIC32 database software and the spectral database for organic compounds (SDBS), the formation of a citrate precursor. Figure 1 shows the FT-IR spectra with their corresponding absorption bands, indicating the formation of a polymeric citrate complex. So, the bands located at 3791 and 3413 cm⁻¹, be associated with vibrational tension modes of O-H links of dimers intermolecularly bonded to hydroxyl groups, which can be moved slightly by the NH_4OH addition effect to the reaction medium [12]. In the same region at 3163 cm⁻¹, is clear a tension mode band associated with the O-H bond in carboxylic acid dimers linked to hydrogen bridges, which contains information from the N-H bond in tension mode. The bands located at 2340 and 2360 cm⁻¹, correspond to stretching modes associated with the presence of occluded CO_2 , in the material pores, derived of thermal treatment of precursor foam, while the band located around 1855 cm⁻¹, can be identified with a secondary vibration and vibration tension of the C=O bond.

The band at 1729 cm⁻¹, corresponds to the tension mode of the C=O bond in carboxylic acid dimers saturated, its intensity increases in proportion to the concentration of iron in the material, which is associated with increased pH of the system during the precursor consolidation. On the other hand, the signal located at 1591 cm⁻¹, is associated with asymmetrical tension mode of a COO^- unidentate coordination compound, which can eventually move to lower wave numbers are also related to the same vibrational mode [13]. The band at 1385 cm⁻¹, correspond to the symmetric tension mode of COO^- bond associated with bidentate coordination compounds, and likewise, may contain information related to the NH_4^+ functional group. Another band to be increased to lower amount of chromium in the precursor, is located at 1231 cm⁻¹, which corresponds to the C-O mode stress related to presence of a acetic acid esters (CH_3COOR), which can form in the drying process of the citric acid foams. The signals corresponding to the band at 1078 and 896 cm⁻¹, corresponding to the C-O mode bond stress associated with acetals and unsaturated aliphatic primary alcohols, as well as bending out of plane C-H bond, which are present in the precursor and may contain information about the NH_4OH added in the process of adjusting the pH of the reaction medium. The bands located at

low wave number at 843, 667 and 410 cm⁻¹, corresponding to the binding of different metal cations of La^{3+} , Sr^{2+} , Cr^{3+} and Fe^{3+} with OH groups and oxygen atoms, whose vibrational modes $\nu(\text{O-M-O})$ may be strengthened in terms of pH, also suffered slight shifts to lower wavelengths. This confirms that the pH of the medium chosen for the synthesis of oxide favors the formation of dimeric species of carboxylic acids, and the establishment preferred bidentate coordination compounds by COO^- group and strengthening M-O links [13] as show in Table 1.

Figure 1.- Infrared spectrum of lanthanum and strontium chromite precursor in KBr pellet obtained at 25° C, with its main absorption bands.

Table 1. The position of the infrared absorption band precursor, obtained through the OMNIC32 software and SDBS database.

Band	Frequency (cm ⁻¹)	Bond	Vibration mode
1	410	M-O	Flexion (<i>m</i>)
2	607	M-O	Tension (antisimétrica <i>m</i>)
3	843	M-O	Tension (symmetrical <i>m</i>)
4	896	C-O	Tension (symmetrical <i>m</i>)
5	1078	C-O, C-H	Tension (<i>f</i>)
6	1231	C-O	Tension (<i>f</i>)
7	1385	COO^-	Deformation (<i>m</i>)
8	1591	COO^-	Deformation (<i>v</i>)
9	1729	C=O	Tension (<i>f</i>)
10	1855	C=O	Secondary vibrations, tension (<i>f</i> , 2 bands)
11	2340	O=C=O	Tension (<i>m</i>)
12	2360	O=C=O	Tension (<i>m</i>)
13	3163	N-H O-H	Tension (<i>m</i>)
14	3413	O-H	Tension (<i>f</i> , wide)
15	3791	O-H	Tension (<i>f</i> , wide)

Thermal analysis of precursor between 25 and 1000 °C, revealed a slight increases in enthalpy associated with the evaporation of water retained by physical adsorption, additionally this stage demonstrated the presence of OH ligands, whose first stage of deprotonation occurs between 50 and 140 °C (zone I), which suggests differences in the mode of binding of water molecules, and end up between 150 and 200 °C (zone II) as indicated in Figure 2.

Figure 2. Thermal analysis (TGA-DTA) of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ precursor.

Dehydration continues until 210 °C and additionally in the case of citrate precursor, starts the formation of C=C double bonds, with partial conversion of citrate to aconitate while ammoniacal species formation begins to appear between 200 and 235 °C (zone III), together with the elimination of R-O radical species, accompanied by an endothermic event until 280 °C. Then, the system reach a maximum level of exothermicity, related to the combustion of organic matter between 280 and 335 °C (zone IV), and the weight loss over 80%. At this point, when most of the organic matter is destroyed and the removal of organic carbonates formed during the process is complete, start the consolidation of the oxide compound. The nature of the compounds that persist in this stage have been discussed in the literature [14, 15] and according to different reports, is clear the formation of carbonate species, and other intermediate oxo-carbonates formed in the synthesis process (zone V) [16, 17]. Slight variations of mass that appear in IV and V zones at 488 and 626 °C, respectively, corresponding to decomposition of secondary species and solid oxide reorganization (Figure 2). Consequently, the analysis allowed us to find an ideal temperature calcination, which not only facilitated the obtention of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ system, also avoids the possible volatilization of chromium species.

Further analysis by X-ray diffraction, indicates that the $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ system has an adequate chemical composition and crystallographic structure, indicating a high correlation with respect to proposed system, with a preferential crystal orientation in the (011) plane, as shown in Figure 3. The crystallite size estimation was done using the highest diffraction signals, by Debye-Scherrer equation, taking the value of half peak width (β), adjusted to a Lorentzian function and using a constant of 0.89 as reference, resulting in an average crystallite size of 39.0 nm. The tolerance factor structure of the composition studied, was determined by the SPuDS software (Structure Prediction Diagnostic Software) [18], suggesting the stabilization of a perovskite structure. The search performed by the program X'Pert ® High Score in ICCD databases indicates a classification according to the $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ reference oxide, JCPDS 00-035-1480, space group *Pbn* (62) orthorhombic crystal system with cell parameters $a = 5.532 \text{ \AA}$, $b = 5.553 \text{ \AA}$, $c = 7.835 \text{ \AA}$ and cell volume $240.68 \text{ \AA}^3$.

Figure 3.- X-ray pattern of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ powder sample, obtained by the method of polymerization-combustion.

The subsequent refinement and indexing was done through Cellref3.0® software under the parameters mentioned above, using the 8 intensity highest signals, verifying that there are differences in about $0.045 \text{ \AA}$, in terms of standard deviation for each indexed line with respect to those shown by the reference compound, which is explained by distortion that can generate the iron cation in the structure of chromite, situation that can be observed when comparing the unit cells of crystalline systems $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$, calculated using the DiamondV3.1 software and the corresponding diffraction patterns as shown in Figure 4.

Figure 4.- Unitary cells of the $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ systems, calculated using the DiamondV3.1 software.

The $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ perovskite was studied by scanning electron microscopy, to analyze the different morphological and surface characteristics of particles; for that, the specimen was evaluated at different magnifications and some results are shown in Figure 7. From these micrographs it is clear that at the microscopic level, the solid is composed of irregular aggregates, distributed with particle sizes between 0.5 to 200 μm as shown in Figure 5. In principle, this picture is related to the texture and the relief created by the elimination of volatile substances that are produced in the combustion of organic compounds during thermal treatment (drying and calcination), also is notable that the obtained materials suffered some degree of densification, a fact that favored a compact morphology and it is reflected in the intensity of the (011) signal, but did not affect the size of the crystallites. The elemental analysis of the sample was studied by X-ray dispersive energy analysis, showing an adequate compositional profile, the results are discussed below along with those obtained by X-ray fluorescence.

Figure 5.- Scanning electron micrographs for $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ sample.

The results of transmission electron microscopy, allowed us developing a statistical count in all micrographs obtained in a population of 300 particles, based on equation (1). Where n_i is the number of particles and d_i is the characteristic diameter of particle.

$$d = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \quad (1)$$

The data were normalized, confirming the presence of nanometric crystallites with regular morphology, and a average size of 41 nm, crystallite outer areas of ca. $12,000 \text{ nm}^2$ and interplanar distances of 0.32 nm for the (011) plane and grain boundary widths of at least 1 nm as shown in Figure 6. Similarly, the Figure 7 shows the histogram of particle size, which indicates that the distribution is unimodal with a strong Gaussian behavior.

Figure 6.- Interplanar distances and grain boundary widths for the $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ system.

Figure 7.- Particle size distribution data determined from transmission electron microscopy.

The elemental analysis of the oxide, measured by XRF microanalysis and energy dispersive X-ray fluorescence, showed that the composition of the oxide is closely related to the expected values. These results are significant in the analysis of subsequent characterization tests, because provide information relating to the success of the synthesis in aqueous medium.

The analysis by impedance spectroscopy (IS), in order to evaluate the capacitance and resistance of the system in order to provide information related to the concentration of charge carriers and the diffusion rate of ions in the material, measured at 25 °C and displayed as Nyquist plot confirm that the solid have a semiconductor behavior with conductivities of $2.1 \times 10^{-3} \text{ ohm}^{-1}\text{cm}^{-1}$ as shown in table 2.

Table 2.- Comparison of frequency values, resistance, capacitance and conductivity obtained at 25° C for $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ system, derived from the analysis by Zplot software.

Component	Frequency (Hz) $\times 10^6$	Resistance (ohm)	Capacitance (Farads) $\times 10^{-10}$	Correlation	Conductivity ($\text{ohm}^{-1}\text{cm}^{-1}$) $\times 10^3$
LSCF	3.7	471	4.6	0.997	2.1

The detailed analysis of the results derived from Zplot software and showed at Table 2 indicates that the electrical behavior of solid is consistent with the desired characteristics for anodic materials, in which it is important to provide adequate levels of conductivity, with the purpose of allow reactant gases to diffuse to the electrolyte interface, since the oxidation reactions occur only in the three-phase boundary (TPB), where the gas phase, the metallic phase, and the anodic material are all in contact. The main results indicate that the oxide has high electrical conductivity, and the transport properties in this material are strongly dependent on the relative volume fraction of the phases, microstructure, and used calcination temperature. The behavior of resistivity, conductivity and capacitance, determine that both the capacitance as the

permittivity are essentially independent of the frequency, it allows to perform a preliminary classification of material in the way of evaluating their behavior at higher temperatures. Based on these results, the sample was used to perform a study of impedance at 450 °C to obtain the corresponding conductivity profile as a function of temperature as shown in Figure 8.

Figure 8.- Nyquist Plot of impedance, which represent the electrical behavior of the $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ system to 450°C with its corresponding equivalent circuit.

The equivalent circuit shown in Figure 8 indicates that a diffusional impedance related to charge transport phenomena in the material, functionally equivalent to a Warburg impedance, can arise at nonzero frequency. The element R_p in Figure 8 represents the geometrical, or bulk resistance, while C , is the corresponding geometrical capacitance. Values for R_p , and C and values of the equivalent circuit elements, can be estimated using the Zplot software. The representation of these results, together with that derived from that at room temperature, allowed to obtain the data in Table 3, where we can observe that the increase in temperature has a proportional effect in the conductivity of the $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ system in more of two magnitude orders.

Table 3.- Comparison of frequency values, resistance, capacitance and conductivity obtained at 450°C for the $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ sample derived from the analysis by Zplot software.

Component	Frequency (Hz) $\times 10^6$	Resistance (ohm)	Capacitance (Farads) $\times 10^{-7}$	Correlation	Conductivity ($\text{ohm}^{-1}\text{cm}^{-1}$) $\times 10^{-1}$
LSCF	2.1	1.3	3.7	0.999	7.6

Under these conditions, it is clear that the level of conductivity obtained for $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ system, are strongly related with high electrical conduction levels similar to the state of the art of typical anodic materials as Ni-YSZ, which confirm that it is possible to obtain polycationic perovskite materials, using the citric acid self-combustion method.

CONCLUSIONS

The main results indicate that the $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.2}\text{Fe}_{0.8}\text{O}_3$ oxide has high electrical conductivity, and that the transport properties in this material are strongly dependent of the relative volume fraction of the phases, microstructure, and temperature. These parameters should hence be taken into consideration for the optimized design of anodic materials. Additionally, it is clear that self-combustion method with citric acid is suitable for tuning the properties according to optimized parameters for specific applications.

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