INFLUENCE OF THE SYNTHESIS METHOD OF NANOSTRUCTURED $La_{1-x}Sr_xMnO_3$-BASED MATERIALS FOR SOLID OXIDE FUEL CELL CATHODES [1]

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Abstract
The Sr-doped lanthanum manganites ($La_{1-x}Sr_xMnO_3$, LSM) have been studied as a promising material for cathodes in solid oxide fuel cells (SOFC). This material presents interesting properties such as chemical and thermal stabilities, high catalytic activity for the oxygen reduction, thermal expansion coefficient similar to that of solid electrolyte (YSZ) and high electrical conductivity. In this context, the present work is aimed to contribute to the synthesis and characterization of nanostructured powders to produce SOFC cathodes, by different chemical synthesis methods. The LSM (x = 0.3) was synthesized by combustion, citrate and solid-state methods. All powders obtained were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), textural analysis determined by physical adsorption of N_2 (BET), scanning electron microscopy (SEM), and X-ray fluorescence (XRF) analysis. Preliminary results indicate that the synthesis of LSM by the citrate method provided the production of smaller nanoparticles than to combustion and solid state methods, which produced particles with sizes around 12-21 nm. The SEM shows that the citrate method resulted in narrower particle size distribution than the other methods. The BET surface area was around 10 m^2/g for the samples prepared by the method of citrate, slightly larger than the other methods.
Key words: Lanthanum manganites; Nanopowder synthesis; SOFC cathode.

INFLUÊNCIA DO METODO DE SÍNTESE DE MATERIAIS NANOESTRUTURADOS TIPO- $La_{1-x}Sr_xMnO_3$ PARA CATODOS DE CÉLULAS A COMBUSTÍVEL DE ÓXIDO SÓLIDO

Resumo
Manganitas de lantânio dopadas com Sr foram estudadas como um importante material para uso como catodos de células a combustíveis de óxido sólido (SOFC). Este material apresenta boas propriedades, como estabilidade térmica e química, alta atividade catalítica para a redução de oxigênio, coeficiente de expansão térmica semelhante ao do eletrólito sólido (YSZ) e alta condutividade elétrica. Neste contexto, o presente trabalho tem como objetivo contribuir para a síntese e caracterização de pós nanoestruturados para serem utilizados como catodos de SOFC, por diferentes métodos de síntese. $La_{1-x}Sr_xMnO_3$ LSM (x = 0.3) foi sintetizado pelos métodos de combustão, citrato e estado sólido. Todos os pós obtidos foram caracterizados por difração de raios-X (DRX), análise termogravimétrica (ATG), análise textural por adsorção física de N_2 (BET), microscopia eletrônica varredura (MEV) e análise de fluorescência de raios-X (FRX). Os resultados preliminares indicam que a síntese de LSM pelo método citrato proporciona a obtenção de pós com diâmetros de partícula menores, em relação aos métodos de combustão e estado sólido, que produziram partículas com dimensões da ordem de 12-21 nm. A MEV mostrou que o método citrato resulta em maior formação de aglomerados devido à quantidade de partículas pequenas e com distribuição de tamanho mais estreita. A área superficial (BET) apresentou valores de cerca de 10 m^2/g para a amostra preparada pelo método de citrato, um pouco maior que os outros métodos.
Palavras-chave: Manganitas de lantânio; Síntese de nanopós; Catodo de SOFC.

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INTRODUCTION

In recent decades, the world turned to discussions on increasing global warming, the so-called "greenhouse effect", caused mainly by the emission of toxic gases, such as carbon dioxide, resulting from the burning of fossil fuels used as a source of generation of energy. The climate of the planet is bringing economic and environmental challenges, providing a strong interest in research aimed to alternative ways of producing electricity.

Accordingly, one of the biggest challenges ahead is to increase the quantity and quality of energy system, maintaining and expanding its economic environmental sustainability, emphasizing the efficient use of renewable energy resources. Within this approach it is essential developing new technologies for power generation, particularly those coming from renewable sources. Among them as new technologies the micro turbines, use of biomass, photovoltaic cells, wind power, geothermic systems and the fuel cells. Among these systems, the fuel cell is presented as a very promising technology.[1-3]

The fuel cell is a device that electrochemically converts combustible chemicals into electricity, it is essentially a battery that never ceases to provide electric current because of the continuing external power fuels. In short, it is a battery in which the two electrodes are not consumed during unloading, but simply act as sites for the reaction between fuel and oxidant.[4-7]

Solid Oxide Fuel Cells (SOFCs) are promising efficient, energy-saving, and environment-friendly energy conversion devices that generate electricity and heat (4). This instigates research in the area of novel synthetic methods for ceramic powders for cathode materials used in SOFC. Sr-doped $LaMnO_3$ (LSM) attracts substantial interests as a promising material for a cathode in the SOFCs. In nanosized crystals, this material presents good properties such as chemical and thermal stabilities, high catalytic activity for the oxygen reduction, thermal expansion coefficient reasonably similar to that of solid electrolyte (YSZ) and high electrical conductivity. Thus, there is considerable interest in particle size reduction which maximizing the electrode surface increases the number of pores that affects the catalytic performance of SOFC materials.

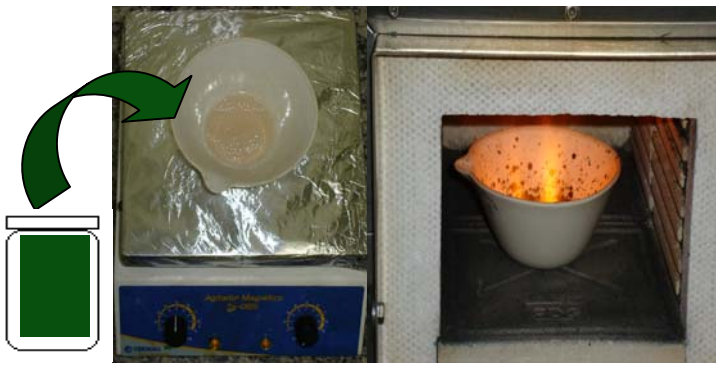
A number of promising preparation methods such as, solid-state reaction, sol-gel, hydrothermal, spray-drying, co-precipitation, combustion and gel-combustion have been used for ceramic powder synthesis.[8-13] In this context, the present work is aimed to contribute to the synthesis and characterization of LSM ($La_{1-x}Sr_xMnO_3$, x = 0.3) nanostructured powders to produce SOFC cathodes. The objective is to study the influence of different chemical synthesis methods (combustion, citrate and solid state) on the structural and morphological properties of LSM.

EXPERIMENTAL

The starting materials used in this study were metal nitrates, $La(NO_3)_3.6H_2O$, $Sr(NO_3)_2$ and $Mn(NO_3)_3.4H_2O$, urea ($CO(NH_2)_2$), ethylene glycol ($C_2H_6O_2$) and citric acid ($C_6H_8O_7$). All reagents are from Vetec.

Some cathode powders were synthesized by the combustion method (LSMCB), mixing the nitrate precursors in the required amounts, which were melted on a hot plate (150ºC) and the propellant was added to the molten nitrates (2:1 fuel/oxide). The basin was then introduced in a muffle furnace at 600°C, where the combustion

reaction took place (Figure 1). The powder was finally calcined at 750°C for 10h in flowing air (60mL/mim).



Heating Plate 150°C **Combustion Reaction 600ºC**

Figure 1. Picture of the preparation process of the LSM by combustion method.

For the citrate method (LSMCI) (Figure 2) the nitrates were mixed with a solution of citric acid and ethylene glycol 6:1 (acid + ethylene / oxide) by 24h, with formation of a resin, which was calcined at 900°C in flowing air.

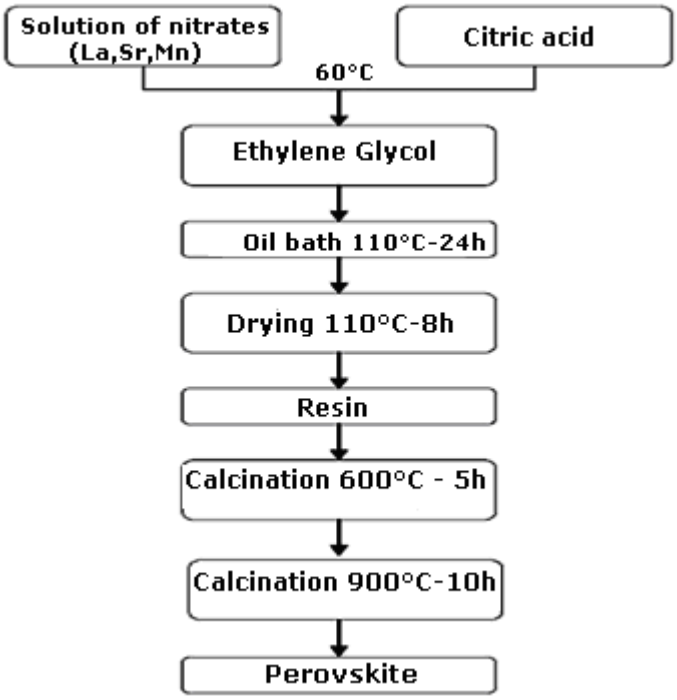


Figure 2. Schematic flow diagram of citrate method process.

A solid-state synthesis (LSMSS) method (Figure 3) was carried out in a ball mill, where the oxides were mixed with balls equivalent to 8 times the weight of the sample, for 24 h, then calcined at 1000°C, according to the synthesis study of ceramic materials made by Furtado et. al. [(14)]

Figure 3. Picture of the ball milling step of the preparation process of the LSM by solid-state method.

The prepared materials were analyzed by X-ray powder diffraction (XRD), in a PANalytical X'Pert PRO diffractometer, with Cu Kα radiation and filter of Ni (λ = 1.54055 Å), with speed of 2°mim^{-1} and variation of the angle between 2° and 100^{o}. Thermo-gravimetric analysis (TGA) of the powder was carried out using a Perkin-Elmer Thermo gravimetric Analyzer 7, a heating rate of 5°C mim^{-1} in air from room temperature to 1400°C. The morphology of the cathode powders and the microstructure of cathode compacts were investigated by scanning electron microscopy (SEM) Jeol KAL 64602 LV. The chemical composition of cathodes was determined by X-ray fluorescence spectroscopy (XRF, Rigaku - RIX 3100) and textural analysis was determined by physical adsorption of N_2 (BET method).

RESULTS AND DISCUSSION

The results of X-ray fluorescence (XRF) of the LSM synthesized by different routes are shown in Table 1. The values of the concentrations of the elements calculated stochiometrically before the reaction are very similar the values found experimentally.

The results obtained by XRD (Figure 4) showed the presence of perovskite $La_{1-x}Sr_xMnO_3$ (ICDD 47344) and $SrCO_3$ phases (JCPDS 50418) for the sample synthesized by citrate method. The lattice parameters of the hexagonal structure of the perovskite are shown in Table 2I. The small formation of $SrCO_3$ for the sample synthesized by the method of citrate is due to incomplete polymerization and low calcination temperature, according to Gaoke et al.[15]

Table 1. Values obtained by the XRF analysis for the LSM materials synthesized by different routes.

Sample	Route of synthesis	Nominal content	Experimental content
LSMCI	Citrate	$La_{0.7}Sr_{0.3}MnO_3$	$La_{0.67}Sr_{0.33}MnO_3$
LSMCB	Combustion	$La_{0.7}Sr_{0.3}MnO_3$	$La_{0.66}Sr_{0.34}MnO_3$
LSMSS	Solid-state	$La_{0.7}Sr_{0.3}MnO_3$	$La_{0.67}Sr_{0.33}MnO_3$

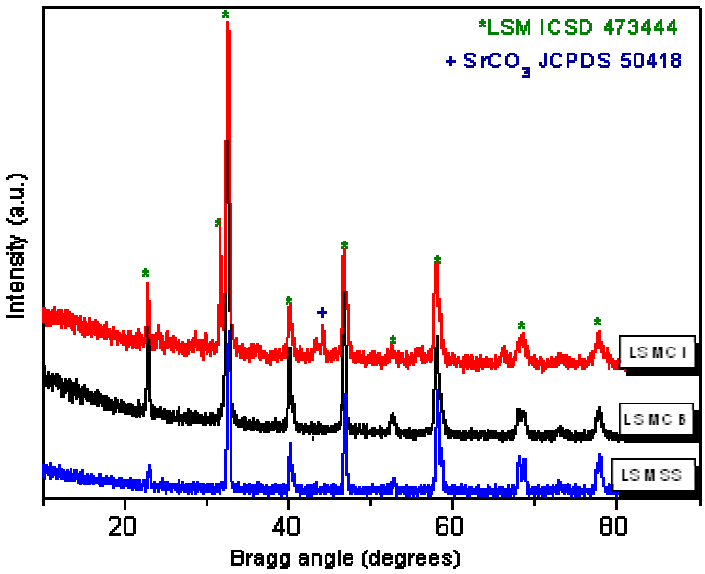


Figure 4. XRD for LSM synthesized by combustion (LSMCB), citrate (LSMCI) and solid-state (LSMSS) methods.

The crystallite size of LSM prepared from different methods is shown in Table 2. The citrate synthesis method presented the best results, with crystalline nanoparticles around 12 nm, indicating that a better definition of crystalline arrangement of the structure of LSM.

For the combustion synthesis the particle size is affected by the combustion temperature, with the product powder size increasing with the rise of temperature.[16] In this case, the crystallite size, surface area (Table 3) and the extent and nature of the agglomeration of products are governed primarily by the temperature of the flame generated during combustion, which is dependent on the of fuel/oxidant ratio. Large particle sizes are formed due to the high temperature of reaction when using urea, as the low volume of gas generated prevents the dissipation of heat.[17] The nanosize and area of particular ceramics materials synthesized by the solid-state method is also influenced by the temperature and time of mixing in the grinder of balls.[18]

Table 2 – Crystallite sizes calculated by Scherer equation and lattice parameters from XRD.

Samples	Crystallite size (nm)	Lattice parameters*	Lattice parameters of LSM (Å)**
LSMCI	12.3	a= 5.777 c= 13.4305	a= 5.4943 c= 13.3422
LSMCB	16.0	a= 5.4989 c= 13.4000	
LSMSS	21.3	a = 5.4994 c = 13.3719	

** Calculated from XRD; ** LSM JCPDS ICDD 47344*

Table 3 shows the values of the surface area and pore volume of the LSM synthesized by different methods. One can observe that the method of citrate presented best results in relation to other methods, in accordance to the results already described in the literature. In general, specific areas of the LSM varies from 10 to 40 m^2/g,[19] when chemical methods are used.

Table 3 - Values of specific surface area and pore volume for samples of LSM synthesized by different methods.

Sample	S_{BET} (m^2/g)	V_{pore} (cm^3/g)
LSMCI	10	0.038
LSMCB	<10	0.004
LSMSS	<10	0.017

Figure 5 shows the TGA curves for the as-synthesized LSMCB, LSMCI and LSMSS powders. For the sample prepared by combustion there was a weight loss of about 12% between 600 and 850°C that was likely due to oxidation of carbon residues.[20] Temperatures above 850°C are necessary for complete decomposition, but when the powder is calcined at 750°C for a long time a unique phase of LSM was obtained, as observed by XRD.

The TGA of LSM synthesized by the citrate method presents the following decomposition steps: from 50°C to 350°C, loss of hydration water; from 350 to 550°C, decomposition of citrate, and possible formation of carbonates; and finally from 550 to 850°C, decomposition of carbonate.

For the solid-state method TGA curve shows the decomposition of strontium carbonate between 250-750°C with small weight loss (14%).The relevant difference in the weight loss between the citrate method (56%) and the other methods is the largest quantity of citric acid and ethylene glycol for the formation of chelating and etherification of the material.[21]

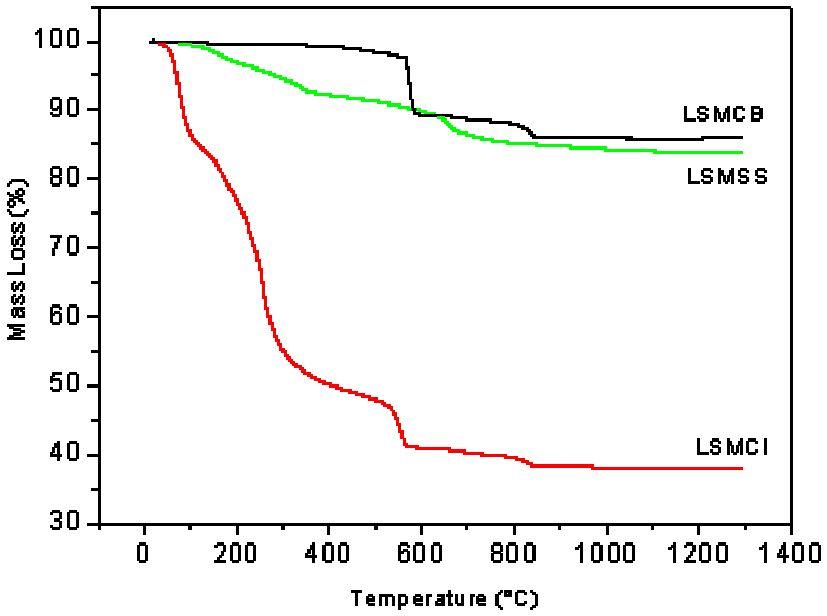


Figure 5. Thermogravimetric analysis of the samples of LSM synthesized by different methods.

From scanning electron microscopy (SEM) analysis, shown in Figure 6, it is observed the morphology of the particles synthesized by different methods. The form of clusters obtained in the ceramic material is consequence of the preparation method, and the method of citrate has advantages in obtaining nanoparticles, because the reactions of chelating are slower and produce material more homogenized, forming uniform particles.

The nanopowders prepared by combustion were highly porous and particles were linked together in agglomerates of different shapes and sizes. According to Bansal et. al.,[21] substantial particle growth was observed upon calcination above 800°C, but the structure remained highly porous until 1000°C. For materials obtained by solid-state method the particles sizes depend mostly on the milling time and calcination temperature. Nanometric sizes are obtained by milling time between 24 and 96 h, and calcination temperature of 1000-1200°C.[18]

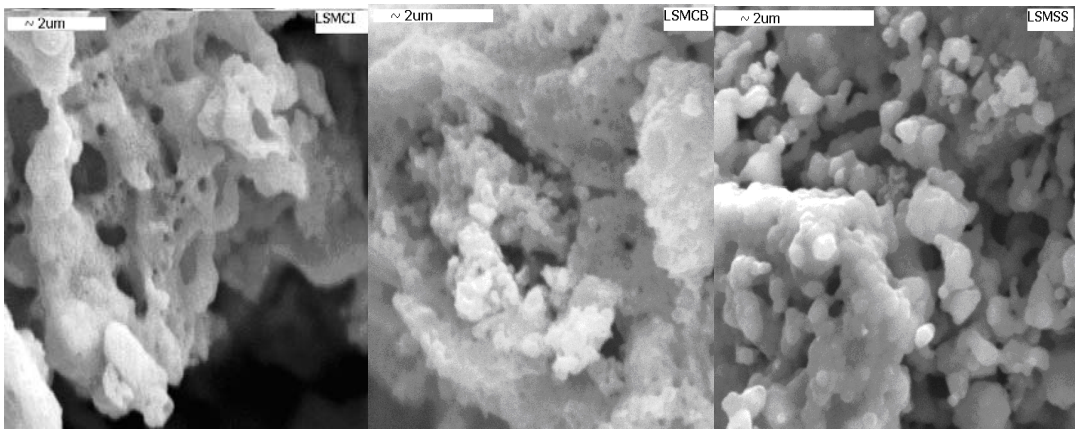


Figure 6. SEM of the samples synthesized by citrate (LSMCI), combustion (LSMCB) and solid-state (LSMSS) methods.

CONCLUSIONS

The XRD results indicate that the synthesis of LSM by the method of citrate resulted in smaller nanoparticles (12 nm) than the methods of combustion (16 nm) and solid state (21 nm). The SEM analysis also presents a better distribution of the particles and the textural analysis showed a slight increase in surface area for the citrate method. All methods produced powders with chemical compositions very close to the nominal ones. From these characterizations we can conclude that all materials are good candidates to be used as cathode of SOFC, especially those prepared by citrate method. However, it is necessary further specific electrical conductivity analysis to confirm the potential of these materials.

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