Surface behaviour and stability of strontium and cobalt doped-lanthanum chromite powders in water

Luiz Fernando Grespan Setz [a,*], Sonia Regina Homem de Mello-Castanho [1], María Teresa Colomer [b,2], Rodrigo Moreno [b,2]

[a] Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN, Av. Lineu Prestes 2242, Cidade Universitária, CEP: 05508-000, São Paulo, SP Brazil
[b] Instituto de Cerámica y Vidrio, ICV/CSIC, C/Kelsen, 5 Madrid, E-28049, Spain

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ABSTRACT

In this paper, the surface behaviour and stability in water of a powder with the composition $La_{0.8}Sr_{0.2}Cr_{0.92}Co_{0.08}O_3$ prepared by combustion synthesis were studied. The isoelectric point of as-prepared suspensions occurs at pH near 8, while the maximum zeta potentials of 40 to 50 mV are reached at pH 3, but suspensions are not stable as the pH tends to move towards the isoelectric point. Solubility of ions occurs at acidic pH, although chromium and strontium are detected at basic pH, also. If the pH of the suspensions is periodically readjusted, the highest solubility is reached at very acidic conditions and only chromium is detected at basic pH. The effect of 1 wt.% of an anionic polyelectrolyte (ammonium polyacrylate, PAA) on suspension stability shifted down the isoelectric point to pH 6 and very high zeta potentials ($> |-50|$ mV) were attained at pH 9–10, where the moderate pH assures that the solubility is low.

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1. Introduction

The study of colloidal phenomena has led to important advances in many areas of technology, including paper coatings, paints, cosmetics, pharmaceuticals, polymers, food technology [1,2] as well as ceramic processing and powder metallurgy [3–5].

Colloidal processing has proved to be a useful way for manufacturing near-to-net shaped ceramic bodies with complex microstructure and improved reliability [3,6,7]. The surface behaviour of oxidic materials mainly depends on the pH and the concentration of electrolyte, including counterions that can be introduced as contamination, but dissolution in water is negligible. The surface chemistry of non oxides is more difficult to evaluate since not only oxidation phenomena but also dissolution can occur [5]. Other materials that exhibit a complex surface chemistry are the mixed oxides in which two or more cationic species are present each one being stable at different pH conditions. This is the case of suspensions that contain several oxides or complex substances such as superconductors, manganites, PLZT related materials, chromites, etc.

Doped-lanthanum chromites have been extensively studied as ceramic interconnects [8] or as coatings for metallic interconnects [9] for use in high temperature Solid Oxide Fuel Cells (SOFCs) because they

exhibit good mechanical and electrical properties as well as chemical stability at high temperatures in oxidizing and reducing atmospheres [10,11].

SOFC devices can be designed according to different geometries to produce a planar or a tubular configuration, but the manufacture of these complex structures often requires the use of colloidal processing techniques, which have received increased attention in the last years for obtaining complex parts with controlled microstructure and high reliability [12].

There is a broad body of work dealing with the processing of different parts of the SOFC by colloidal routes, mostly referred to the electrolyte layer or the electrodes. However, facing the manufacture of the stack, it is also necessary to study the colloidal behaviour of the other components of the stack to allow global integration. In this sense, there is very scarce work dealing with the processing and, in particular, with the colloidal behaviour of the interconnect material. Stakkestad et al. [13] studied the surface behaviour of lanthanum chromite powders doped with different cations, i.e., Ca in position A of the perovskite structure ABO_3, Ni and Zn in position B and Sr in position A combined with Ni, Cu or Mg in position B. They measured the zeta potential of the resulting aqueous suspensions and determined the IEP for the 20% Ca-doped $LaCrO_3$ at pH 5.6. Compounds doped with Ni or Zn gave higher isoelectric points (IEPs) of 7.6. Compounds co-doped with Sr and Ni, Cu or Mg led to lower IEPs of 3.7 to 4.1. The electrophoretic mobility for all doped chromites was maximum at pH 3.0 and decreased at lower pH 2.0 due to the higher dissolution of chromium at the surface [14] and to the increased ionic strength. Stakkestad and Bergflodt [15] studied the dispersion of Ca-doped $LaCrO_3$ powders in organic solvents. To study the dispersing

* Corresponding author. Tel.: +55 11 3133 9200; fax: +55 11 3133 9276.
E-mail addresses: lfsetz@yahoo.com.br (L.F. Grespan Setz), srmello@ipen.br (S.R.H. de Mello-Castanho), tcolomer@icv.csic.es (M.T. Colomer), rmoreno@icv.csic.es (R. Moreno).
[1] Tel.: +55 11 3133 9200; fax: +55 11 3133 9276.
[2] Tel.: +34 91 735 58 40; fax: +34 91 735 58 43.

mechanism, these authors studied also the effect of different types of deflocculants on the zeta potential of aqueous suspensions, namely a polyester/polyamine copolymer, a polymeric fatty ester and a polyvinyl alcohol. The corresponding IEPs changed from 5.6 for the pure compound to 7.5 for the first and to 3.5 for the second, whereas the last seemed not to adsorb.

Kaji and Sakamoto [16] studied the colloidal behaviour of aqueous suspensions of $La_{0.6}Sr_{0.4}CoO_3$, reporting the IEP at pH 5.6, similar to that described before for the chromite. The maximum values of zeta potential (i.e. maximum stability) were found to occur at pH 3.

The presence of several cations in these mixed oxides makes difficult the dispersion in water because of the solubility and the complex surface behaviour. This is the case of barium titanate and barium zirconate powders, which have a similar ABO_3 structure than lanthanum chromite. When immersed in water at acidic pH conditions a surface dissolution of Ba^{2+} ions occurs, and the particle surface becomes TiO_2-enriched (or ZrO_2-enriched). Therefore, it is recommended to work at high pH to reduce Ba^{2+} dissolution, which can lead to significant changes of the surface properties [17,18].

Chromium oxide compounds, as lanthanum chromite, generally have some solubility in aqueous media and the pH values determine the formed species [19]. Cr(VI) was reported to be mainly in the form of H_2CrO_4 at pH < 1.0, as $HCrO_4^-$ at pH 1.0–6.0, and as CrO_4^{2-} at pH > 7.0 [20]. The minimum solubility occurs at the point of zero charge [21].

Considering the few works appeared in the literature much more work is still needed to control the surface behaviour and to reach the best dispersing conditions of these materials.

The aim of the present work was to study the surface behaviour and stability in water of a powder with the composition $La_{0.8}Sr_{0.2-}Cr_{0.92}Co_{0.08}O_3$ prepared by combustion synthesis from the corresponding metal nitrates, as reported in a previous work [22].

2. Experimental

The precursors used for the synthesis of doped lanthanum chromite were the following: 1) chromium (III) nitrate nonahydrated, $Cr(NO_3)_3 \cdot 9H_2O$ (99%, Aldrich, Germany); 2) lanthanum (III) nitrate hexahydrated, $La(NO_3)_3 \cdot 6H_2O$ (99.99%, Aldrich, Germany); 3) strontium nitrate, $Sr(NO_3)_2$ (99%, Aldrich, Germany; and 4) cobalt (II) nitrate hexahydrated, $Co(NO_3)_2 \cdot 6H_2O$ (98%, Vetec, Brazil). Urea $(CO(NH_2)_2$, Nuclear, Brazil) was used as a fuel. The nitrates were stoichiometrically mixed in deionised water until complete solubility in order to obtain the composition $La_{0.80}Sr_{0.20}Cr_{0.92}Co_{0.08}O_3$ [22].

The synthesised powders were attrition milled in ethanol (absolute ethanol, Casa Americana, Brazil) for 2 h using silicon nitride balls.
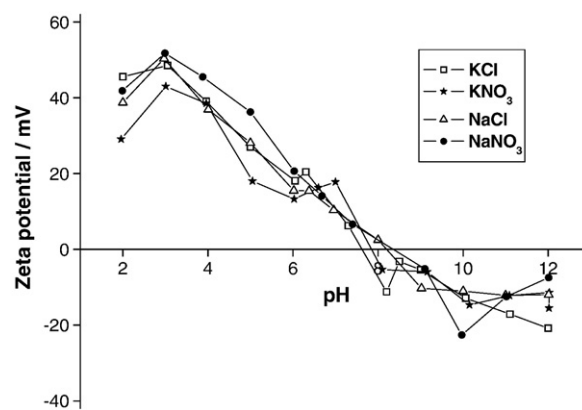

Fig. 1. Particle size distribution of the doped lanthanum chromite powder after 2 h ball milling.

Fig. 2. Variation of ζ-potential with pH for fresh suspensions of strontium and cobalt doped-LaCrO₃ powder in various electrolyte types at a concentration of 10^{-3} M.

The powder was then dried in an oven at 60 °C. The specific surface area of the strontium and cobalt doped-LaCrO₃ powder after milling was 10.2 m² g⁻¹. The particle size distribution, measured by laser diffraction (Mastersizer S, Malvern, UK) is shown in Fig. 1, which has an average particle diameter of ∼2 µm, although a small fraction of unmilled particles still remains. The details of the synthesis through a combustion method and the physico-chemical characterisation of the synthesised powder and its crystallographic analysis were reported in previous work [23].

The stability of the milled powders was studied as a function of pH through zeta potential measurements, which were performed using Phase Analysis Light Scattering (ZetaPALS, Brookhaven Instruments Corporation, USA) and using also the laser Doppler velocimetry technique (Zetasizer Nano-ZS, Malvern Instruments, UK). The samples were prepared to a solid content of 0.065 g l⁻¹ in deionised water produced by a Milli-Q Plus pure water generating system from Millipore (USA). The ionic strength was fixed at 10⁻³ M using KCl, KNO₃, NaCl and NaNO₃ (analytical degree, Casa Americana, Brazil) as indifferent electrolytes. The pH adjustments were made by adding appropriate amounts of HCl and KOH. Prior to measurements, all suspensions were homogenised with an ultrasounds probe (dr. Hielscher 400US, Germany) for 1 min. The polyelectrolyte Duramax D3005 (ammonium salt of a polyacrylic acid (PAA, Rohm and Haas Co., PA, USA) was used as a deflocculant. The stability of suspensions dispersed with polyelectrolyte was studied through ζ-potential measurements. The stability against time was studied for a total time of 7 days for suspensions with and without polyelectrolyte in terms of zeta potential. Three measurements were performed for each value, all three matching very accurately. However, there is a number of error sources that cannot be perfectly controlled, such as ageing, temperature, pH, etc, so that it is widely accepted a typical error in zeta potential measurements of about 5–10%.

To study the dissolution behaviour of the lanthanum chromite powder, suspensions were prepared in deionised water to a concentration of 1 wt.%. These experiments were performed for a total time of 1 week; meanwhile the pH and the stability were measured. Two sets of experiments were performed: 1) using suspensions in which the pH was only adjusted at the beginning of the study and the variation with time was then registered, and 2) by adjusting the pH two times per day to maintain fixed values ranging from 1 to 12 with HCl and KOH. After the period of 7 days, the suspensions were centrifuged and the liquid-phase was analyzed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Iris Advantage, Thermo Jarrel-Ash, USA) in order to determine the concentration of soluble species. The error of the ICP-OES measurements was below 1% of measured value. The average of three measurements is always given.

In general, dilute suspensions were prepared by mechanical mixing with magnetic stirre for 15 min. A series of tests was performed to study the effect of an ultrasounds probe on the stability of the suspensions.
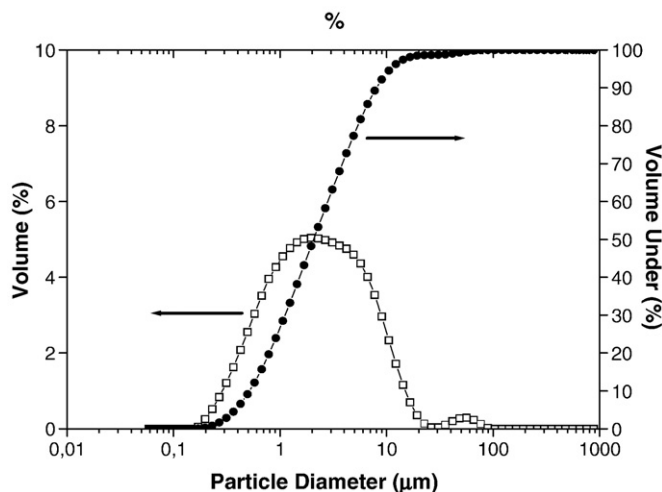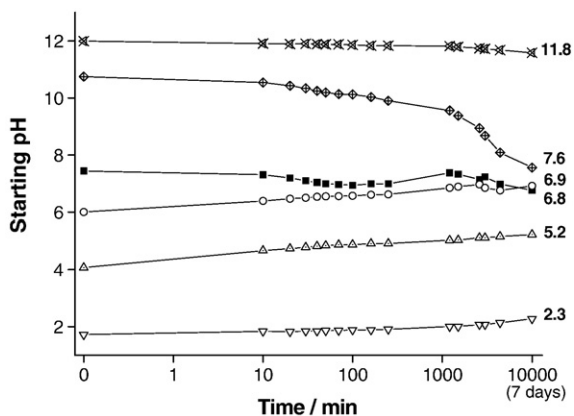
Fig. 3. Evolution of pH vs time for strontium and cobalt doped-LaCrO₃ suspensions prepared at different starting pH. The final pH is indicated in the right column.

This was done by measuring the zeta potentials for fresh and aged suspensions prepared with PAA.

3. Results and discussion

3.1. Suspensions without pH readjustment

The stability of the strontium and cobalt doped-LaCrO₃ aqueous suspensions as a function of pH was studied by measuring the zeta potentials of the suspensions just after preparation and every day later until 1 week. Fig. 2 shows the evolution of zeta potential versus pH for fresh suspensions prepared in four indifferent electrolytes at a concentration of 10^{-3} M. There are no significant variations among the electrolytes, thus meaning that there is no specific adsorption in any case. The isoelectric point occurs at pH by 8, significantly higher than the values 5.6–7.6 reported elsewhere [13] for doped-LaCrO₃ powders, as reported above. It is observed that the maximum zeta potentials are reached at pH 3, with values ranging from 40 to 50 mV. At basic pH values the zeta potential is always lower than in the acidic region, with maximum absolute values of 20–25 mV. The low zeta potentials at basic pH are in good agreement with the behaviour of La₀.₆Sr₀.₄CoO₃ reported by Kaji and Sakamoto [16].

The as-prepared suspensions are not stable against time as the pH tends to move toward the isoelectric point. Fig. 3 shows the free evolution of pH vs time for suspensions prepared in a broad range of starting values. At extreme pH conditions the suspensions maintain stable, and near the isoelectric point they have low stability and tend to flocculate. This is expected because of the acid–base reactions
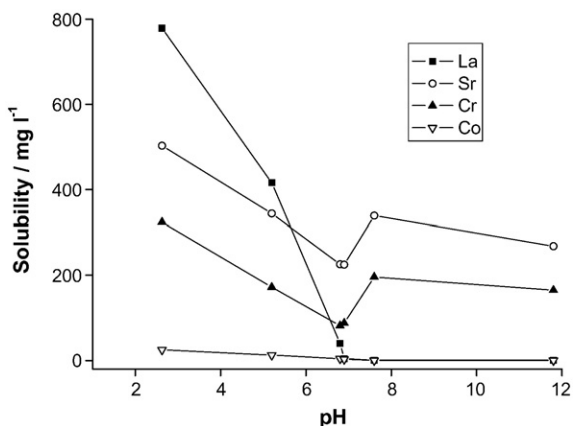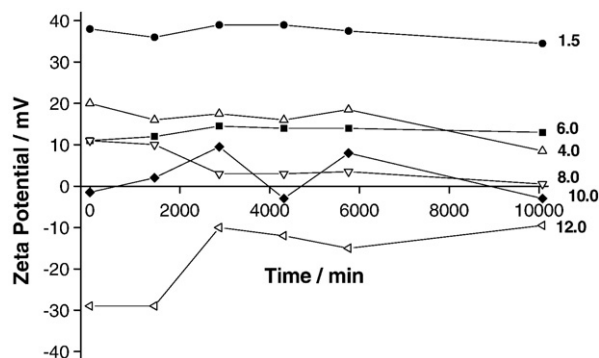

Fig. 5. Evolution of ζ-potential vs time for strontium and cobalt doped-LaCrO₃ aqueous suspensions with continuous readjusting of pH. pH values at the right are the final ones.

occurring at the particle surfaces were a small change of concentration of acid or base leads to a sharp pH variation. The largest variations occur for a starting pH of near 10.5 that moves to 7.6, whereas that at pH 4 shifts to pH 5.2. This suggests that acidic suspensions are more stable than basic ones, in good agreement with the zeta potential curves shown in Fig. 2.

To confirm the stability against pH the suspensions aged for 1 week were centrifuged and the supernatant was analyzed by ICP. The results of the chemical analysis are shown in Fig. 4 as a function of the final pH. The results are not in agreement with previous measurements. The lowest solubility seems to occur for final pH of 7–8, near the isoelectric point, which correspond to starting pH>10. According to these curves, the largest solubility is reached at pH 3, where the concentration of Sr and La is high. This is in opposition to the maximum zeta potential values measured at this pH and the relatively good stability of pH with time. The only possibility to explain the stability of these suspensions containing significant concentrations of multivalent cations is that they could form complexes and do not remain free in the dispersing medium. However, since the starting pH does not maintain constant it is not possible to know when the cations are liberated into the medium. Thus, to control the solubility and the stability it is necessary to avoid pH variations.

3.2. Suspensions with continuous pH readjustment

The evolution of ζ-potential during ageing is plotted in Fig. 5. Acidic suspensions maintain a constant zeta potential during all the testing time. Suspensions with pH 8 and 10 are very unstable and the zeta potentials are near to zero and the sign changes, since they are near to the isoelectric point. The sign changes when pH is readjusted until the suspension destabilises again. The most basic suspension, at
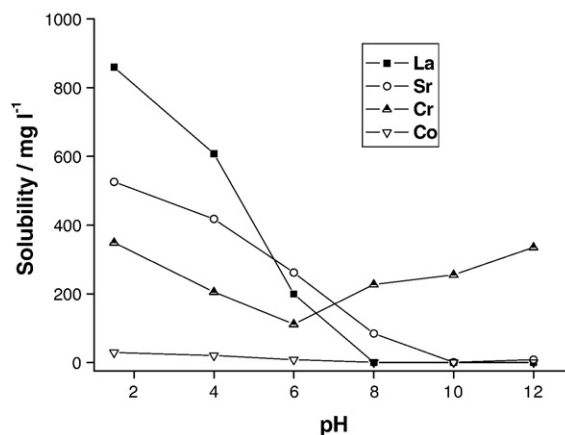

Fig. 4. Concentration of dissolved species for strontium and cobalt doped-lanthanum chromite suspension without pH readjustment.

Fig. 6. Concentration of dissolved species for doped-lanthanum chromite suspension with periodical pH readjustment.
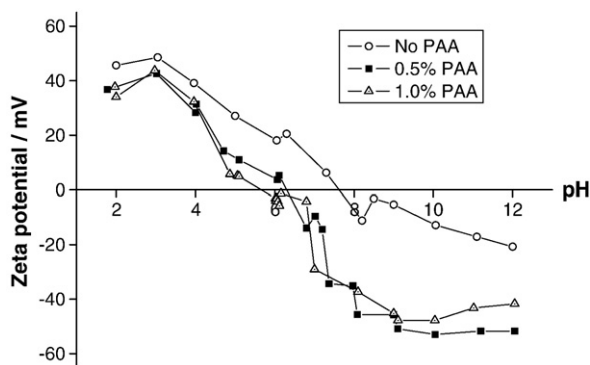
Fig. 7. Variation of ζ-potential with pH for strontium and cobalt doped-LaCrO$_3$ powder with 0.5 and 1.0 wt.% of polyacrylic-based polyelectrolyte (PAA) and without PAA.

pH 12 is the only one where the zeta potential (e.g. the stability) reduces from −30 to −10 mV and maintains at that low value. There is no reason to explain why the zeta potentials at pH 1.5 are higher to that at pH 4 or pH 6. Thus, it could be thought that higher solubility occurs at higher pH.

The solubility studies were also performed for the set of suspensions with continuous pH control. In this case the pH is forced to maintain constant and some relationship between pH and solubility can be obtained. The results are shown in Fig. 6. In this case the highest solubility is reached at very acidic conditions and solubility decreases with increasing pH. At basic pH only Cr is detected that can be as CrO$_4^{2-}$ [20]. At acidic pH the order of concentration of elements in the medium is [La]>[Sr]>[Cr]>[Co], the last one being negligible as compared to the others. This dissolution effect is only observed after a relatively large equilibrium time (from several hours to 1 day). According to this plot the processing of this powder should be done under basic pH conditions since at acidic pH the concentration of different species of the cations in the medium is very large. Considering the low stability at basic pH even for fresh suspensions (Fig. 2) the further step was to study the effect of an anionic polyelectrolyte capable to improve the suspension stability at slightly basic pH.

3.3. Suspensions dispersed with polyelectrolyte

Fig. 7 shows the zeta potentials measured for suspensions without PAA and with 0.5 and 1.0 wt.% PAA as a function of pH. It is observed that the isoelectric point shifts down by 2 units of pH, toward pH 6, which is the expected behaviour when an anionic polyelectrolyte is adsorbed at the particle surface. However, once the surface is covered by the polyelectrolyte there are no differences for the two studied concentrations. Similar results were obtained for Ca-doped-LaCrO$_3$, whose isoelectric point shifted from 5.6 to 3.3 when adding a polymeric fatty ester as dispersant [15].
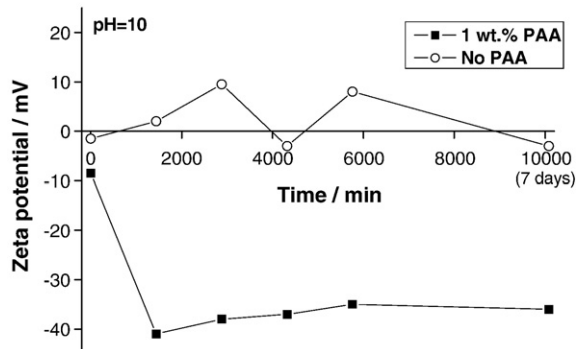

Fig. 8. Evolution of ζ-potential with time for suspensions prepared at pH 10 with 1 wt.% and without PAA.
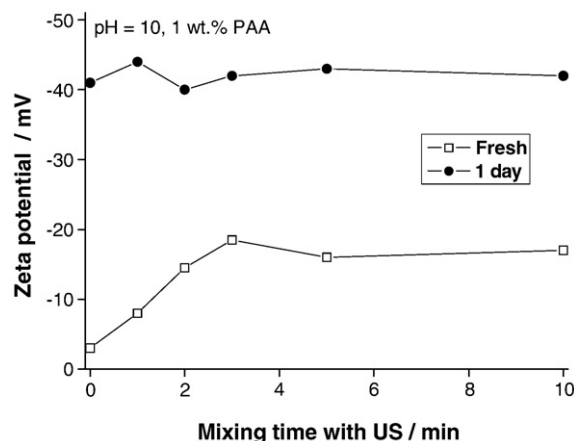

Fig. 9. Effect of the ultrasound's (US) mixing time on the zeta potential of fresh and one day aged suspensions prepared at pH 10 with 1 wt.% PAA.

The values of zeta potential in the acidic region maintain similar to those obtained when no PAA is added. However, the alkaline region changes dramatically. With PAA very high zeta potentials (by −50 mV) are obtained at quite soft conditions (pH 8–9), which is a clear improvement of the processing conditions.

A further step is to evaluate whether the suspensions dispersed with PAA maintain stability against time or not. The evolution of ζ-potential values with time, for suspensions prepared at pH=10 are presented in Fig. 8. The stability of the corresponding PAA-free suspension is also plotted for comparison. In opposition with the latest, which is highly unstable for all the testing time, the suspension with PAA shows a great stability for all the time. The fact that stability is significantly lower for the fresh suspension suggests that mixing/equilibrium time was not sufficient at time zero. It must be remembered that suspensions were prepared by simple magnetic stirring for 15 min, and longer times are probably needed to reach a surface equilibrium. To overcome this problem a new set of suspensions were prepared with 1 wt.% PAA at pH 10 by using an ultrasound (US) probe and different times of mixing. The effect of US time on the zeta potential of the suspensions is plotted in Fig. 9. Measurements were performed using the fresh suspensions and those left to equilibrate for one day. From this plot the following conclusions can be drawn: 1) the stability of fresh suspensions increases as the time of US mixing increases, up to 3 min, and then maintains unchanged for longer US times; 2) all suspensions left under agitation one day after preparation display a similar zeta potential that is about −40 mV, at least twice that of the fresh suspensions, thus demonstrating that surface equilibrium
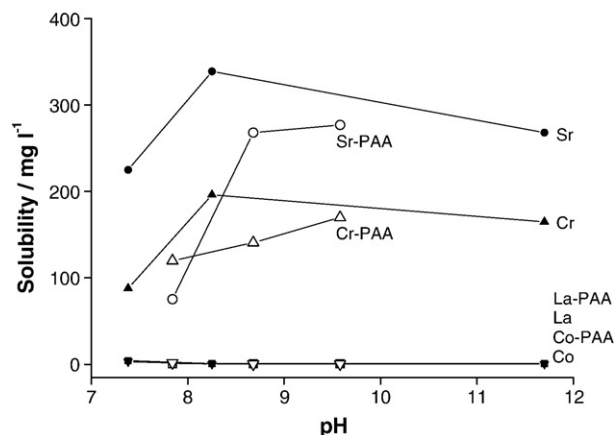

Fig. 10. Concentration of dissolved species for doped-lanthanum chromite suspension with and without PAA addition, without pH readjustment.
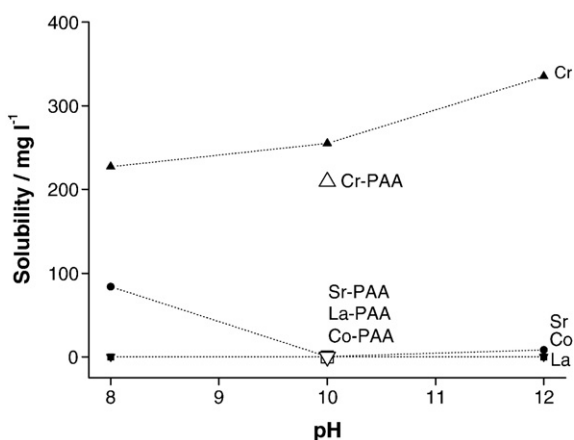
Fig. 11. Concentration of dissolved species for strontium and cobalt doped-lanthanum chromite suspension with and without PAA addition, with continuous pH readjustment.

has been reached that ensures stability. This means that the equilibrium time is the critical factor to obtain stable suspensions while US mixing seems not to have influence. From these results stable suspensions were obtained with 1 wt.% PAA and pH 10.

Fig. 10 shows the concentration of dissolved species for doped-lanthanum chromite suspensions prepared with and without PAA at different pH adjusted in the process beginning. It can be seen that there are neither Co nor La in solution at the considered basic pH interval. Contrarily, Cr and Sr are still present in the basic region, although their concentrations seem to be slightly lower in the PAA containing suspensions. These results could be influenced by the free change of pH during the testing time.

According to the chemical analyses reported in Fig. 11, when the pH is readjusted during the test, the absence of Sr species and an increase in the Cr species concentration could play a role in the adsorption and interaction of the PAA. This paper's focus does not include this but it may be interesting for future research.

Considering that under acidic conditions there were various ions in play, the best conditions for aqueous processing of strontium and cobalt doped-LaCrO$_3$ are moderately basic pH in the presence of adsorbed polyelectrolyte. The polyelectrolyte strongly increases the zeta potential (that is, the stability) while the moderate pH assures that the solubility is low. These would be the basis for the preparation of concentrated suspensions and their further shape forming into bulk bodies or laminates.

4. Conclusions

In this paper, the colloidal behaviour of aqueous suspensions of strontium and cobalt doped-lanthanum chromite is investigated. The isoelectric point of as-prepared suspensions occurs at pH 8, while the maximum zeta potentials are reached at pH 3, with values ranging from 40 to 50 mV. However, the as-prepared suspensions are not stable against time as the pH tends to move towards the isoelectric point. Solubility of ions occurs and according to chemical analysis the largest solubility is reached at pH 3 the same pH than that of the maximum zeta potential. In suspensions with continuous pH readjustment, the highest solubility is reached at very acidic conditions and chromium is also detected at basic pH. The addition of an anionic polyelectrolyte (PAA) capable to improve the suspension stability at slightly basic pH is also studied. Its addition shifts down the isoelectric point toward pH 6 and very high potentials (by −50 mV) are attained at pH 8–9, which are the best pH conditions for aqueous processing of strontium and cobalt doped-LaCrO$_3$ dispersed with 1 wt.% PAA. The PAA increases the zeta potential from about −10 to about −50 mV at pH 8–9, which is low enough to assure a low solubility <10 mg/l, except for Cr, with solubility higher than 300 mg/l.

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