Forming of cathodic ceramic film using airbrush for application in high temperature solid oxide fuel cells

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Abstract. The high temperature solid oxide fuel cell (HTSOFC) can be manufactured in different configurations, which can to detach the planar and tubular. The HTSOFC are composed for four components that are cathode, electrolyte and anode for the formation of the unity cell; and interconnector, that establish connection these unity cells in series and parallel for bigger power generation. Different forming techniques are used for the manufacture of the components that need variable thicknesses for the forming ceramic films in the order of micrometers. In this work, the cathodic ceramic film of strontium-doped lanthanum manganite had been deposited on the electrolyte substrate of yttria-stabilized zirconia using the airbrush. In the forming ceramic film, the powder had been characterized by laser beam scattering granulometry and the suspension characterized by rheometry. The substrate and the ceramic film had been characterized by X-ray diffractometry and scanning electron microscopy. The conclusions of this work show that the airbrush allows flexibility in getting ceramic films with varied thicknesses with good adherence and low manufacture cost.

Introduction

The high temperature solid oxide fuel cells (HTSOFC) operate in the band of 800 to 1000 °C and its 4 components: cathode, anode, electrolyte and interconnector are constituted the base of ceramic oxide. Usually the ceramic composite strontium-doped lanthanum manganite ($La_{0.85}Sr_{0.15}MnO_3$ - LSM) is the cathode, the nickel/yttria-stabilized zirconia cermet ($ZrO_2/Y_2O_3/Ni$ - YSZ/Ni) is the anode, the yttria-stabilized zirconia (ZrO_2/Y_2O_3 - YSZ) is the electrolyte and the lanthanum chromite doped generally with strontium, chromium or cobalt ($LaCrO_3$ - LC) is the interconnector [1-3].

The electrode components (cathode and anode) must be porous for the diffusion of the oxidant and combustible gases. The electrolyte and interconnector, dense to occur the migration of oxygen ions and electrons, respectively. These components have different functions, presenting particular and specific properties for that the SOFC has a good functioning for the electric energy generation [1-4].

In the ceramic processing for manufacture of these components it is necessary to know which techniques are adjusted for application in the different configurations (monolithic, cells in series segmented, planar and tubular) of the cell unity, for the preparation of substrates and ceramic films with thicknesses usually in the band of 50 to 1000 μm and 5 to 250 μm, respectively [5-9].

For forming of cathodic ceramic films, the wet powder spraying technique uses the equipment airbrush, in which it is necessary to know the parameters (pressure, distance, type of nozzle, viscosity, solid concentration of the suspension and powder granulometric distribution) that affects the result for the formation of the layer on the substrate [8,10,11].

In the airbrush is fed a suspension composed of ceramic powders, solvent and additive, that are sprayed for the formation of the cathodic ceramic film on the electrolyte substrate. The layer thickness is controlled for the amount of the material sprayed with drying intermediate steps, preventing the layer breaking, without compromising the desired thickness final [8,10,11].

In this work, ceramic suspension was prepared for forming of cathodic ceramic film of strontium-doped lanthanum manganite on electrolyte substrate of yttria-stabilized zirconia. The LSM powders, contained in the suspension, they had been characterized by laser beam scattering granulometry, the ceramic suspension by rheometry, and the ceramic film and the electrolyte substrate by X-ray diffractometry and scanning electron microscopy.

Materials and Methods

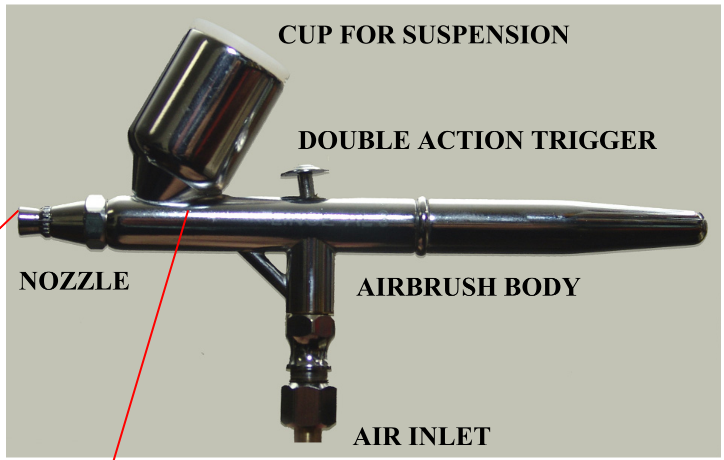
The electrolyte substrate was prepared with 8 mol% yttria-stabilized zirconia powders (Tosoh Corporation, Tokyo, Japan), uniaxially pressed, conformed in pellet, sintered at 1500 °C for 1 hour, getting dense, solid and mechanically resistant pellet, with dimension of approximately 11 mm of diameter and 0.7 mm of thickness. The surface of the sintered YSZ cylindrical pellet was sandpapered and washing with ethanol for surface cleanness. This superficial treatment in the substrate caused grooves, for a better adherence of the deposited layers for formation of the LSM cathodic ceramic films [12].

The suspension was prepared with LSM powders, synthesized by the citrate technique [13], ethanol (solvent) and ethylcellulose (binder). This organic suspension was fed to the equipment double action manual airbrush (Lince, model AL3), whose spraying is carried through with suspension feeding by gravity and air compressor (Schulz, model Twister). When air if mixes to the suspension is formed a unique and homogeneous spurt expelled by the airbrush nozzle as a mist that must be directed to the substrate to be sprayed [8,10-14].

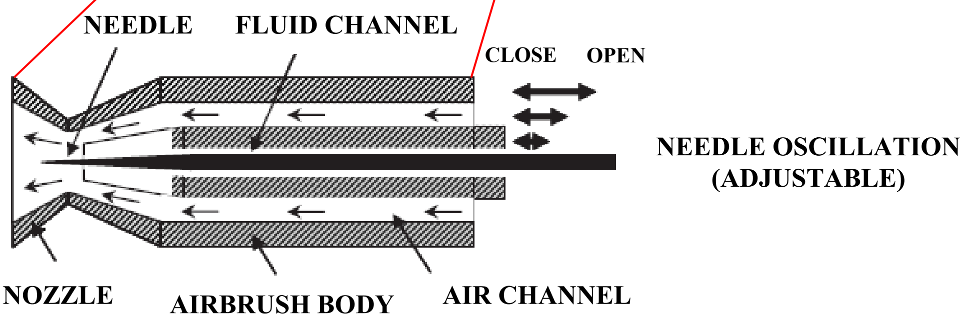
The suspension was sprayed passing for a nozzle with opening of diameter 2 mm with pressure of the compressed air of 100.000 Pa. In Figure 1 is presented the equipment airbrush with a cross section diagram.

During the suspension application on the substrate, the airbrush was horizontally located with the nozzle directed toward low in the distance between the nozzle and substrate of approximately 200 mm.

For the formation of the LSM ceramic film was established depositions in 4 different directions of the airbrush in relation to the plan (horizontal, vertical, right and left diagonal) with drying intermediate stages for to get the desired thickness in the band of micrometers. The conformed LSM cathodic ceramic film was submitted to the drying and sintering at temperature of 1200 °C for 2 hours [12].



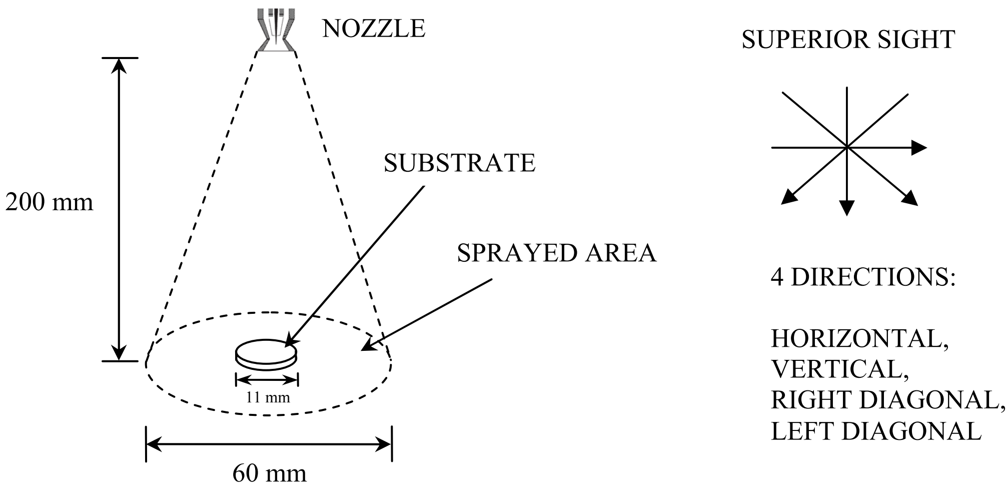
Source: Adapted http://commons.wikimedia.org/wiki/Category:Airbrush.



Source: Adapted ref. OISHI, N.; YOO, Y.; DAVIDSON, I., 2007.

Figure 1 - Equipment airbrush and cross section diagram.

In Figure 2 is presented an esquematization of the distance between the airbrush nozzle and the substrate and the different directions applied for the formation of each layer.



Source: Adapted ref. OISHI, N.; YOO, Y.; DAVIDSON, I., 2007.

Figure 2 – Esquematization of distance between tnozzle and substrate and the directions established for the formation of each layer.

The particle average diameter distribution of the LSM powders were obtained by laser beam scattering granulometry, in a potential zeta analyzer (Brookhaven, model ZetaPALS - Phase Analysis Light Scattering), using software Mas Option/ZetaPlus Particle Sizing.

The rheological behavior study of the organic suspension it was possible by rheometry (HAAKE, model RS600), obtaining resulted of flow and viscosity curves.

The LSM ceramic film and the YSZ electrolyte substrate were characterized by X-ray diffractometry -XRD (Philips, model XL30) and scanning electron microscopy - SEM (Rigaku, model Multiflex), for identification of phases and observation of the morphology and thickness of the cathodic ceramic film.

Results and Discussion

The LSM powders they had presented particle average diameter of 0.463 ± 0,007 µm, making possible the preparation of the organic suspension and the spraying for the forming of cathodic ceramic film.

The flow and viscosity curves for LSM organic suspension contend 10 wt% solid concentration with 10 wt% ethylcellulose binder are presented in Figure 3. In Figure 3a, the organic suspension behavior presents decrease in the viscosity values to the measure that increase the rate shear. In Figure 3b, the curve presents a pseudoplastic rheological behavior, that it's characterized for reduction of the fluid viscosity to the measure that if increases the shear rate and/or stress of the applied [15,16].

The LSM organic suspension is adjusted to be used with the airbrush by wet powder spraying technique, therefore it's advisable to use lesser viscosity that 10 mPa.s to the high shear rate, indicated for ceramic materials used by this technique [8].

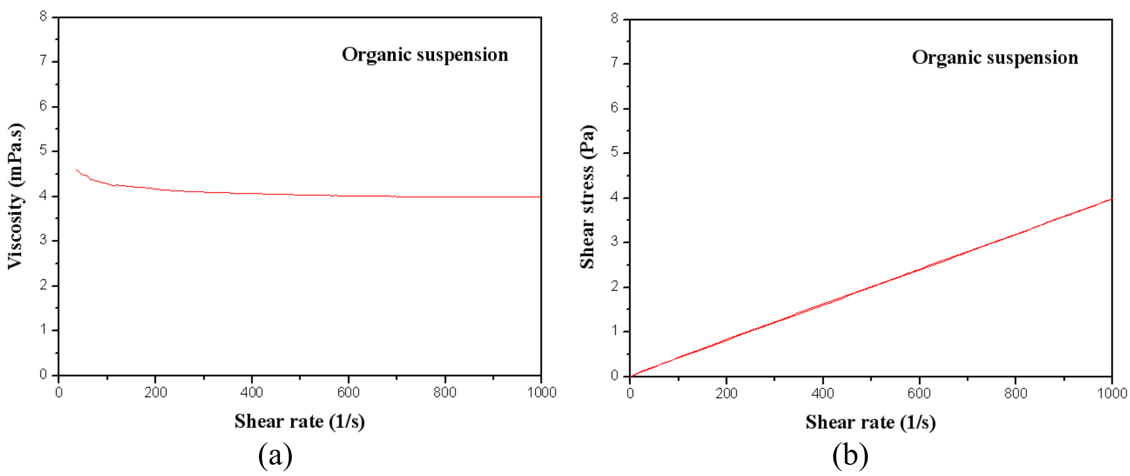
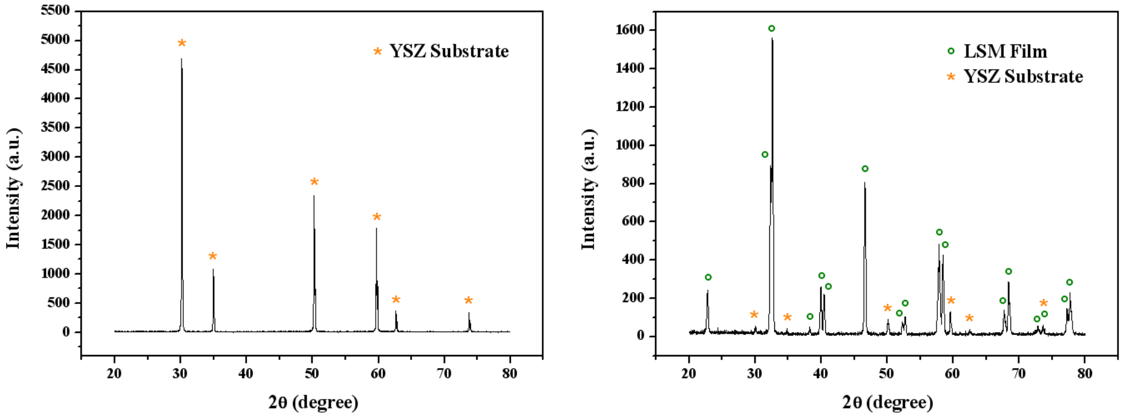


Figure 3 – Flow (a) and viscosity (b) curves of the LSM organic suspension.

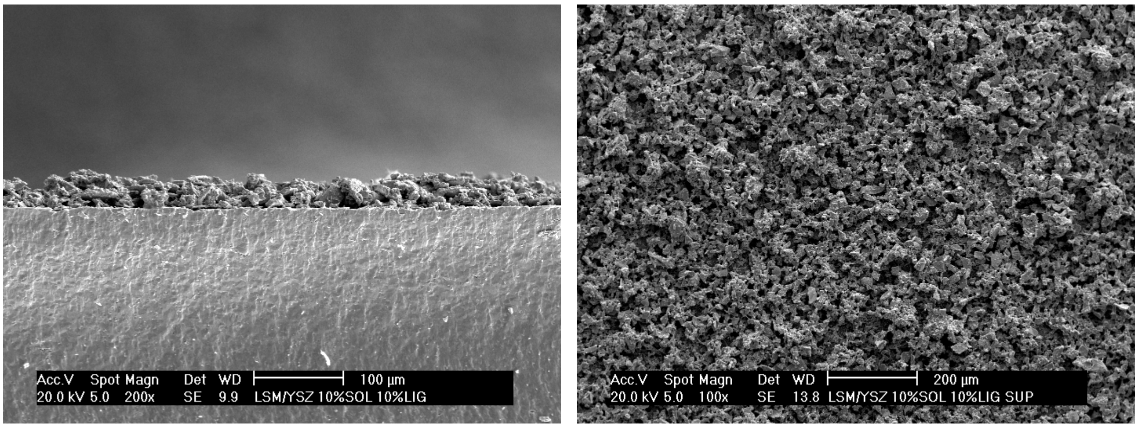
The X-ray diffractograms of the YSZ electrolyte substrate and the LSM ceramic film are presented in Figure 4. In Figure 4a is identified the presence of YSZ single phase of cubic crystalline structure (PDF Nº 81-1551) and in Figure 4b, the presence of LSM phase of hexagonal crystalline structure (PDF Nº 89-648) confirmed for LSM film. The YSZ phase in the LSM film if must to the YSZ substrate, therefore the LSM film is little thick, also analyzing the substrate.



(a) (b)

Figure 4 - Diffractograms of the YSZ electrolyte substrate (a) and of the LSM ceramic film (b).

The micrographs obtained by SEM show the fractured and sintered cross section of the LSM ceramic film on the YSZ electrolyte substrate observed in Figure 5a and the cathodic ceramic film surface is observed in Figure 5b.



(a) (b)

Figure 5 - Micrographs of the cross section of the LSM ceramic film on the YSZ electrolyte substrate (a) and cathodic ceramic film surface (b).

The LSM ceramic film presented thickness of approximately 30 µm with deposition of 15 layers with drying intermediate stages of 30 seconds in air, obtained the final desired thickness observed in Figure 5a [12].

In Figure 5b is observed that the YSZ electrolyte substrate is dense and the LSM ceramic film is porous, presenting good adherence between the cathodic ceramic film and the electrolyte substrate.

Conclusions

The preparation of the suspension contend 10 wt% LSM solid concentration, 10 wt% ethylcellulose binder and ethanol solvent was adjusted for the spraying with airbrush, equipment used by wet powder spraying forming technique.

The suspension viscosity presented value of 4 mPa.s for high shear rate, minor that 10 mPa.s, indicated for ceramic materials used by this forming technique. The suspension rheological behavior is pseudoplastic, considered interesting for the use of the airbrush, therefore the high shear rate, the viscosity diminishes, preventing the clogging during the spraying.

The forming of cathodic ceramic film on the electrolyte substrate using airbrush was possible, obtained film with thickness of approximately 30 μm, as observed by SEM and confirmed to the presence of LSM phase of hexagonal crystalline structure identified by XRD.

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