Synthesis of praseodymium doped cerium oxides by the polymerization-combustion method for application as anodic component in SOFC devices

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Abstract. This work reports the synthesis and the characterization of six oxides; it is based on Ce₁₋ₓPrₓO₂ (x=0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) system, which is obtained by the polymerization-combustion technique for potential applications on design of advanced electrodic components, for solid oxide fuel cells (SOFC). Initially the solid precursors are characterized by infrared spectroscopy (FTIR) and thermal analysis (TGA-DTA), allowing to determine the formation of prevalent citrate species and the optimal temperature for the consolidation of the desired crystalline phases. The X-ray diffraction (XRD) and the transmission electron microscopy analysis (TEM) are performed over calcined samples which provided information about the formation of a fluorite phase with grain distribution, surface, textural and morphological properties consistent with the nanometric obtaining crystallites (30nm), it is oriented along the (1 1 1) facet, with d spacings of 0.31nm for the main diffraction signal. These results indicate the effectiveness of the proposed synthesis method for potential applications in the design of advanced anodic materials for solid oxide fuel cells.

1. Introduction
The operating principle of a fuel cell is based on its three basic components, an anode (fuel electrode), a cathode (air electrode) and an electrolyte (polymer or ceramic) [1, 2]. Depending on the type of electrolyte, the fuel cells can be classified in systems of low, medium and high operation temperature. The first group is integrated by the proton exchange (PEMFC), direct methanol (DMFC) and phosphoric acid fuel cells (PAFC), which operates directly with hydrogen and oxygen, through the catalytic effect that can be achieved by an expensive platinum catalyst in the fuel electrode. In the second group, the molten carbonate fuel cells (MCFC), employ a metallic electrocatalyst of low cost. However, these systems are characterized by a low CO tolerance, which causes a poisoning phenomenon on the anodic catalyst, causing a blockage of active sites of the catalyst and hence, the anode degradation. On the other hand, the solid oxide fuel cells (SOFC), have an incomparable advantage with respect to the systems that works at low and medium temperatures, since these devices have the possibility to use ceramic electrocatalysts (Ni-YSZ), economically more affordable, with possibilities of use for a wide range of fuels without high levels of processing or use of noble metals. However, the carbon deposition, represents the main drawback of this cell, recently, the cerium oxides modified with praseodymium oxide have had a growing interest as anodic components, since fluorite structure allows the movement of cations and charge carriers along structure, producing good levels conductivity and structural stability [3,4], reason of which, the manufacture of anodic components
using rare earth oxides for fuel cells has increased in order to produce more efficient devices that help to reduce the emissions of greenhouse gases and the consumption of fossil fuels [5,6].

However, it is clear that chemical routes used to obtain the ceramic electrodes of these devices do not allow the generation of acceptable properties, at textural, morphological and surface levels for developing catalytic processes. So, it is clear that in the materials science's context, it is necessary the search of new synthesis methods that allow the obtain of new and improved materials for the applications in solid oxide fuel cells technology [7,8]. In this context, the present work is focused on the synthesis and characterization of 6 cerium oxides based on the Ce_{1-x}Pr_{x}O_{2} (x=0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) system, by a chemical route of polymerization-combustion, with the aim of studying the effect on structural, morphological, electrical and catalytic properties for use as potential anodic components in SOFC technology.

2. Experimental

For the synthesis of cerium oxides, it is started from corresponding nitrates of Ce(NO_{3})_{3} 1.0molL^{-1}, Pr(NO_{3})_{4} 1.0molL^{-1} and citric acid monohydrate 99.99%. The dissolutions of metal ions were measured in glass reactors equipped with magnetic stirring (150rpm), temperature control and reflux. In this way, the proposed systems remained on simultaneous heating for 2 hours at 80°C, after which it is added a solution of citric acid at a ratio of 1:0.5, with respect to the total content of metal cations, in order to enable the formation of the corresponding coordination compounds [9]. The solutions were treated between 100 to 250°C to evaporate the solvent and obtain gels, which were treated at 350°C until the beginning of a combustion process, which generates a cluster of heterogeneous solids. The obtained precursors are treated at 500°C under oxygen flow (10mLmin^{-1}) for three hours in order to remove carbonaceous residues from previous combustion stage and to form the crystalline phase [10].

The metal-organic precursors (before calcination), were analysed by FT-IR technique in a Shimadzu prestige-21 spectrophotometer to confirm the presence of citrate species [11]. The relationship between weight change and heat exchange in function of temperature (TGA-DTA) were carried out in a simultaneously Mettler Toledo equipment TG-APMS TGA/SDTA851e/LF/1600, under air flow conditions (50mLmin^{-1}), in platinum crucibles with a heating rate of 5°Cmin^{-1} between 25 and 1000°C to evaluate the optimal temperature for the consolidation of the crystalline phases [12]. The chemical composition and crystallographic structure of calcined solids were determined by X-ray diffraction, on a PANalytical X’Pert PRO MPD diffractometer equipped with an Ultra fast X’celerator detector and a Bragg-Brentano configuration, using the Cu Kα radiation (λ=1.54186Å), between 10 and 90° with steps of 0.02°. The measurements are developed with a voltage of 40kV and a current of 20mA. The analysis by transmission electron microscopy was performed on a JEOL 2100 microscope equipped with a LaB_{6} thermo-ionic gun, operated with accelerating voltage of 200kV equipped with a CCD image acquisition system crystalline phase.

3. Results and discussion

The Figure 1 presents the FT-IR spectra of one of the precursors with their corresponding absorption bands, which point out the formation of a polymeric citrate complex for all synthesized precursors. Showing the same absorption bands, it is possible to identify the main signals as follow: The band located at 3431cm^{-1} is associated with vibrational tension modes of O-H group of dimers intermolecular bonded to hydroxyl groups, which can be moved on slightly by the NH_{4}OH addition effect to the reaction medium. In the same region at 3241cm^{-1}, it is clear, a tension band associated with the vibrational mode of O-H bond in carboxylic acid dimers linked to hydrogen bridges, which contain information from the N-H bond in a tension mode [4]. The band located at 2360cm^{-1}, corresponds to the stretching modes associated with the presence of occluded CO\(_{2}\) in the material pores, derived of thermal treatment. The bands associated with asymmetric stretching and bond deformation (COO-M) are in the region at 1300-1500cm^{-1} and a band that arises from the symmetric deformation of the groups (COO-M) at 1653cm^{-1} [13]. The signal at 1040cm^{-1} corresponds to the C-O bond tension associated with acetals and primary alcohols, as well as bends out of plane of C-H bond,
which are present in the precursors and that contain information about the NH$_4$OH addition during the process of adjusting the pH [14]. The bands located at low wavenumber correspond to the bonds of the different metal cations of Ce$^{3+}$ y Pr$^{3+}$ with OH groups and oxygen atoms [15,16].

The TGA-DTA analysis is shown in Figure 2. In the first stage, occurs the de-protonation of OH groups between 50 and 60°C, while in the second stage occurs the elimination of water molecules present until achieving a temperature of 150°C. Dehydration continues until 210°C and additionally in the case of the citrate precursor, it 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 230°C, together with the elimination of O-R radical species, it is accompanied by an endothermic event until 285°C [4]. At that moment, the system reach a maximum level of exothermicity, which is related to the combustion of organic matter between 285 and 340°C and the weight loss upper to 70%. At this point, it is initiated the removal of formed carbonates and consolidation of the crystalline phase, in this way, most of organic species are removed when the temperature reaches 505°C [17].

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The analysis by means of transmission electron microscopy (TEM), confirms the presence of nanometric agglomerates of regular morphology, with an average size of 30 nm, outer areas of 1853 nm², and interplanar distances of 0.31 nm for the (1 1 1) facet [4,18] (see Figure 4).

4. Conclusions
The FT-IR and TGA-DTA analysis performed over citrate precursors allows evaluating the formation of intermediate coordination complexes and the optimal temperature for the consolidation of the crystalline phase, in accordance with the synthesis method used. The characterization by X-ray diffraction and transmission electron microscopy on calcined samples provide information about the formation of a prevalent fluorite phase with morphological and surface properties which consistent with the obtaining of nanometric crystallites (30 nm) oriented along (1 1 1) facet and interplanar distances of 0.31 nm for the main diffraction signal. The effect of citric acid is a critical parameter to establish the compounds coordination, which favours the development of highly homogeneous materials with improved properties for potential applications, since it involves the preservation of surface properties of relevance in the development of catalytic properties for eventual applications as anodic electrocatalysts in solid oxide fuel cells.

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Figure 4. Transmission electron microscopy images of the Ce₁₋ₓPrₓO₂ (x=0.0, 0.2, 0.4, 0.6, 0.8 and 1.0) systems respectively.