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Short communication

Effect of propellant on the combustion synthesized Sr-doped $LaMnO_3$ powders

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Abstract

Lanthanum strontium manganite (LSM) powders of composition $La_{0.7}Sr_{0.3}MnO_3$ are good candidates for cathode application in solid oxide fuel cells. This paper reports the synthesis of LSM powders from nitrate precursors by the combustion method, using two different propellants (urea and glycine) and varying the propellant/nitrate ratio. Thermogravimetric analysis (TGA) revealed two or three decomposition stages of the as-synthesized samples, with complete burn out of organics at about 850–900 °C. X-ray diffraction (XRD) patterns showed formation of only LSM phase for the sample synthesized with excess of urea, whereas $SrCO_3$ and $MnCO_3$ phases were also found for the samples prepared from glycine. The powder is better crystallized when a homogeneous gel is formed before burning. The crystallite size calculated using the Scherrer equation is in the range of 15–20 nm. Scanning electron microscopy (SEM) revealed the presence of agglomerates, formed by fine particles of different shapes.

Keywords: A. Powders: chemical preparation; B. X-ray methods; D. Perovskites; E. Fuel cells

1. Introduction

Solid oxide fuel cells (SOFCs) are promising, efficient, and environmentally friendly energy conversion devices that generate electricity and heat [1]. These features have stimulated research on developing ceramic powders for cathode materials used in SOFCs. Sr-doped $LaMnO_3$ (lanthanum strontium manganites—LSM) has particularly attracted substantial interest as a promising material for cathode in SOFCs. This material has good properties such as chemical and thermal stability, and high catalytic activity for oxygen reduction. Additionally, it has a thermal expansion coefficient similar to that of a solid electrolyte (yttria-stabilized zirconia, YSZ), and high electrical conductivity [2].

A number of preparation methods such as solid-state reaction, sol–gel technique, hydrothermal synthesis, spray-drying, co-precipitation, and combustion, have been used for perovskite synthesis [3]. The combustion method is particularly useful in the production of ultrafine ceramic powders with a small average particle size. This is a simple method with the advantage of using inexpensive precursors and of producing nano-sized, homogeneous, highly reactive powders.

The most commonly used fuels in the combustion process for the synthesis of LSM are glycine and urea. However, citric acid, oxalyl-hydrazine and sucrose have also been recently employed as complexing agents and fuels in the combustion synthesis [4–6]. The combustion synthesis technique consists in bringing a saturated aqueous solution of the desired metal salts and a suitable organic fuel to boil, until the mixture ignites and a self-sustaining and fast combustion reaction takes off, resulting in a dry, usually crystalline, fine oxide powder [7]. The large amounts of gases formed can result in the appearance of a flame, which can reach temperatures above 1000 °C [7].

This work focuses on the preparation of LSM powder materials by the combustion method. Our aim is to assess the influence of the nature and amount of two different propellants (urea and glycine) and the formation of a gel before burning on the structural and morphological properties of the prepared powders.

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2. Experimental

2.1. Powder synthesis

The materials used in the synthesis were metal nitrates: $La(NO_3)_3{\cdot}6H_2O$, $Sr(NO_3)_2$, $Mn(NO_3)_3{\cdot}4H_2O$, and the propellants were urea ($CO(NH_2)_2$) and glycine (NH_2CH_2COOH). All reagents were from VETEC, Brazil.

LSM was prepared by combustion and gel combustion methods. In the method of combustion, the nitrates and the propellant were mixed on a hot plate (150 °C). The mixture was shaken to obtain a homogeneous solution, which was then introduced to a muffle furnace pre-heated at 600 °C, where the combustion reaction took place. The powder was calcined in flowing air (60 mL min^{-1}) at 750 °C for 10 h.

The propellant was used in a stoichiometric amount and twice the theoretical amount (1:1 and 2:1 ratio of propellant/metallic oxide). The stoichiometric amount of the propellant was determined based on the valencies of oxidizing and reducing elements, according to the propellant chemistry [8].

In the method of gel combustion, a solution of nitrates was heated slowly at 60 °C in oil bath, and then the propellant was added. The heating was kept for 6 h, obtaining a homogeneous gel, which was introduced to a muffle furnace (600 °C) to burn the material. The powder was then calcined at the same conditions previously described.

All $La_{1-x}Sr_xMnO_3$ powder materials were prepared with nominal composition of $x = 0.3$, because this composition has shown better performance as cathode in SOFC [2,9]. The prepared perovskites will be referred to as LSMCUxx and LSMCGxx for those prepared by combustion with urea and glycine, respectively, where xx can be 11 or 21, depending on propellant/metallic oxide ratio (1:1 or 2:1). Samples LSMGCU and LSMGCG were prepared by gel combustion.

2.2. Characterization

X-ray powder diffraction (XRD) patterns were recorded in a PANalytical X'Pert PRO diffractometer, with Cu Kα radiation and filter of Ni, with speed of 2° min^{-1}.

Thermogravimetric analysis (TGA) of the powders were carried out using a TA thermal analyzer (SDT Q600 model) with heating rate of 5 °C min^{-1} in air flow from room temperature up to 1400 °C.

BET specific areas were determined by N_2 adsorption–desorption at −196 °C in a Micromeritics ASAP 2000. Prior to analysis, the samples were outgassed for 24 h at 300 °C.

The microstructure of the prepared materials was investigated by scanning electron microscopy (SEM), using a Jeol KAL 64602 LV (20 kV) microscope.

3. Results and discussions

3.1. Thermal decomposition

Fig. 1 shows TGA curves of the as-synthesized LSM powders by the combustion method, before calcination. As can be seen, thermal decomposition takes place in two or three stages, depending on the fuel, and burn out of organics is complete at about 850–900 °C for all samples.

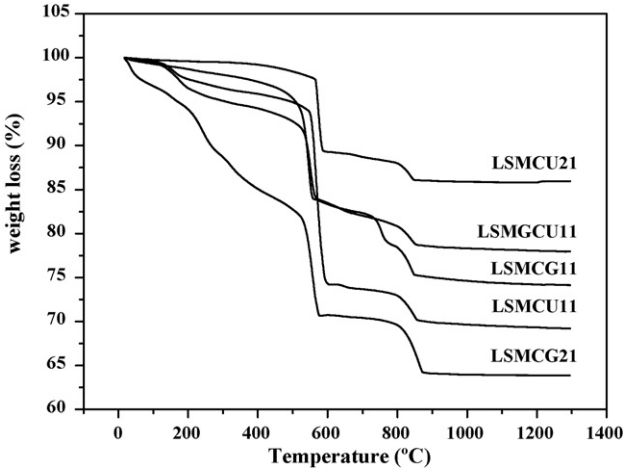

Fig. 1. TGA curves of the as-synthesized LSM powders prepared by the combustion and gel combustion method.

When urea is used as fuel, two steep decomposition stages can be distinguished: the first, at about 600 °C, can be

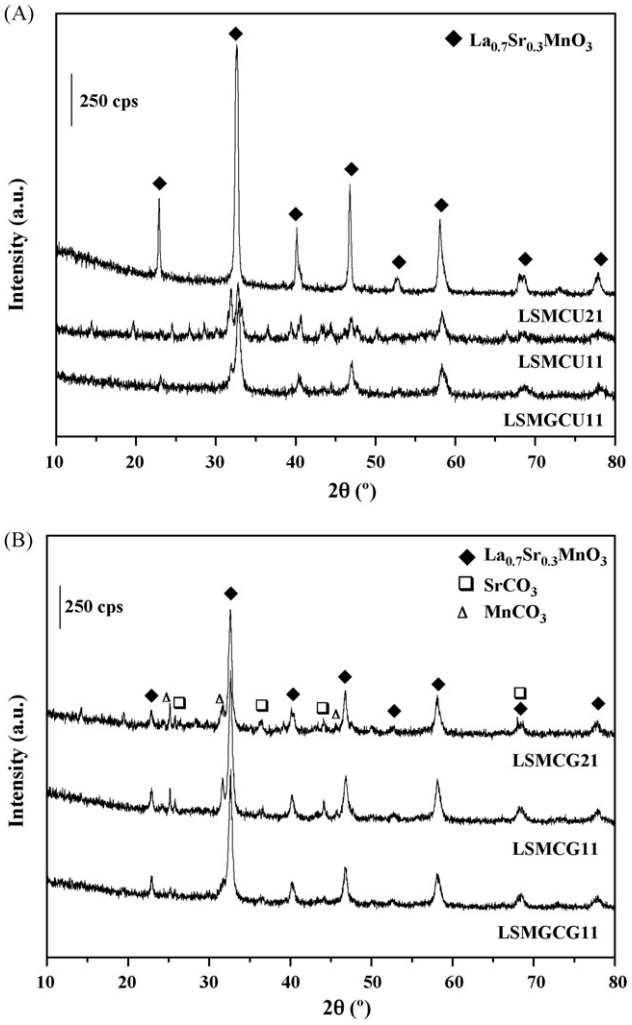

Fig. 2. XRD patterns of the powders after calcination, prepared with urea (A) and glycine (B).

associated with the oxidation of combustion residues, mainly fuel that was not burnt during the fast combustion reaction; the second, at 850 °C, may be due to complete dissociation of carbonates produced during combustion and formation of LSM phase [10]. The total weight loss of sample LSMCU21 is 15%, much lower than that of LSMCU11 (30%), showing that combustion is more complete in excess of the fuel, forming a more crystalline material, as will be shown by XRD analysis.

TGA profile of LSMGCU11 sample, prepared by the gel combustion method, is also shown in Fig. 1. We found that the formation of a gel before burning allows a more complete reaction, with a smaller weight loss during thermal decomposition.

For the samples prepared from glycine, TGA profiles (Fig. 1) show at least three decomposition steps: the first, at 200 °C, can be assigned to water loss and also to reaction between glycine and nitrate anions with formation of hydroxy-species [11]. The second and third decomposition steps, at 600 and 850 °C, can be associated as described previously for urea route. In the case of glycine, weight loss increases with the increase of fuel amount. The heat of combustion for glycine is higher than that for urea [12], and the combustion reaction remains localized and incomplete in the glycine route, justifying the large weight loss observed for the sample prepared with excess of glycine.

Although TGA profiles have shown that thermal decomposition is only complete at 850–900 °C, all samples were calcined at 750 °C for 10 h. This condition is sufficient for LSM phase formation and total burn out of organics, as verified by TGA analysis of the calcined sample (not shown).

3.2. Phase formation and microstructure

XRD patterns of the powder samples after calcination are shown in Fig. 2. For urea (Fig. 2(A)), XRD patterns are strongly dependent on the fuel/oxide ratio; the use of stoichiometric ratio results in a poorly crystallized sample, with weak diffraction peaks and secondary phases besides LSM. The combustion reaction is far more complete when excess of urea is used, resulting in a crystalline material with single LSM

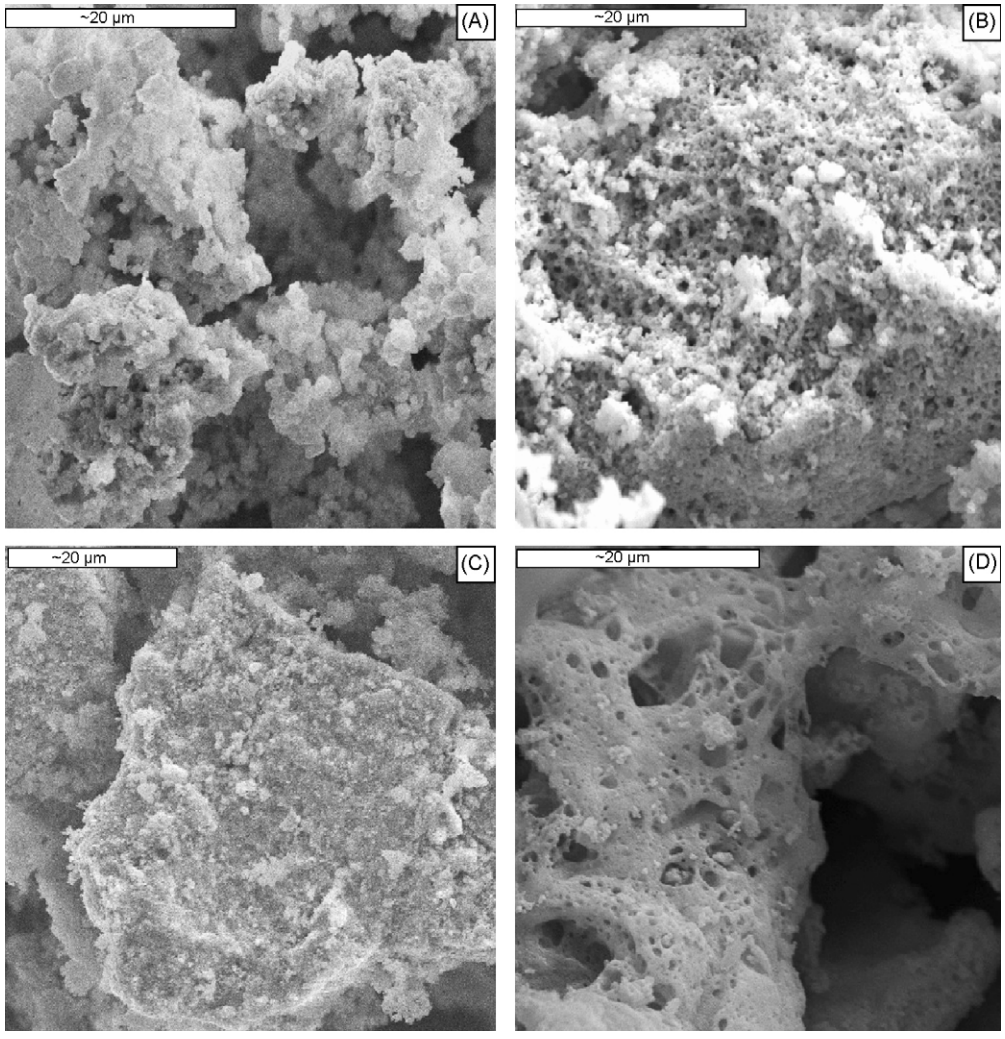

Fig. 3. Micrographs of (A) LSMCU11, (B) LSMCU21, (C) LSMCG11 and (D) LSMCG21 samples.

Table 1
Crystallite sizes calculated from XRD data using the Scherrer equation and lattice parameters of LSM samples.

Samples	Crystallite size (nm)	Lattice parameters[a] (Å)
LSMGCG11	17.7	$a = 5.4918$, $c = 13.3754$
LSMCG11	17.3	$a = 5.4924$, $c = 13.3888$
LSMCG21	19.6	$a = 5.5041$, $c = 13.3813$
LSMGCU11	14.9	$a = 5.4876$, $c = 13.2745$
LSMCU11	–	–
LSMCU21	16.0	$a = 5.5193$, $c = 13.3222$

[a] Calculated from XRD data considering (1 0 4) plane.

phase formation (ICSD 473444). The phase formation can be improved by the gel combustion method, which indicates that intimate mixing of the fuel and oxidant in the form of a stable gel is useful for preparation of crystalline materials.

For the samples prepared from glycine, $SrCO_3$ (JCPDS 50418) and $MnCO_3$ (JCPDS 441472) phases were formed, as can be seen in Fig. 2(B). The formation of carbonate phases may be due to reaction between SrO or MnO and CO_2 decomposed from organic compounds at elevated temperatures during the combustion reaction [6,13]. These secondary phases slightly increased with increasing fuel amount. The higher crystallinity of the LSMCG11 sample as compared to that of LSMCU11 shows that glycine is a stronger complexing agent and forms more stable gels in nitrate solution. Also in the glycine route, the powder is better crystallized when the gel combustion method is used.

Table 1 shows the crystallite sizes, calculated from XRD data using the Scherrer equation, and the lattice parameters. All products obtained in this work were nanocrystalline with sizes ranging between 14.9 and 19.6 nm. The crystallite sizes of LSM samples prepared from urea were smaller than those derived from glycine. It is well known that the crystallite size is affected by combustion temperature, with the product powder size increasing with the rise of temperature [14,15]. Larger crystallite sizes of the powder produced by glycine route can be attributed to the higher flame temperature. Moreover, crystallite size slightly increases with fuel amount, closely related to a higher combustion temperature [6]. The lattice parameters calculated from XRD data have proved that rhombohedral perovskite structure was obtained, with values very close to those of ICSD No. 473444 ($a = 5.4953$ Å and $c = 13.3422$ Å).

The specific surface areas, determined by BET method, of all calcined samples were lower than 10 m^2/g, consistent with other values reported in the literature [11,16].

Fig. 3 shows the typical SEM micrographs of LSM samples prepared by the combustion method. Note that the powders have a spongy aspect, with formation of agglomerates of fine particles of different shapes. Voids and holes can be observed, which result from the escaping of gases during combustion synthesis [17]. By SEM observation, it was found that the porosity of the powders increased with the increase in fuel amount, which can be explained by the evolution of more gas during the combustion reaction [15].

4. Conclusions

A combustion synthesis method from nitrate precursors has been used to prepare nanocrystalline LSM powders. According to our results, thermal stability, phase formation and crystallite size are strongly dependent on the nature of the propellant (urea or glycine) and the propellant/nitrate ratio. The samples prepared from glycine have higher crystallinity because glycine is a stronger complexing agent and forms more stable gels in nitrate solution. However, samples from glycine route presented carbonate phases besides LSM phase. LSM single phase formation is observed when urea is used in excess (2:1 propellant/nitrate ratio). As we have shown, phase formation can be improved when a homogeneous gel with an intimate mixing of the fuel and oxidant is formed before burning.

Particularly, crystallite sizes, between 15 and 20 nm, slightly increase with the increase in fuel amount, closely related to higher combustion temperatures. All samples have a specific surface area smaller than 10 m^2/g and a microstructure with agglomerates formed by fine particles of different shapes.

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References

[1] M.S. Dresselhaus, I.L. Thomas, Alternative energy technologies in nature insight, materials for clean energy, Nature 414 (2001) 332–337.
[2] S.C. Singhal, K. Kendall, High Temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications, 2nd ed., Elsevier, 2004.
[3] R.J. Bell, G.J. Millar, J. Drennan, Influence of synthesis route on the catalytic properties of $La_{1-x}Sr_xMnO_3$, Solid State Ionics 131 (2000) 211–220.
[4] K. Prabhakaran, J. Joseph, N.M. Gokhale, S.C. Sharma, R. Lal, Sucrose combustion synthesis of $La_xSr_{(1-x)}MnO_3$ ($x \leq 0.2$) powders, Ceramics International 31 (2005) 327–331.
[5] L.A. Chick, L.R. Pederson, G.D. Maupin, J.L. Bates, L.E. Thomas, G.J. Exarhos, Glycine–nitrate combustion synthesis of oxide ceramic powder, Materials Letters 10 (1990) 6–12.
[6] R.S. Guo, Q.T. Wei, H.L. Li, F.H. Wang, Synthesis and properties of $La_{0.7}Sr_{0.3}MnO_3$ cathode by gel combustion, Materials Letters 60 (2006) 261–265.
[7] D.A. Fumo, J.R. Jurado, A.M. Segadães, J.R. Frade, Combustion synthesis of iron-substituted strontium titanate perovskites, Materials Research Bulletin 32 (1997) 1459–1470.
[8] A. Ringuedé, J.A. Labrincha, J.R. Frade, A combustion synthesis method to obtain alternative cermet materials for SOFC anodes, Solid State Ionics 141/142 (2001) 549–557.
[9] S. Otoshi, H. Sasaki, H. Ohnishi, M. Hase, K. Ishimaru, M. Ippommatsu, T. Higuchi, M. Miyayama, H. Yanagida, Changes in the phases and electrical conduction properties of $(La_{1-x}Sr_x)_{1-y}MnO_{3-\delta}$, Journal of the Electrochemical Society 138 (1991) 1519–1523.
[10] A. Ghosh, A.K. Sahu, A.K. Gulnar, A.K. Suri, Synthesis and characterization of lanthanum strontium manganite, Scripta Materialia 52 (2005) 1305–1309.
[11] D. Berger, C. Matei, F. Papa, D. Macovei, V. Fruth, J.P. Deloume, Pure and doped lanthanum manganites obtained by combustion method, Journal of the European Ceramic Society 27 (2007) 4395–4398.

[12] C.-C. Hwang, T.-Y. Wu, J. Wan, J.-S. Tsai, Development of a novel combustion synthesis method for synthesizing of ceramic oxide powders, Materials Science and Engineering: B 111 (2004) 49–56.

[13] N.M. Nagabhushana, R.P.S. Chakradhar, K.P. Ramesh, C. Shivakumara, G.T. Chandrappa, Low temperature synthesis, structural characterization, and zero-field resistivity of nanocrystalline $La_{1-x}Sr_xMnO_{3+\delta}$ ($0.0 \leq x \leq 0.3$) manganites, Materials Research Bulletin 41 (2006) 1735–1746.

[14] A.M. Segadães, M.R. Morelli, R.G.A. Kiminami, Combustion synthesis of aluminium titanate, Journal of the European Ceramic Society 18 (1988) 771–781.

[15] X. Pingbo, Z. Weiping, Y. Kuo, J. Long, Z. Weiwei, X. Shangda, Size-controllable glynitrate low temperature combustion synthesis (LCS) of nanocrystalline $La_xSr_{1-x}MnO_3$, Journal of Alloys and Compounds 90 (2000) 90–92.

[16] M. Gaudon, C. Laberty-Robert, F. Ansart, P. Stevens, A. Rousset, Preparation and characterization of $La_{1-x}Sr_xMnO_{3+\delta}$ ($0 \leq x \leq 0.6$) powder by sol–gel processing, Solid State Sciences 4 (2002) 125–133.

[17] C.-C. Hwang, J.-S. Tsai, T.-H. Huang, C.-H. Peng, S.-Y. Chen, Combustion synthesis of Ni–Zn ferrite powder—influence of oxygen balance value, Journal of Solid State Chemistry 178 (2005) 382–389.