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Synthesis Characterization and Sintering of Cobalt-Doped Lanthanum Chromite Powders for Use in SOFCs

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Abstract. Doped lanthanum chromite is a promising as interconnect material because of its good conductivity at high temperatures and its stability in oxidizing and reducing atmospheres. Perovskite oxide powders of Co-doped lanthanum chromite were synthesized by dispersing precursor metal salt solutions in a polymer matrix followed by a thermal treatment. XRD patterns showed that a highly crystalline cobalt-doped lanthanum chromite was obtained. Fine perovskite powder with a surface area of 6.15 $m^2 g^{-1}$ calcined at 700°C for 1 h, were obtained. After the sample sintered at 1450°C for 3h, the powder reached high densities exceeding 97% of the theoretical density. The proposed here has proved to be a very promising technique for the synthesis of lanthanum chromite powders.

Introduction

Cobalt-doped lanthanum chromite is of interest as an interconnect material for solid oxide fuel cells (SOFCs) [1, 2, 3]; mainly in cells composed of yttria-stabilized zirconia (YSZ) as a solid electrolytes and electrodes of Sr-doped $LaMnO_3$ (cathodes) and Ni/YSZ cermets (anodes). The SOFC interconnect must have sufficient chemical and mechanical stability at oxidizing and reducing atmospheres close to 1000°C, high electronic conductivity and low ionic conductivity, and a thermal expansion coefficient that matches that of the electrolyte, YSZ. Several types of ABO_3 chromites, including $La(M)CrO_3$, where M is Mg, Ca, Sr or Co have been developed that meet these requirements. High density is also required to provide gas-tightness in the interconnection. Most Cr-containing oxides are known to be difficult to sinter in air to high densities because of vapor-phase transport, during the process, which causes grain growth without densification [4, 5, 6]. Sintering of chromites in air is dependent on the formation of liquid phases, which develop through the introduction of sintering aids such as Co, Ni or Ca, resulting in the formation of secondary perovskite phase, although some problems resulting from such additives in SOFC applications have been reported [7, 8, 9]. The addition of $LaCoO_3$ favors the densification of $LaCrO_3$ in air at low temperatures. The reason for adding $LaCoO_3$ is that it has a perovskite structure with high conductivity similar to that of $LaCrO_3$, but it is sintered at lower temperatures than those required for $LaCrO_3$ because its melting point occurs at around 1400°C. In addition to sintering processing, the characteristics of the precursor powder are crucial to obtain high dense interconnects. These characteristics depend on the method of synthesis. There are a variety of methods for the synthesis of multi-cation oxide precursor powder. The conventional method for the preparation of multi-cation oxides is based on the solid-state reaction technique. In this method, the ball milling and grinding steps are time consuming and energy intensive. Moreover, the grinding media may contaminate the final product. In addition, calcining and sintering with long holding times at high temperatures make the method expensive [10, 11, 12]. Multi-cation oxides can also be produced by the combustion method with urea [13, 14], but long holding times and high temperatures are

required to obtain a single phase. The citrate method (Pechini) [15] is another way to synthesize multi-cation oxides. Popa [15] synthesized $LaCoO_3$ powders by a polymerizable complex technique based on the Pechini-type reaction route. A mixed solution of citric acid and ethylene glycol with La and Co ions was polymerized. The product obtained by the polyesterification between citric acid and ethylene glycol was compared with that obtained by the nonpolymerizable route using only citric acid as complex-forming agent, without ethylene glycol. The latter method offered advantages over the former. Zhigalkina et al. [16] proposed a method to synthesize lanthanum chromite by the sol-gel method, using aqueous solutions of lanthanum and chrome nitrates in the presence of a high-molecular-weight compound, polyvinyl alcohol (PVA). PVA was used as a gel-forming agent. The effects of the amount of PVA and of the heat treatment time and temperature on the completion of synthesis were studied, and the aforementioned authors obtained dispersed lanthanum chromite powder with a homogeneous composition and particle size. The optimum process parameters were as follows: $La(NO_3)_3$.$6H_20$ and $Cr(NO_3).9H_20$, PVA:$LaCrO_3$ = 0.3:1, and a gel calcination temperature of 900ºC. In the present work, cobalt-doped lanthanum chromite was also obtained by dispersing the nitric metal precursor solutions in a polymer matrix. The constituent metal ion solutions were mixed with the polymeric matrix, which consisted of an aqueous solution of polyvinyl alcohol (PVA). The ratio of the PVA mass to the mass of the resulting product $La_{0.7}(Co)_{0.3}CrO_3$ was 0.03:1. This ratio, which is 10 fold lower than that used in a previous study [16], enabled us to obtain a highly dispersed, homogeneous and nanosized cobalt-doped lanthanum chromite powder. Sintering of the achieved powder resulted in a highly dense crystalline material.

Experimental

The aqueous nitric solutions of the metals were prepared by dissolving their respective nitric salts, $La(NO_3)_3.6H_2O$ (>99%, Aldrich), $Cr(NO_3)_3$.$9H_2O$ (98%, Aldrich) and $Co(NO_3)_3$.$6H_2O$ (98%, Aldrich), in distilled water.

A polymeric solution was prepared by dissolving polyvinyl alcohol (PVA, Casa Americana, 200 – 500 $g.mole^{-1}$) (8 weight %) in distilled water.

The prepared nitric metal salt solutions were then mixed in stoichiometric amounts to obtain $La_{0.7}(Co)_{0.3}CrO_3$. These salt solutions and the aforementioned polymeric solution were mixed in a ratio of 0.03:1 of PVA mass to the rated mass of the resulting $La_{0.7}(Co)_{0.3}CrO_3$ product. The resulting mixture was heated on a hot plate (~250ºC) under continuous stirring until the water evaporated and a dark brown easy-broken dry gel was obtained. This material, which is the precursor of $La_{0.7}(Co)_{0.3}CrO_3$, was crushed into a powder in an agate mortar with a pestle and calcined in air for 2h at 500, 600 and 700ºC. The specific surface area of calcined powders was determined by the BET method (Quanta Chrome, Nova-2000). The crystalline phase was identified by the X-ray diffraction technique (XRD) (Bruker AXS-D8). The measurements were performed in the 2θ range of 20º –75º, using CuK_α radiation. The morphology of the powders was observed by scanning electron microscopy (SEM). Calcined powder pellets with a diameter of 10mm were uniaxially pressed at 300MPa and then sintered in air at 1450ºC for 3h in a covered alumina crucible. The densities of the sintered pellets were determined by the Archimedes method. The crystalline phases of the sintered samples were analyzed by XRD on the polished surface.

Results and discussion

Table 1 lists the BET surface area and particle size of calcined powders and the densities of samples sintered in air at 1450ºC for 3h. The surface area ranged from 6 to 19 $m^2\ g^{-1}$. It can be observed that the higher the calcination temperature the smaller the surface area, indicating the high reactivity of

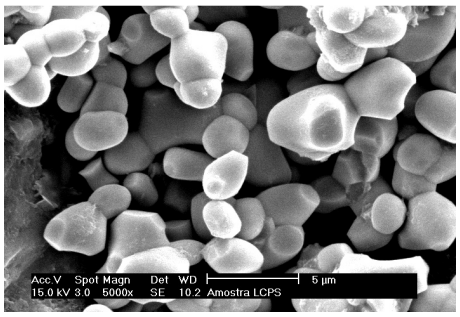
the powders. The particle size values calculated from the surface areas (Table 1) confirm that nanometric powders can be produced by the present method.

Table 1 – BET surface area and particle size of calcined powders and densities of samples sintered in air at 1450°C for 3h.

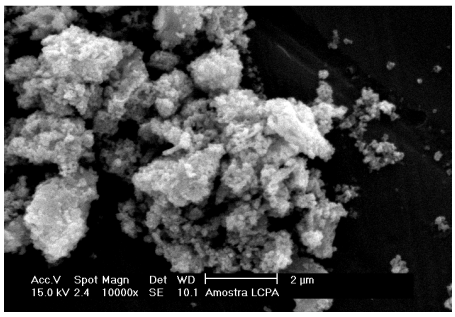
Sample	Temperature of calcining [°C]	Surface area [$m^2\ g^{-1}$]	Particle size from surface area [D*] [nm]	Density [$g.cm^{-3}$]	% of theoretical density
A	500	18.4	48	6.38	94.99
B	600	12.54	71	6.47	96.30
C	700	6.15	145	6.57	97.83

*($D = 6.\ (S.\rho)^{-1}$, where D is the diameter, S is surface area and ρ is density of material

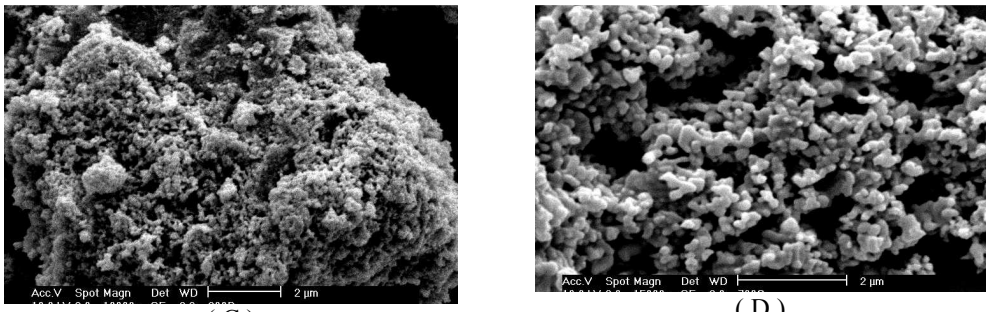
In the present process, the dispersion of the metal salt solutions in the polymer matrix (PVA) resulted in a homogeneous product, yielding uniformly sized fine particles because the material was dispersed evenly throughout the polymeric structure, preventing the segregation of oxide components while gases and water vapor were eliminated. It is extremely important to determine the minimum quantity of PVA solution to be used in the process, since long holding times and high temperatures are required to remove residual carbon from the polymeric matrix, despite reports in the literature that 500°C suffices [17]. The quantity of PVA used here was considerably less than that used in an earlier work [16]. The amount of PVA used in that work [16] was tenfold higher, and the specific surface area was 1.2 and 1.68 $m^2.cm^{-3}$ for the powder calcined at 800 and 900ºC, respectively. In the present work, calcining at 500, 600 and 700ºC resulted in specific surface areas of 18.4, 12.54 and 6.15 $m^2.g^{-1}$, respectively. We found with a minimum quantity of PVA, the specific surface area reached much higher values, thus resulting in a highly reactive powder. The densities of the samples sintered in air at 1450°C for 3h, as listed in Table 1, indicate that all the samples reached a relatively high percent of the theoretical density in the range of 94-98 %. These results are important, since high density provides gas-tightness when the material is applied as an interconnect material for SOFC. Fig. 1 shows SEM micrographs of samples dried at 120°C (A), and calcined at 500°C (B), 600°C (B) and 700°C (D). All the micrographs in this figure show spherical particles.



(A)



(B)



(C) (D)

Fig. 1 - SEM micrographs of samples dried at 120°C (A), calcined at 500°C (B), 600°C (B) and 700°C (D)

In Fig. 1 (A) they are micron sized, and in the other micrographs, (B), (C) and (D), the particles are submicron sized. Increasing the calcination temperature caused the spherical particles to transform into tight agglomerates, as shown in (C), which is congruent with the decreasing BET surface area values listed in Table 1.

Fig. 2 shows XRD patterns of powders calcined at 700°C for 2h and the same sample sintered at 1450°C for 3h.

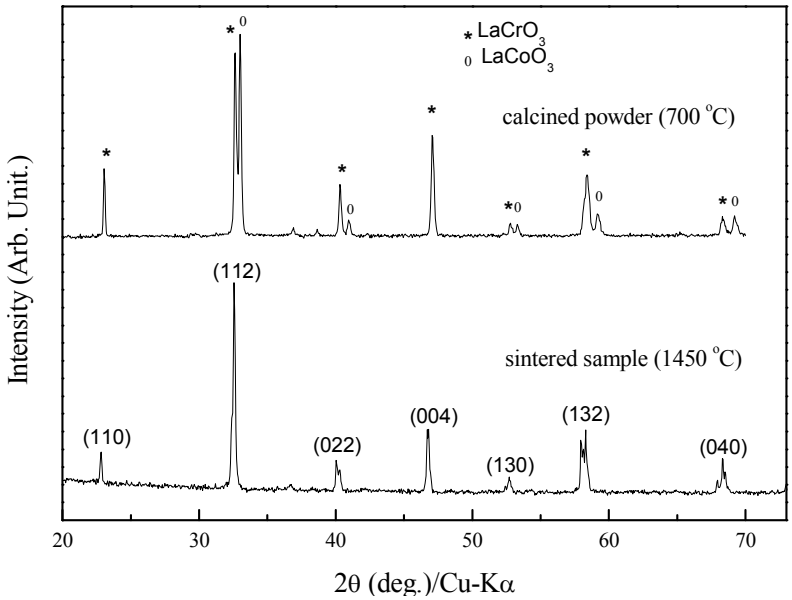


Fig. 2 - XRD patterns of powders calcined at 700°C for 2h and the same sample sintered in air at 1450°C for 3h.

The diffraction peaks of XRD pattern of calcined powder precursors depicted in Fig. 2 correspond to $LaCrO_3$ and $LaCoO_3$ crystalline phases. The formation of solid solution was confirmed by the characteristic XRD pattern of the sintered sample, which corresponds to $LaCrO_3$ crystalline phase. An XRD analysis of powders calcined at 980°C for 2h showed an identical XRD pattern that obtained to the sintered sample. This indicates that the solid solution can be achieved at 980°C, temperature below the sintering temperature (1450°C).

Conclusions

A simple method for synthesizing La(Co)CrO_3 from aqueous solutions at an ordinary temperature and pressure was presented here. La (Co)CrO_3 was obtained using aqueous solutions of lanthanum, cobalt and chrome nitrates in the presence of PVA aqueous solution. The ratio of PVA mass to the rated mass of the resulting product $La_{0.7}(Co)_{0.3}CrO_3$ was 0.03:1. Fine La (Co)CrO_3 precursor powder with a high surface area was obtained. Crystalline La(Co)CrO_3 was synthesized at temperatures as low as 980^{o}C. After sintering, the calcined precursor powders reached densities exceeding 95% of the theoretical values. The synthesis method presented here is an easy way to obtain highly crystalline La(Co)CrO_3. It does not involve the rigorous process control usually required by other chemical processes. The advantage of the method compared to others is its simplicity. This method is promising for the preparation of La(Co)CrO_3 for SOFC applications.

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