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POROUS $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ – BASED CATHODE MATERIALS FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS, DEPOSITED BY SCREEN-PRINTING METHOD

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In this paper, are presented our results on the deposition of porous $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (LSFC) based-cathode thick films for intermediate temperature solid oxide fuel cells (IT-SOFCs) by a simple and efficient method, the screen-printing technique. LSFC single-phase powder with perovskite structure and rhombohedral symmetry has been obtained by citrate-EDTA method. LSFC and LSFC-based composite (containing 80% LSFC and 20% $Ce_{0.8}Gd_{0.2}O_{2-\delta}$) powders were screen-printing deposited as layers on $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CG20) electrolyte ceramic bodies using polyethyleneglycol as binder. LSFC and LSFC-based composite layers were investigated by X-ray diffraction and scanning electron microscopy. The cathode layers sintered at 1200 °C, 4h present high porosity, small particles and chemical stability, as well as good adherence on the substrate.

INTRODUCTION

The solid oxide fuel cells (SOFCs) are being developed as efficient power generators having the ability to use a wide variety of fuels including hydrocarbons, alcohols, hydrogen, and carbon monoxide.[1,2] Advances in SOFC materials for high specific power density and reduced operating temperature have been pursued for the improvement of SOFC technology and the development of intermediate temperature solid oxide fuel cells (IT-SOFCs).

The cathode material should exhibit an acceptable ionic-electronic conductivity in both oxidising and reducing atmospheres, it has to be catalytically active towards oxygen reduction, it should be compatible with the other fuel cell components and its porosity must be controlled to allow an optimum gas transient to the electrochemically active sites.[3] Cathode materials obtained by wet chemical methods usually show better performance due to their high homogeneity in composition, small particles size and high purity.[4-6] $La_{1-x}Sr_xFe_{1-y}Co_yO_{3-\delta}$ perovskite oxides fulfill the conditions to be used as cathode material for IT-SOFCs with doped ceria or lanthanum gallate-based electrolyte.[3,4] It has been generally accepted that the electrochemical performance of IT-SOFC cathodes can be improved by mixing the cathode materials with electrolyte materials.[7]

Cathode materials for IT-SOFCs can be deposited on the electrolyte by different methods such as electrochemical vapor deposition, which is used commercially, chemical vapor deposition, physical vapor deposition, flame assisted vapor deposition, screen-printing, electrophoretic deposition, etc.[8,9] The screen-printing method is one of the most simple techniques to obtain cathode thick films. Process parameters may affect the electrochemical active area, the electronic conductivity of the cathodes and the gas diffusion for oxygen.[9]

The paper deals with the obtaining and characterization of LSFC ($La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$) powder by the citrate-EDTA method and the deposition of this, and a composite powder containing 80% LSFC and 20% $Ce_{0.8}Gd_{0.2}O_{2-\delta}$, respectively on CG20 ceramic bodies by screen-printing technique.

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EXPERIMENTAL

LSFC powder preparation. $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ powder was synthesized by citrate-EDTA method starting with stoichiometric volumes of 0.2 M aqueous solutions of lanthanum, strontium, iron and cobalt nitrates, ethylenediamine tetraacetic acid (EDTA) dissolved in ammonia solution, and citric acid. The molar ratio, metallic ions : citric acid : EDTA has been 2 : 1.5: 1. The reaction mixture was heated under magnetic stirring at the boiling temperature until the water was slowly evaporated. One of the most important parameter in the case of the citrate-EDTA method is the pH of the reaction mixture that should be kept at 6. Inadequate pH of the reaction mixture leads to the formation of cobalt ferrite as secondary phase. After the water evaporation, a brown gel-type compound has formed (the precursor), which has been separated and dried in vacuum for crystallization. The precursor was burn at 350 ^oC, 2h, in air, in order to decompose the organic parts and then it was annealed at 950 °C, 5h to obtain LSFC single-phase compound.

CG20 ceramic pellet obtaining. $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (CG20) powder has been obtained by solution combustion method the corresponding metallic nitrates and α-alanine as fuel. $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ single phase with fluorite structure and cubic symmetry was obtained direct by combustion reaction. The as-prepared powder (the powder resulted direct by the combustion reaction) was annealed at 500 °C, 3h for removing the traces of the residual carbon. The calcined CG20 powder was uniaxial pressed and sintered at 1400 °C, 4h to obtained dense ceramic bodies. More details about the synthesis and characterization of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ ceramics are presented elsewhere.[10]

LSFC deposition on ceramic bodies by screen-printing. For screen-printing deposition of LSFC-based cathode powders, CG20 ceramic bodies were used. All the ceramic supports were initially polished (using fine grain sand paper), washed with ethanol to have a good, uniform surface and then dried in an oven. LSFC powder obtained by citrate-EDTA method at 950°C and LSFC-based composite a mixture of 80% (wt.) LSFC and 20% (wt.) CG20 (obtained at 500 °C), respectively, have been used for deposition. Slurries from LSFC or LSFC-based composite powders, ethanol and polyethyleneglycol (PEG200) were prepared. The weight ratio between LSFC-based powder and PEG200 has been 1:0.88. PEG200 was added as binder to control the viscosity of the mixture, to assure a well adherence of perovskite powder to ceramic support and to increase the porosity of the cathode layer. The binders used for preparing the screen-printing slurries greatly influenced the microstructure of the screen-printed electrode layers. It was reported that by using a linear polymer as a binder, homogeneous pore size distribution is obtained.[9] The deposited layers were sintered at 1200°C, 4h.

The oxide powders and ceramics were analyzed by X-ray diffraction (XRD) using Rigaku Miniflex II X-ray diffractometer with CuKα radiation at a step of $0.01°\cdot s^{-1}$ in the range 2θ =10 - 80^o. The synthesized powders morphology, ceramics and layers microstructure were investigated by Hitachi S-2600N scanning electron microscope.

RESULTS AND DISCUSSION

LSFC powder obtained at 950°C was analyzed by X-ray diffraction and scanning electron microscopy. The X-ray diffraction data of LSFC powder (Figure 1) have showed the formation of LSFC single-phase compound with perovskite structure and rhombohedrally symmetry. The crystallite size calculated by Rigaku PDXL software from diffraction peak (0 1 2) is 25 nm. The scanning electron microscopy analysis of LSFC powder shows a microporous morphology of the oxide powder with fine primary particles with tendency of agglomeration forming irregular shape aggregates (Figure 2).

LSFC and LSFC-CG20 composite layers were deposited on CG20 ceramic bodies previously obtained from powders synthesized by solution combustion technique and sintered at 1400°C, 4h. Figure 3 presents XRD patterns for CG20 ceramic body used as support for LSFC and LSFC-CG20 composite layers and confirms that CG20 ceramic pellet has fluorite structure and cubic symmetry (*a* = 5.418 Å). The investigation of CG20 ceramic body by SEM shows grains with polyhedral shape with a bimodal distribution in the range of 0.5 – 2 μm and some intergranular pores (Figure 4). The ceramic pellets used as support are well sintered with a relative density of 90% determined by Arhimede's method in alcohol.

Two different layer compositions, LSFC and LSFC-based composite containing 80% (wt.) LSFC and 20% (wt.) CG20, have been deposited on CG20 ceramic pellets. The cathode layers sintered at 1200°C, 4h were analyzed by XRD and SEM. The thickness of the cathode layers on CG20 ceramic pellet was determined by measuring the thickness of the sample with a micrometer before and after five layers deposition. The average LSFC layer thickness on CG20 was found 12 μm, whereas the average thickness of composite deposited on CG20 was 14 μm. These samples were analyzed by XRD to check the structure and by SEM to investigate the microstructure.

No structural modifications of LSFC compound or chemical reactions between LSFC and CG20 have been noticed during the deposition and sintering steps (1200°C, 4h), as XRD data confirm (Figure 5). The substrate, CG20 pellet, has no contributions to the XRD patterns of the obtained LSFC layer. The XRD patterns of LSFC-CG20 composite (with 80% LSFC and 20% CG20 composition) deposited on CG20 pellet prove the formation of the composite thick film containing both phases, the perovskite one, $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$, with rhombohedrally symmetry and the fluorite phase, $Ce_{0.8}Gd_{0.2}O_{2-\delta}$, with cubic symmetry, respectively. In the Figure 7, one can observe both LSFC and CG20 characteristic X-ray diffraction peaks.

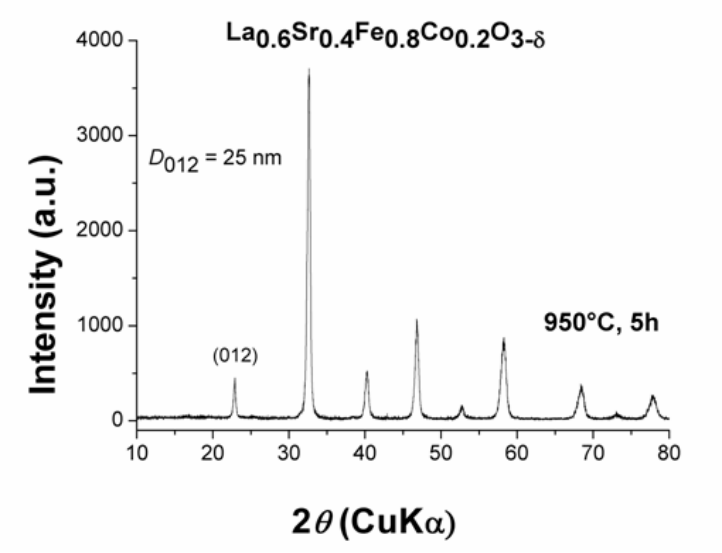

Fig. 1 – XRD patterns of LSFC powder obtained at 950°C, 5h.

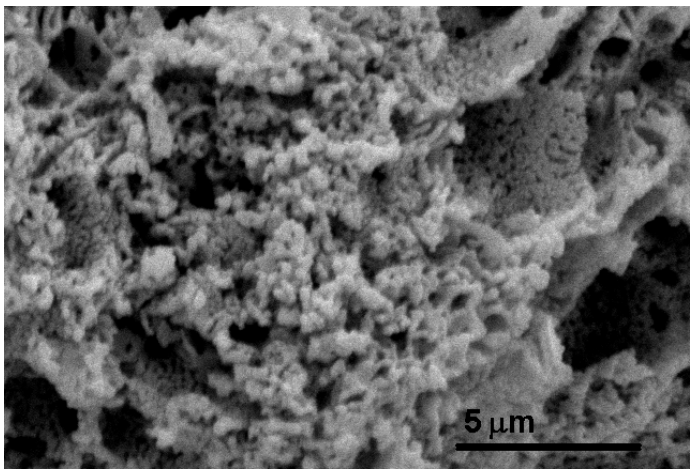

Fig. 2 – SEM micrograph of LSFC powder obtained at 950°C, 5h.

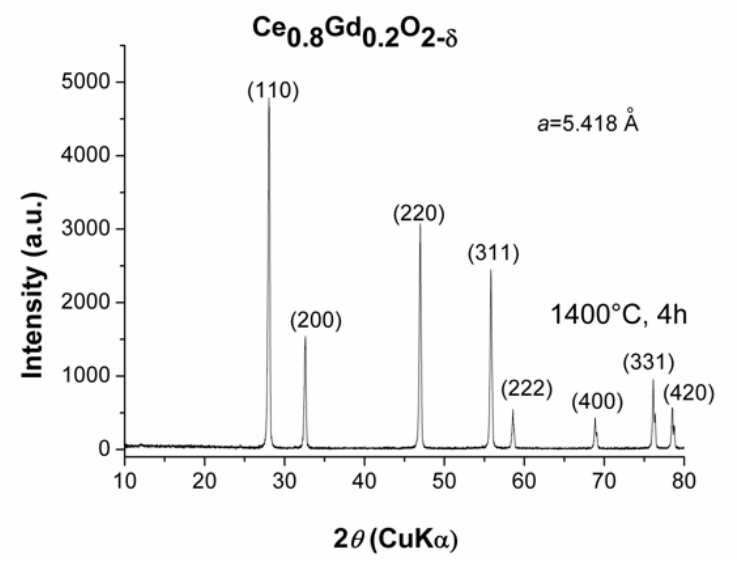

Fig. 3 – XRD patterns of CG20 ceramic pellet sintered at 1400°C, 4h.

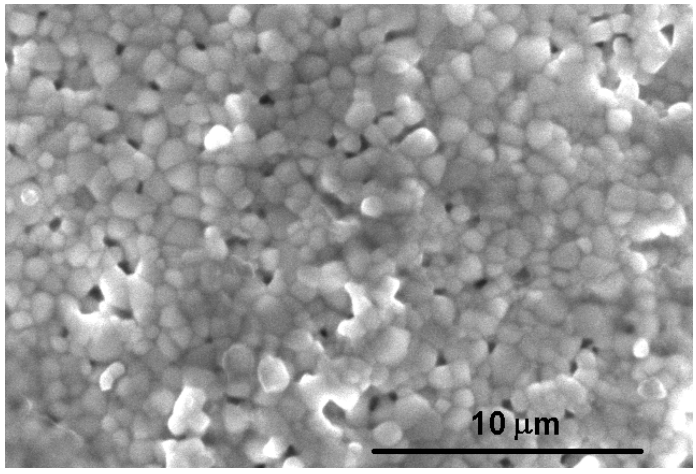

Fig. 4 – SEM picture of CG20 pellet sintered at 1400°C, 4h.

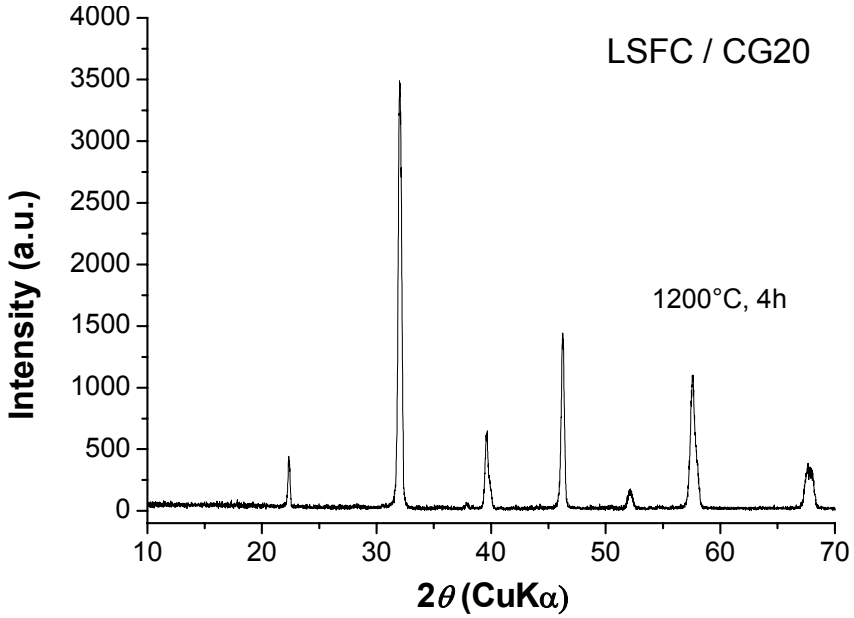

Fig. 5 – XRD patterns of LSFC deposited on CG20 ceramic pellet treated at 1200°C, 4h.

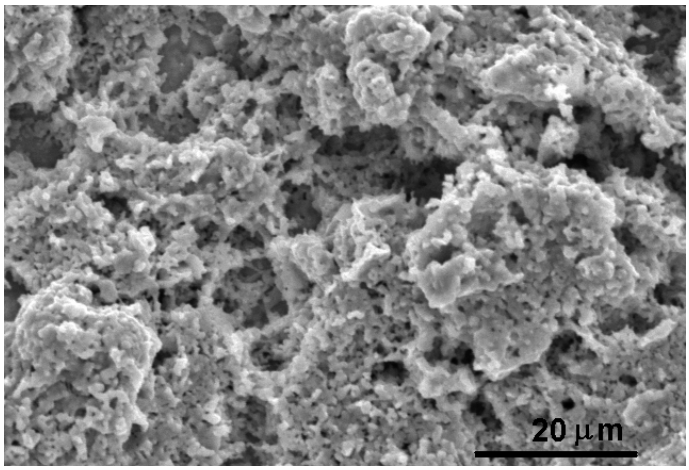

Fig. 6 – SEM micrograph of LSFC deposited on CG20 ceramic pellet treated at 1200°C, 4h.

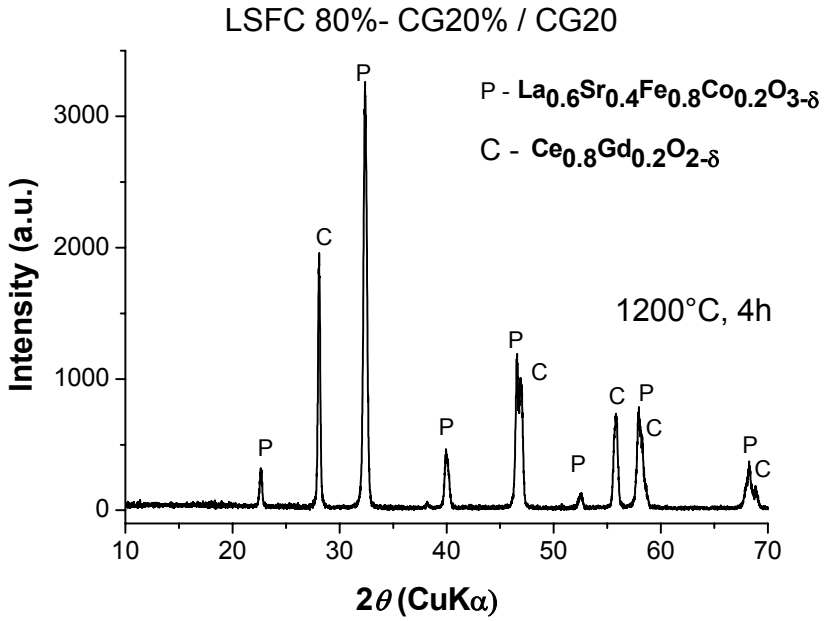

Fig. 7 – XRD patterns of LSFC-CG20 composite deposited on CG20 ceramic pellet treated at 1200°C, 4h.

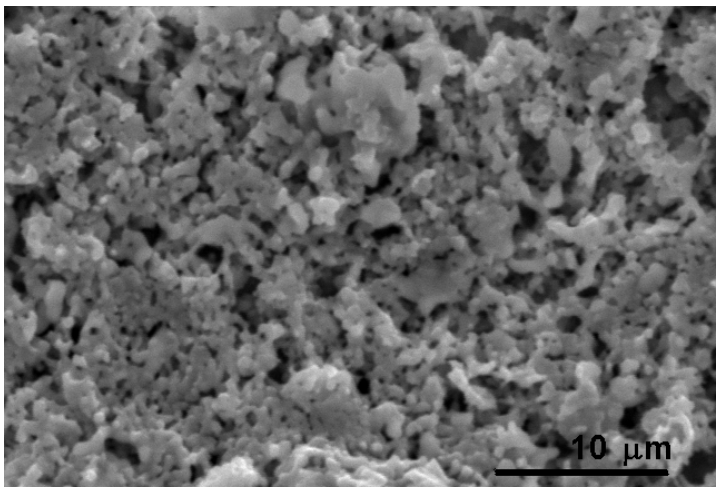

Fig. 8 – SEM micrograph of LSFC-CG20 composite deposited on CG20 ceramic pellet treated at 1200°C, 4h.

The SEM examination of LSFC, and LSFC-CG20 composite respectively, deposited on CG20 ceramic pellets treated at 1200°C, 4h (Figures 6 and 8) shows similar microstructures. One can notice high porosity of both types of layers with relative uniform distribution of intragranular pores.

CONCLUSIONS

$La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ (LSFC) single-phase powder has been successfully synthesized by a soft chemistry route, citrate-EDTA method. Two types of layers, LSFC and LSFC-based composite (80% LSFC and 20% CG20) have been deposited on CG20 ceramic pellets by screen-printing method using PEG200 as binder. The thick films sintered at 1200 °C keep high porosity, small particles and good physical contact between LSFC or LSFC-based composite particles and CG20 electrolyte.

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REFERENCES

1. L. Blum, W.A. Meulenberg, H. Nabielek and R. Steiberger Wilckens, *Int. J. Appl. Ceram. Technol.*, **2005**, *2,* 482-492.
2. M. Yano, A. Tomita, M. Sano and T. Hibino, *Solid State Ionics,* **2007,** *177,* 3351-3359.

3. P. Holtappels, U. Vogt and T. Graule, *Adv. Eng. Mater.,* **2005**, *7,* 292-302.
4. Z. Liu, M.-F. Han and W.-T. Miao, *J. Power Sources,* **2007**, *173*, 837–841.
5. L. Ge, W. Zhou, R. Ran, Z. Shao and S. Liu, *J. Alloys Comp.,* **2008**, *450*, 338-347.
6. W. Zhou, Z. Shao, R. Ran, H. Gu, W. Jin and N. Xu, *J. Am. Ceram. Soc.,* **2008,** *91,* 1155-1162.
7. H.S. Song, S.H. Hyun, J. Kim, H.W. Lee and J. Moon, *J. Mater. Chem.*, **2008**, *18*, 1087–1092.
8. S. Charojrochkul, K.L. Choy and B.C.H. Steele, *J. Eur. Ceram. Soc.* **2004,** *24*, 2515-2526.
9. J. Piao, K. Suna, N. Zhang and S. Xu, *J. Power Sources,* **2008,** *175*, 288–295.
10. C. Matei, D. Berger, S. Stoleriu, D. Neagu and E. Stefan, *J. Optoelectron. Adv. Mater*., **2010**, *2*, 1524-1529.