

Determining the Lanthanum Chromite Zeta Potential in Aqueous Media

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Abstract: Lanthanum Chromite may be used as interconnect for SOFC's applications due to its particular intrinsic properties as stability in both oxidant and reducing environments and electrical conductivity. However to manufacture these devices that generally present complex shapes as grooved plates and fine pipes, they are necessary the use of the conformation techniques such as screen printing, slip casting, tape casting, extrusion moulding, etc. that are related with colloid processing. Independent of the processing techniques chosen the control of the suspension conditions is important to obtain reproducibility and homogeneous products as final result. In this sense, all contribution to understand the behaviour of the LaCrO_3 fine particles in liquid suspension as the surface state using the Zeta's Potential concepts may supply information by the forecast of the behaviour during the shaped processing. The aqueous suspensions behaviour was studied utilizing doped lanthanum chromite powders, attained by combustion synthesis. The electrophoretic mobility measurements of particles in suspension, prepared with the different conditioned powders were made. The electrolyte compositions as function of the pH varying from 2 to 12 were tested. The Zeta potentials and the stability conditions for stable suspensions prepared were determined. The viscosity curves are also appraised.

Introduction

The lanthanum chromite (LaCrO_3) is one of the materials that have received particular attention for applications in SOFC. It is due to its present unique properties, such as good chemical compatibility with other components, good electric conductivity (p-type) and stability during the fuel cell operation, that are: to resist both the reducing conditions at the anode side and the oxidant conditions of the cathode [1-3]. These characteristics make it especially indicated to be used as membranes between the electrodes [4].

Many are the geometries suggested for solid oxide fuel cell, however the fine plates and pipes configurations have been received more attention in last years. For these and other more complex configurations the use of colloidal processing techniques as slip casting, tape casting, screen print, extrusion moulding, have been receiving special attention to attain highly efficient for obtaining complex parts with controlled microstructure and high reliability.

Lanthanum chromite colloidal suspensions have been studied normally using non-aqueous media suspension [5-10], This work shows same results from the Lanthanum Chromite aqueous suspensions.

Experimental Procedure

The Sr,Co-doped lanthanum chromite, used in this work were attained in our laboratories using combustion synthesis route from commercial nitrates of the respective metals (Aldrich, PA) and Urea as fuel. The prepared base compositions were $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.92}\text{Co}_{0.08}\text{O}_3$. To verify the particle size influence on the stability of the suspension, samples of the lanthanum chromite powders were prepared by milling process using different time period up to 5 hours. Tetramethylammonium hydroxide (TMAH, Rohm and Haas Comp.) and nitrate acid solutions, and Duramax D3005 as dispersant, to preparing the suspensions were used.

The doped-LaCrO₃ powders were characterized by surface specific area determinations (CG Instruments, BR) and particle size distribution (90Plus, Brookhaven Instruments Corp., US).

Electrophoretic measurements of doped-LaCrO₃ powder were made using the Zetapals equipment (Brookhaven Instruments Corp., US). Measurements were performed using aqueous solution with 6.5×10^{-3} g/l doped-LaCrO₃ powders. The ionic strength was maintained constant at 10^{-3} M using KCl and NaNO₃ as electrolyte. HCl and NaOH solutions to shift the pH from 2 to 12 were used.

The suspensions were prepared in aqueous media (milli-Q water) containing the desired amounts of polyelectrolyte. The suspensions were stirred for 20h. before measurements to establish an equilibrium dispersion system. Suspension rheological characteristics were determined using a reometer (ThermoHaake RS600, Gm) and aqueous slips with 50 wt.% solids content (13 vol.%). The measurements were performed using a double cone and plate system, at a constant temperature of 22°C.

Results and Discussion

Fig. 1 shows the doped-LaCrO₃ specific surface area values (SSA) measured, after milling. As observed the SSA values remain practically constant after 2 hours milling. These values tend to increase for steps higher than 4 hours milling. However for long milling periods the contamination by erosion from media mill may occur. For this study 2 hours were chosen that results powders with $10.2 \text{ m}^2/\text{g}$.

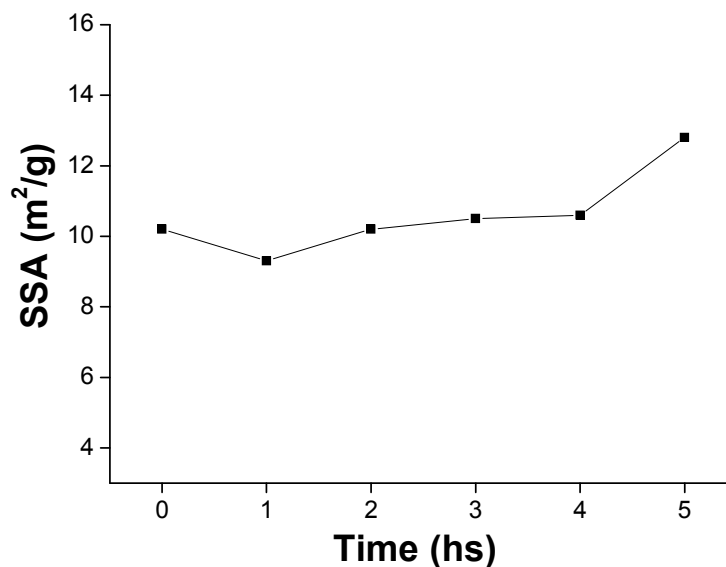


Fig. 1. Specific surface area values in function of the milling time from doped-LaCrO₃ powders samples.

The doped-LaCrO₃ particles size in the diverse times of milling, is showed in Fig. 2. In this figure is possible to observe that, increasing the milling time, the average particles size, being to nanometric dimensions.

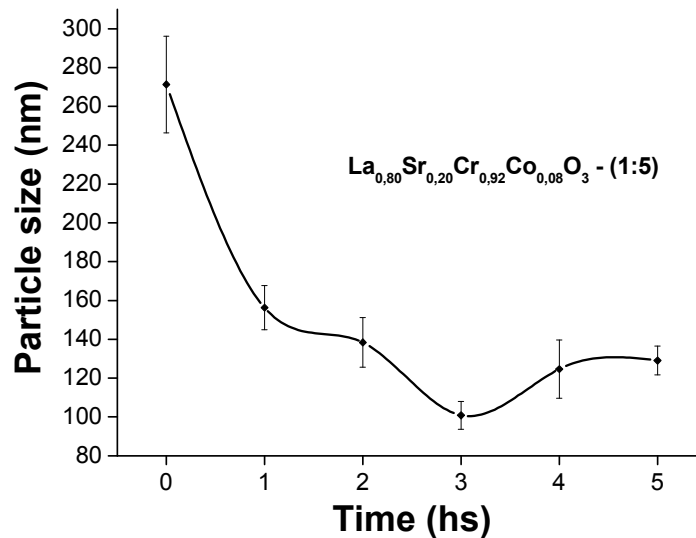


Fig. 2. Doped-LaCrO₃ size particle measured in function of the milling time.

Doped-LaCrO₃ suspension stability, from different size particles specimens, as a function of pH were evaluated by ζ -potential determinations. Fig. 3 shows the ζ -potential curves by using NaNO₃ solutions as electrolyte media. These figure shows that the isoelectric point (IEP) occurs at pH ~8.5. The largest values of ζ -potential and thus, maximum stability, occur at acid pH values; a value of ζ ~27mV is obtained at pH below at 5.0. The IEP with this electrolyte is keeping at the different sizes particles and the ζ -potential values are increased when the particle size is reduced. The alkaline pH values for suspension stability are reduced (< 20mV).

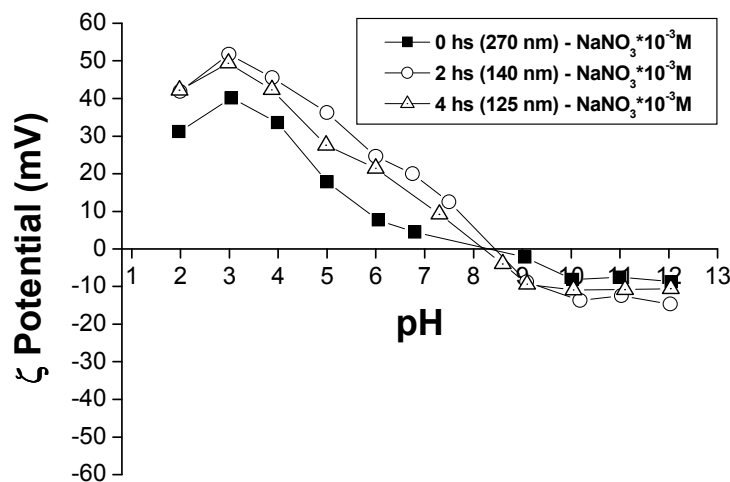


Fig. 3. Variation of ζ -potential with pH suspensions from different conditioned powders.

Fig.4 shows the ζ -potential variation with pH using KCl as electrolyte media. It is possible to observe the similar ζ -potential behaviour for NaNO₃ electrolyte. The IEP is next the previous electrolyte used and occurs at pH ~8.0. The ζ -potential values at acid conditions is the same with NaNO₃ electrolyte, the largest values are obtained at pH below 5.0 (~27 mV).

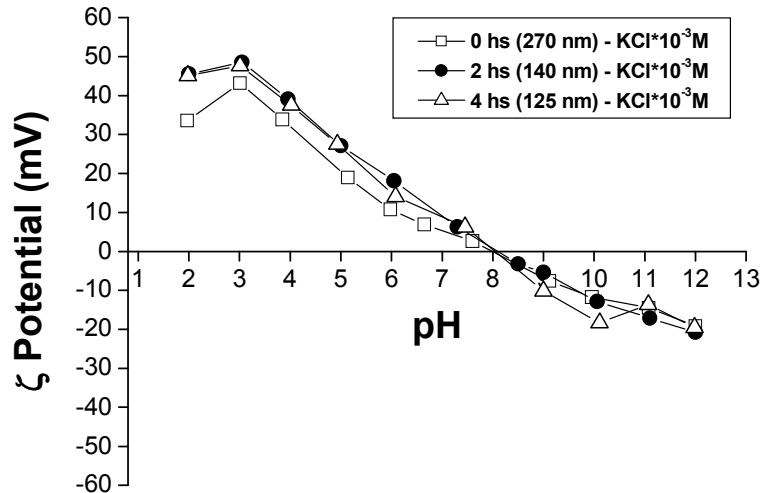


Fig. 4. ζ -potential variation as pH for different conditioned powders using KCl as indifferent electrolyte.

Ammonium salt of polyacrylic acid (PAA) is a very effective dispersant for the suspension stabilization [13-16]. This polyelectrolyte is formed by monomer units as carboxyl function whose dissociation degree depends on the pH of the solution [17]. Under alkaline conditions, a dissociation degree is reached that enhances adsorption of anionic polymer chains onto the particles surface, thus allowing an efficient dispersion through an electrosteric mechanism [18]. The combined effect of polyelectrolyte and pH was studied by ζ -potential determinations.

The variation of ζ -potential as function of pH for doped-LaCrO₃ suspension (0.065 wt.%) containing 0.5 and 1.0 wt.% of polyelectrolyte compared with the suspension without polyelectrolyte is showed in Fig. 5. The doped-LaCrO₃ IEP is shifted until pH ~5.5 when the polyelectrolyte concentration is increased, as expected when anionic polyelectrolytes are adsorbed on the particle surface. In the acid condition, values of ζ -potential remain high and similar to those obtained for the powder without dispersant until pH ~4.0. The ζ -potential in alkaline condition are changed, the values now, is high enough to produce a stable suspension at pH above 8.0 (~35 mV).

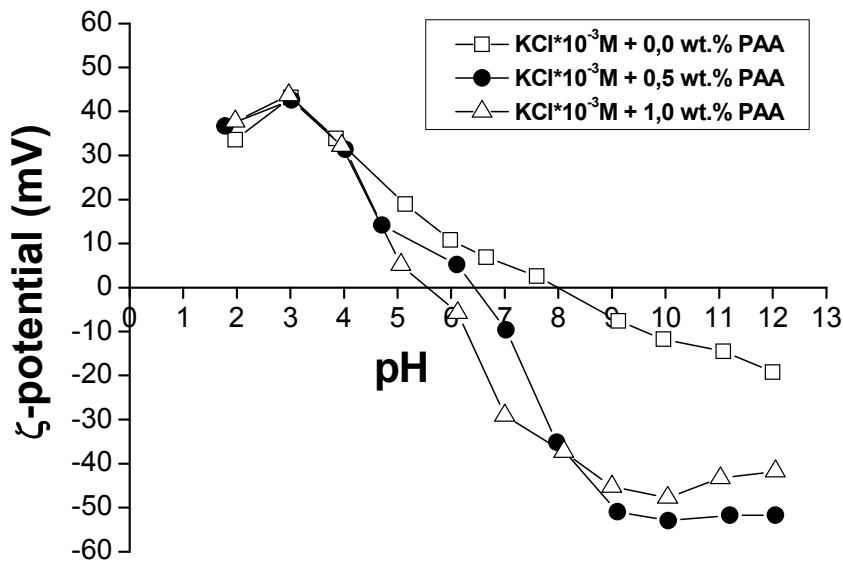


Fig. 5. Variation of ζ -potential with pH for the doped-LaCrO₃ with polyelectrolyte adds.

High solids content doped LaCrO₃ suspension, 50 wt.% (13 vol.%) have been successfully prepared using PAA (1 wt.%), TMAH (1 wt.%) and adequate amounts of ammonia for pH adjustment.

Fig. 7 shows the flux curve behaviour and viscosity variation for doped-LaCrO₃ suspensions with 45%wt solids, prepared with PAA (1 wt.%) and TMAH (1 wt.%). Same tixotropy with the shear rate increasing was observed for the shear rate up to 900 s⁻¹ revealed by the slight hysteresis with the shear stress decreasing. Viscosity curve shows that the kinetic viscosity tends to decrease values with increasing shear rate. The viscosity at 500s⁻¹ determined is 100 mPa.s.

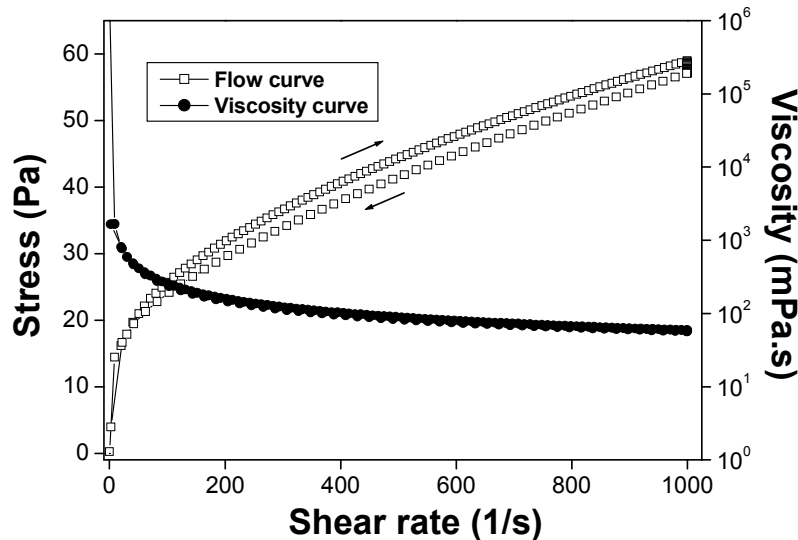


Fig. 6. Rheological curves of aqueous suspensions of lanthanum chromite (50 wt.%).

Conclusions

Lanthanum chromite aqueous suspension was studied using aqueous media through by ζ -potential and the rheological behaviour was determined. The isoelectric point of doped lanthanum chromite synthesized from combustion reaction route has been identified to occur at pH \sim 8.0 and decrease until pH de pH \sim 5,5 when the polyelectrolyte is added.

Adequate ζ -potential values to produce a stable suspension was obtained at pH below 5.0 and when polyelectrolyte was added, the suspension stability may be prepared at pH above 8.0.

The doped lanthanum chromite aqueous suspension stability using concentrated suspension (50 wt.%, i.e. 13 vol.%) using the polyelectrolyte and TMAH, both with concentration of 1.0 wt.% were obtained.

The rheological curves shows flux behaviour and viscosities adequate during the shear.

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