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Fabrication of Sr- and Co-doped lanthanum chromite interconnectors for SOFC

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ABSTRACT

Many studies have been performed dealing with the processing conditions of electrodes and electrolytes in solid oxide fuel cells (SOFCs). However, the processing of the interconnector material has received less attention. Lanthanum chromite (LaCrO₃) is probably the most studied material as SOFCs interconnector. This paper deals with the rheology and casting behaviour of lanthanum chromite based materials to produce interconnectors for SOFCs. A powder with the composition La_{0.80}Sr_{0.20}Cr_{0.92}Co_{0.08}O₃ was obtained by combustion synthesis. Aqueous suspensions were prepared to solids loading ranging from 8 to 17.5 vol.%, using ammonium polyacrylate (PAA) as dispersant and tetramethylammonium hydroxide (TMAH) to assure a basic pH and providing stabilization. The influence of the additives concentrations and suspension ball milling time were studied. Suspensions prepared with 24 h ball milling, with 3 wt.% and 1 wt.% of PAA and TMAH, respectively, yielded the best conditions for successful slip casting. Sintering of the green discs was performed in air at 1600 °C for 4 h leading to relatively dense materials.

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1. Introduction

Nowadays, the study of materials to be used as interconnectors in solid oxide fuel cells (SOFC), has focused on the lanthanum chromite (LaCrO₃) based materials because of their unique properties, such as good chemical compatibility with other components, good electrical conductivity and stability during the fuel cell operation, i.e. their ability to resist both the reducing conditions at the anode side and the oxidant conditions of the cathode at temperatures of about 1000 °C [1–4]. Different geometries have been used for the production of SOFC configurations; however those configurations involving plates and pipes have received special attention in the last years [5,6]. For these and other complex configurations the use of colloidal processing techniques, such as slip casting in plaster molds, tape casting, gel casting, and screen printing, becomes more and more necessary, since they have demonstrated to be efficient in the manufacture of complex geometries with reproducible and controlled microstructures [7,8].

Some papers have been published in the literature concerning the colloidal processing of doped-LaCrO₃ powders by tape casting or slip casting in non-aqueous media [9–12]. In previous works the authors have studied the surface behaviour and stability in water

of a powder with the composition La_{0.80}Sr_{0.20}Cr_{0.92}Co_{0.08}O₃ prepared by combustion synthesis [13–15]. The present work deals with the preparation and optimisation of concentrated aqueous suspensions of doped-LaCrO₃ powders and their further processing by a slip casting route. Suspensions were firstly prepared to a solids loading of 10 vol.% to study the best dispersion and homogenisation conditions, and then the solids loading was increased to achieve higher densities.

2. Experimental procedure

A powder with the composition La_{0.80}Sr_{0.20}Cr_{0.92}Co_{0.08}O₃ was obtained by combustion synthesis as described elsewhere [15]. The following precursors were used: (1) lanthanum (III) nitrate hexahydrated, La(NO₃)₃·6H₂O (99.99%, Aldrich, Germany); (2) strontium nitrate, Sr(NO₃)₂ (99%, Aldrich, Germany); (3) chromium (III) nitrate nonahydrated, Cr(NO₃)₃·9H₂O (99%, Aldrich, Germany); and (4) cobalt (II) nitrate hexahydrated, Co(NO₃)₂·6H₂O (98%, Vetec, Brazil). Urea (CO(NH₂)₂, Nuclear, Brazil) was used as a fuel.

The synthesised powders were attrition milled in ethanol media (absolute ethanol, Casa Americana, Brazil) using silicon nitride balls for 2 h and further dried in a muffle at 60 °C.

Suspensions of the doped-LaCrO₃ powder were prepared in deionized water to a solids concentration of 42 wt.% (corresponding to a 10 vol.%). To reduce powder agglomerates, the slurries were ball milled for milling times up to 24 h, using alumina balls.

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For stabilizing the slurries an ammonium salt of a polyacrylic acid (PAA, Duramax D-3005, Rohm and Haas, USA) with concentrations ranging from 0 to 3.5 wt.% (referred to dry solids) was used. Basicity was provided by adding tetramethylammonium hydroxide (TMAH), supplied by Aldrich-Chemie (Germany). These products are supplied as aqueous solutions with active matter concentrations of 35 and 25 wt.%, respectively. The concentration of these additives is expressed as active matter present, referred to dry solids.

The rheological behaviour of all prepared slurries was studied with a rheometer (Haake RS50, Thermo, Germany) capable to operate at either controlled shear rate (CR) or controlled shear stress (CS) modes. The sensor system consisted on a double-cone rotor and a stationary plate, this system being surrounded by a cylindrical wall. The chamber is protected with a solvent trap to reduce evaporation phenomena. For characterising the slurry dispersion the flow curves were determined in controlled rate mode (CR). Measurements were performed by increasing the shear rate from 0 to 1000 s^{-1} in 5 min, maintaining at 1000 s^{-1} for 2 min and returning to 0 in 5 min. CS measurements were performed by increasing the stress from 0 to a value higher than the yield point estimated by direct observations of the CR flow curves (i.e. 10–15 Pa). The up and the down curves were measured without any intermediate step. For both ramps the measuring time was 200 s. Temperature was maintained constant at $25\text{ }^{\circ}\text{C}$ during these experiments.

Small ceramic discs with 2 cm in diameter were obtained by slip casting suspensions prepared at different conditions (concentrations of PAA and TMAH) on plaster of Paris moulds. The green density of the disc-shaped specimens was measured by mercury immersion after drying for 48 h at room conditions and the values are reported as percentage of theoretical density of $\text{La}_{0.80}\text{Sr}_{0.20}\text{Cr}_{0.92}\text{Co}_{0.08}\text{O}_3$ (6.50 g cm^{-3}).

Sintering of the green discs was performed in air at $1600\text{ }^{\circ}\text{C}$ for 4 h with a heating and a cooling rate of $5\text{ }^{\circ}\text{C min}^{-1}$. The crystalline phases present were identified by X-ray diffraction using two powder diffractometers Rigaku-RINT2000 and Rigaku-DMAX, operating at 50 kV and 30 mA, using the K_{α} radiation of Cu and Cr rotating anodes, in the range of $2\theta = 10\text{--}110^{\circ}$. The scanning step was 0.020° , with a 5 s/step.

FESEM-EDX observations of the fracture surfaces were performed by field emission scanning electron microscopy (FESEM) (Hitachi S-4700 type I, Japan).

3. Results and discussion

As reported in a previous work the average particle size of the milled powders measured by laser diffraction is $2.1 \pm 0.1\text{ }\mu\text{m}$, but according to scanning electron microscopy observations these are agglomerates consisting of nanometer sized particles that behave as unitary particles [15].

The isoelectric point of this powder was reported to occur at $\text{pH} \sim 8$ leading to high zeta potential values at acidic pH. However, the stability against time was poor because of the high solubility of the powder, especially at acidic conditions. Hence, basic pH is preferred and the addition of PAA is necessary to provide stability at $\text{pH} \sim 8\text{--}9$, where zeta potential was about -50 mV and the solubility was low [14].

With these considerations in mind, the effect of pH control and PAA additions were studied separately. In all cases the optimisation of the rheological behaviour was studied for suspensions prepared to a solids loading of 10 vol.%. Fig. 1 shows the flow curves of the suspension as-prepared and after the addition of KOH to pH 9.5, with and without the application of ultrasounds for 1 min. It can be seen that the application of ultrasounds produces an increase of viscosity. The use of an ultrasound probe for dispersion is deleterious, probably due to local overheating, so that ball milling was tested. Since the presence of PAA is needed to achieve

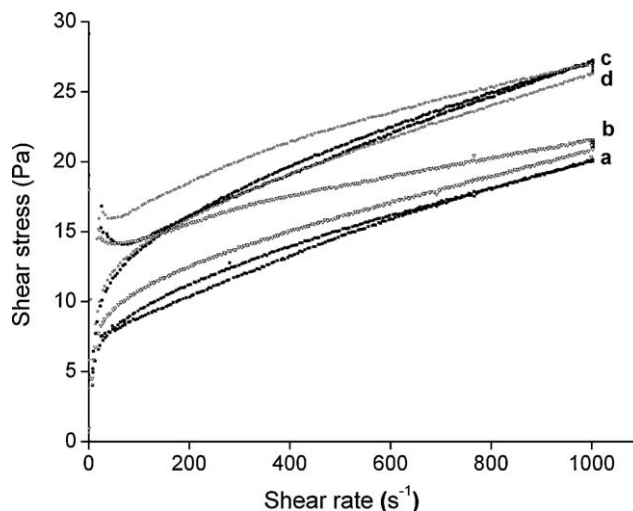


Fig. 1. Flow curves of the as-prepared suspension, whose natural pH was 8.5, before (a) and after (b) 1 min of ultrasound; and the suspension after the addition of KOH to pH 9.5 before (c) and after 1 min of ultrasounds (d).

stability, suspensions with a concentration of PAA of 1 wt.% were prepared to different milling times. The corresponding flow curves can be seen in Fig. 2. The viscosity tends to increase with milling time, the lowest being for that milled for a few minutes (5–10 min), but the time stability is low and settling occurs spontaneously or after few minutes.

These results suggest that dispersion requires the use of both PAA, to promote electrosteric stabilisation, and a strong base that allows a pH control at basic conditions in order to promote deflocculant chains to extend toward the liquid and to maximise the number of surface sites available for adsorption. In previous works it has been demonstrated that TMAH is useful to provide a better dispersion to ceramic suspensions because it is a strong base and can adsorb as a quaternary ammonium [16,17]. Fig. 3 shows the flow curves of suspensions prepared with 1 wt.% PAA and different additions of TMAH. The incorporation of TMAH up to 1 wt.% decreases the viscosity of the suspensions, that maintains nearly constant with further additions.

Only the suspension without TMAH, which has the highest viscosity and thixotropy, exhibits an apparent yield point (5.4 Pa). Suspensions with TMAH have no significant yield stress and their viscosity is very low (23–24 mPa s at 100 s^{-1} for 1–2 wt.% TMAH).

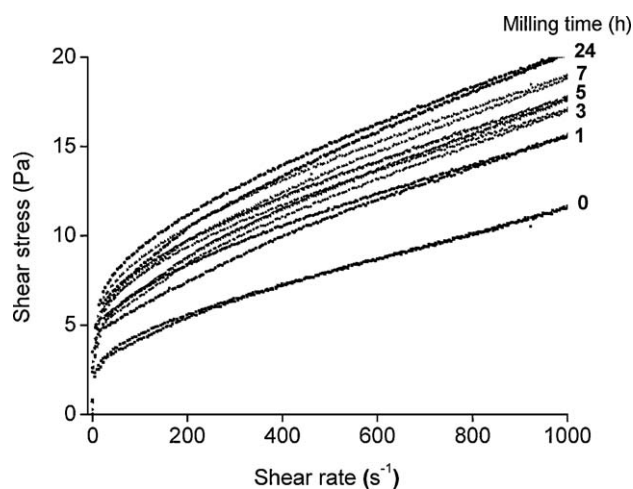


Fig. 2. Flow curves of 10 vol.% suspensions with 1 wt.% PAA measured after different ball milling times.

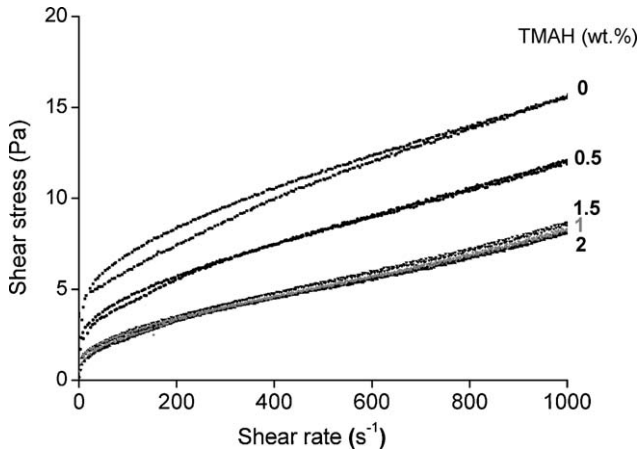


Fig. 3. Flow curves of 10 vol.% suspensions prepared with 1 wt.% PAA and different additions of TMAH.

These suspensions were slip cast and the dried green bodies displayed very low relative densities, by 20% of theoretical, as a consequence of the excessively low solids loading of the suspensions (10 vol.%).

In order to optimise the PAA content, other set of suspensions was prepared with 1 wt.% TMAH and different concentrations of PAA. However, to enhance dispersability, ball milling is often required. As it is well known, ball milling reduces particle size and increases the surface area, so that more amount of deflocculant will be needed to provide stabilisation. The resulting flow curves are

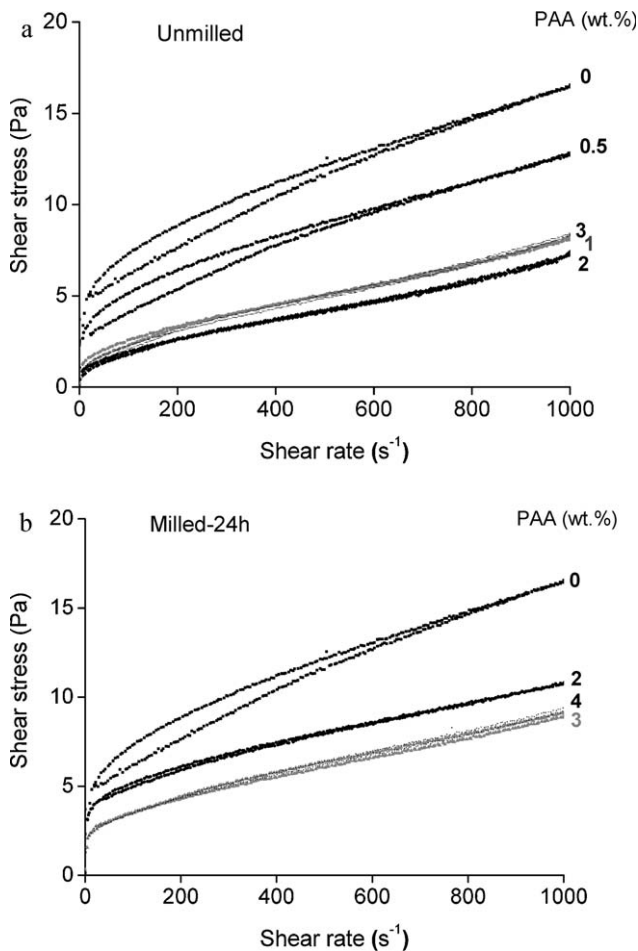


Fig. 4. Flow curves of 10 vol.% suspensions prepared with 1 wt.% TMAH and different concentrations of PAA before (a) and after (b) 24 h ball milling.

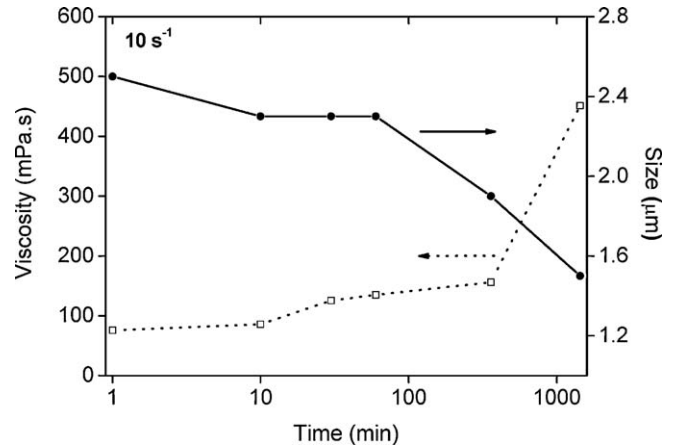


Fig. 5. Variation of viscosity and average particle size with milling time, of 10 vol.% suspensions with 1 wt.% PAA and 1 wt.% TMAH.

plotted in Fig. 4 for suspensions without (Fig. 4a) and with 24 h ball milling (Fig. 4b). In the case of unmilled suspensions, the highest viscosity occurs for the suspension without PAA, which has also the largest thixotropy. The minimum viscosities are obtained for suspensions with 2.0 wt.% PAA (~ 20 mPa s at 100 s $^{-1}$). The

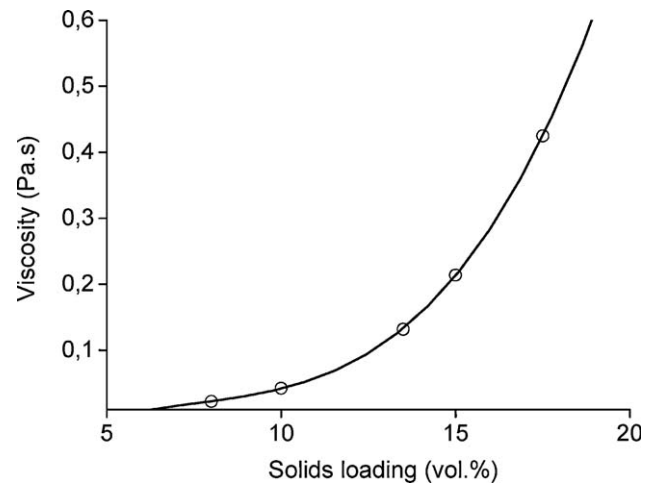


Fig. 6. Variation of relative viscosity with solids loading for optimised suspensions (1 wt.% TMAH and 3 wt.% PAA, after 24-h ball milling).

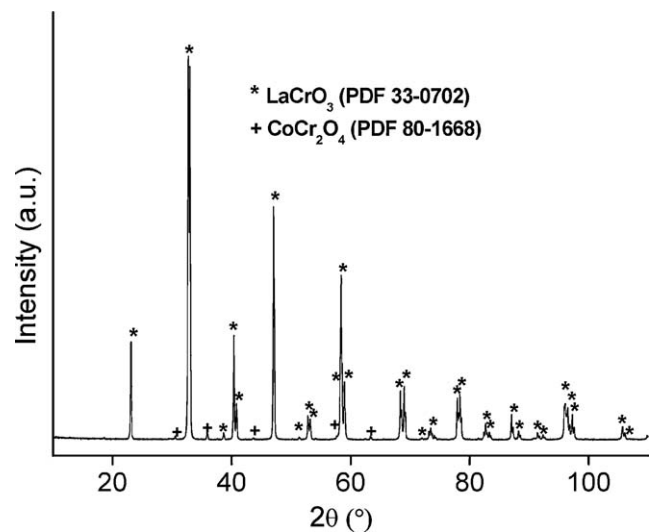


Fig. 7. XRD pattern of the sintered $\text{La}_{0.80}\text{Sr}_{0.20}\text{Cr}_{1.92}\text{Co}_{0.08}\text{O}_3$ sample.

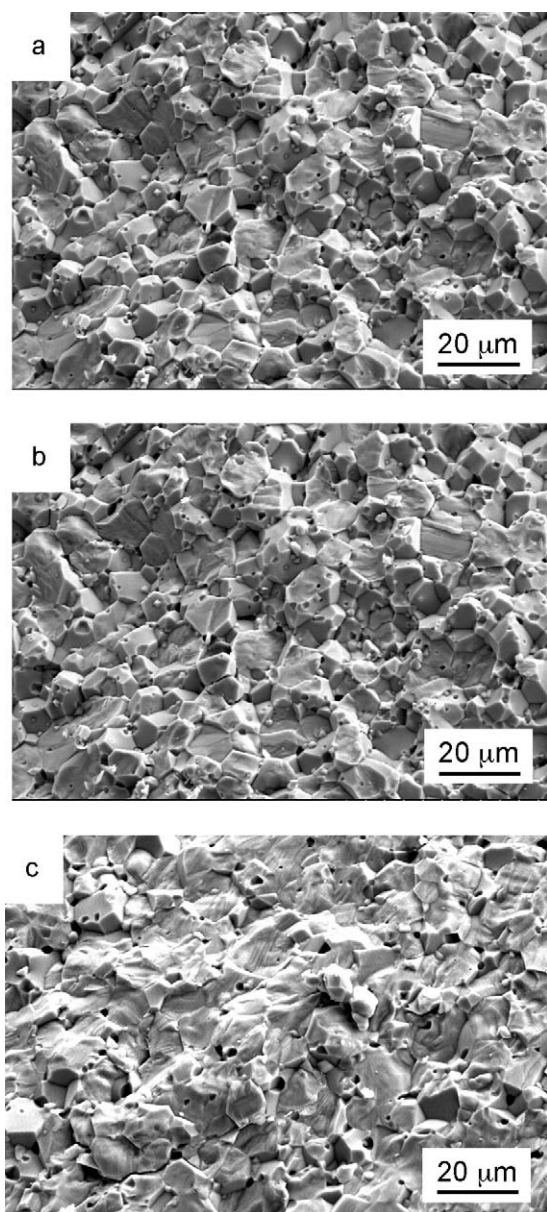


Fig. 8. FESEM micrographs of the fresh fracture surfaces for the sintered specimens cast from optimised suspensions with 13, 15 and 17.5 vol.% solids loading.

behaviour is complex being shear thinning at the low-medium shear rate region and becoming shear thickening at the high shear rate region. This is characteristic of complex fluids in which a suspension structure develops or breaks down depending on the shearing conditions. In the case of suspensions milled for 24 h thixotropy disappears for any addition of PAA and the viscosity reduces significantly for PAA contents of 3–4 wt.%, the flow behaviour becoming nearly Newtonian. This suggests that milling must be accomplished of an increasing PAA concentration.

This can be demonstrated in Fig. 5, which shows the variation of the average particle size with milling time, compared with the variation of viscosity. It can be seen that both parameters present an opposite trend. The particle size decreases with milling time whereas viscosity increases. This suggests that agglomerates are breaking down leading to the formation of new surfaces that increase the viscosity. Then, particles have higher free surface that is now available for the adsorption of more deflocculant.

Once all the dispersion parameters were optimised (1 wt.% TMAH, 3 wt.% PAA after 24 h ball milling) suspensions with different solids

contents were prepared. Fig. 6 shows the evolution of the relative viscosity with solids loadings in the range from 8 to 17.5 vol.% solids. The viscosity increases from 23 to 425 mPa s for volume fractions of 8 and 17.5%, respectively. No significant yield points are obtained and negative values of thixotropy are obtained, that is, the up-curve is below the down-curve thus indicating that the most concentrated suspensions maintain a solid-like structure after shearing.

Fig. 7 shows the XRD pattern of the sintered $\text{La}_{0.80}\text{Sr}_{0.20}\text{Cr}_{0.92}\text{Co}_{0.08}\text{O}_3$ sample. It can be seen that a rhombohedral perovskite, indexed according to LaCrO_3 (PDF 33-0702), is the major phase present. A second phase is also present and is identified as CoCr_2O_4 (PDF 80-1668) with a cubic spinel structure.

Fig. 8 shows the microstructures of the fresh fractures of cast specimens prepared with suspensions with 13.5, 15 and 17.5 vol.% solids, all treated at 1600 °C/4 h. They show inter and intragranular porosity with an increase of the grain size for the sample with the highest solids content (17.5 vol.%). Relative densities are in all cases higher than 97% of the theoretical density and EDX analysis are in accordance with the perovskite composition.

4. Conclusions

Doped-lanthanum chromite aqueous suspensions with solid concentrations ranging from 8 to 17.5 vol.% have been prepared and characterised through rheological measurements performed at different dispersing conditions. The most suitable rheological properties are obtained dispersing with both polyacrylic acid and tetramethylammonium hydroxide to promote electrosteric stabilization and basic pH to align the polymer chains. The best results were obtained for relative contents of 3 wt.% of PAA and 1 wt.% of TMAH after 24 h of ball milling.

The green density values (~30% TD) lead to sintered materials with relatively high density, although the microstructures show some inter and intragranular remaining porosity. However, considering that there are no studies dealing with the processing of this material using aqueous suspensions, the presented results are very promising for the manufacture of the interconnectors.

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