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Use of sucrose in the synthesis of cathodes used in fuel cells

Uso da sacarose na síntese de cátodos usados em células a combustível

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Abstract

Perovskite powders with composition $La_{1-x}Sr_xMnO_3$ (x=0.1) were obtained via combustion synthesis using sucrose as fuel. In the X-ray diffraction patterns it was observed that in order to obtain a single phase material calcination in 750ºC was necessary. BET analysis detected a specific surface area of 45 m²/g, which means an increase when compared with other fuels. SEM micrographs revealed a very spongy aspect with great porosity in the agglomerates and TEM micrographs showed micro and nano bubble shaped particles in the as-obtained manganite. The powder compacted and sintered at 125 MPa and 1050ºC for 2 hours, respectively, presented a 31% open porosity and the SEM micrographs showed a fine interconnected porosity.

Keywords: Sr-doped lanthanum manganite; Sucrose combustion synthesis; Solid oxide fuel cell.

Resumo

Pós de perovskitas com composição $La_{1-x}Sr_xMnO_3$ *(x=0.1) foram obtidos via síntese por combustão utilizando sacarose como combustível. Nos padrões de DRX foi observado que para a obtenção da fase é necessária uma calcinação a* 750°C *foi necessária. Pelos resultados de BET foi determinada uma área superficial específica de* 45m²/g*, maior do que o reportado com o uso de outros combustíveis. Micrografias de MEV revelaram um pó na forma de aglomerados porosos e com aspecto esponjoso e micrografias de MET mostraram que o pó como obtido apresenta partículas nanométricas com formato esférico e oco. O pó compactado a* 125 MPa *e sinterizado a* 1050°C *por duas horas, apresentou uma porosidade aparente de 31% e micrografias de MEV mostraram a formação de uma fina porosidade interconectada.*

Palavras-chave: *Manganato de lantânio dopado com* Sr*; Síntese por combustão de sacarose; Célula a combustível óxido sólido.*

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Introduction

Solid oxide fuel cells (SOFC) that operates at high temperatures are devices that can reach an efficiency up to 85% when used with co-generation and, due to its reliability, are being used in telecommunications, computers and internet hosts as a source of stationary power generation[1]. Strontium-doped lanthanum manganite is a suitable material for use as SOFC's cathodes owing to its chemical stability and good properties at high temperatures and, manly, to the physical compatibility with yttria-stabilized zirconia (YSZ), the most common electrolyte material[2]. In this sense, combustion synthesis emerges as an potential method to obtain perovskite powders, such as LSM, with good crystallinity and high purity, and can also provide interesting morphological characteristics that may improve its performance as a cathode[3,4]. This because an increase in the specific surface area and a porous and stable microstructure promote an increase in the triple phase boundary (TPB) and optimize the air flow through the electrode[5]. Thus, the aim of this study was to obtain single phase LSM powders through combustion synthesis using sucrose as fuel, to form and sintering ceramic bodies to evaluate the appropriate temperature to reach between 30 and 40% open porosity.

Materials and Methods

The LSM powders were synthesized from $La(NO_3)_3.6H_2O$, $Mn(NO_3)_3.4H_2O$ and $Sr(NO_3)_2$ with a calculated strontium fraction of 10% and using a nitrates to sucrose ($C_{11}H_{22}O_{11}$) stoichiometric ratio of 1:2[6]. The use of less than 200% of oxidizers excess could lead to the formation of undesirable secondary phases[7]. After the complete dissolution of the reagents in distilled water the recipient containing the precursor solution was kept on a hot plate at 110ºC until the formation of a gel and heated up to 300ºC, where the reaction took place. The resulting as-obtained material was analyzed in a X-ray diffractometer (XRD) and had its specific surface area measured using the Brunauer-Emmet-Teller gas adsorption technique (BET). The powder morphology was observed through Scanning and Transmission Electron Microscopy (SEM and TEM, respectively). Also, a calcination at 750ºC for 3 hours was held and the powder was again analyzed by XRD. The as-obtained powder was uniaxially compacted at 125 MPa with only glycerin as a lubricant. The green ceramic bodies were sintered at temperatures between 1000 and 1200ºC for 2 hours and a under a heating rate of 10ºC/min. The Archimedes method was used to determinate the influence of sintering temperature on the sintered bodies' apparent porosity (A.P.) and also, the sample sintered at 1050°C had its microstructure evaluated by SEM micrographs.

Results and Discussion

A dark-colored powder resulted from the reaction, highly agglomerated and with a spongy aspect. The XRD patterns of the as-obtained and the calcined powder are shown in Fig. 1. Before the calcination the powder is completely amorphous with no peaks, but after the calcination at 750ºC for 3 hours the generated pattern presents well defined peaks of the LSM rhombohedral perovskite (ICDD 01-089-0648), being also a very pure material.

SEM micrographs of the as-obtained powder revealed the agglomerates morphology which is very spongy and porous, as seen in Fig. 2(A). In Fig. 2(B) is the SEM micrograph of the calcined powder, very similar to the powder without any thermal treatment, which means that calcination did not modified significantly the agglomerates morphology, remaining a highly porous material.

This morphology in the agglomerates was expected since combustion synthesis can lead to superior interconnected porosity when compared to other methods such as solid state reaction[8], co-precipitation[9] and sol-gel[10], where the agglomerates tend to appear denser. The BET results indicated a specific surface area of 45 m²/g, demonstrating the influence of the fuel in the obtained powder morphology[4], which means that for the obtaining of porous materials for SOFC the combustion synthesis is, in fact, very promising due to the influence of the fuel in the powder morphology. It is possible that the use of sucrose leaded to a more viscous solution, trapping the gases that evolve from the reaction outlining this peculiar morphology.

TEM micrographs, in Fig. 3, also showed a very porous aspect in the particles. The formation of gas bubbles during the synthesis allowed this interesting morphology and putting together the SEM and TEM micrographs it is possible to comprehend the significant increase in the specific surface area over other methods[10] and other fuels[4].

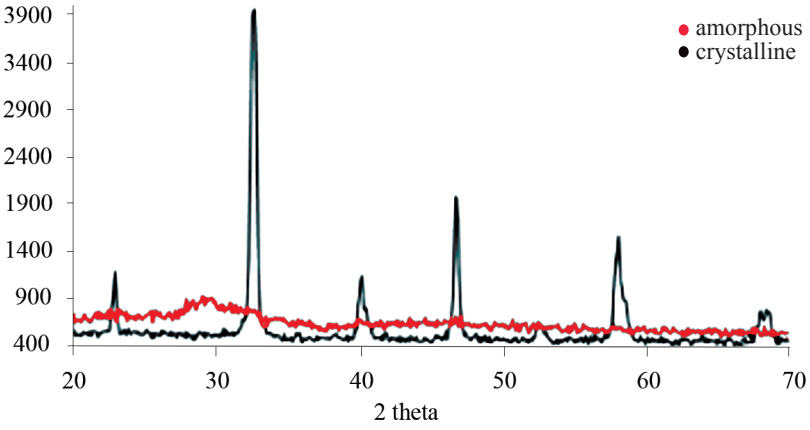

Figure 1. X-ray diffraction patterns of LSM as-obtained (amorphous) and after calcination (crystalline).

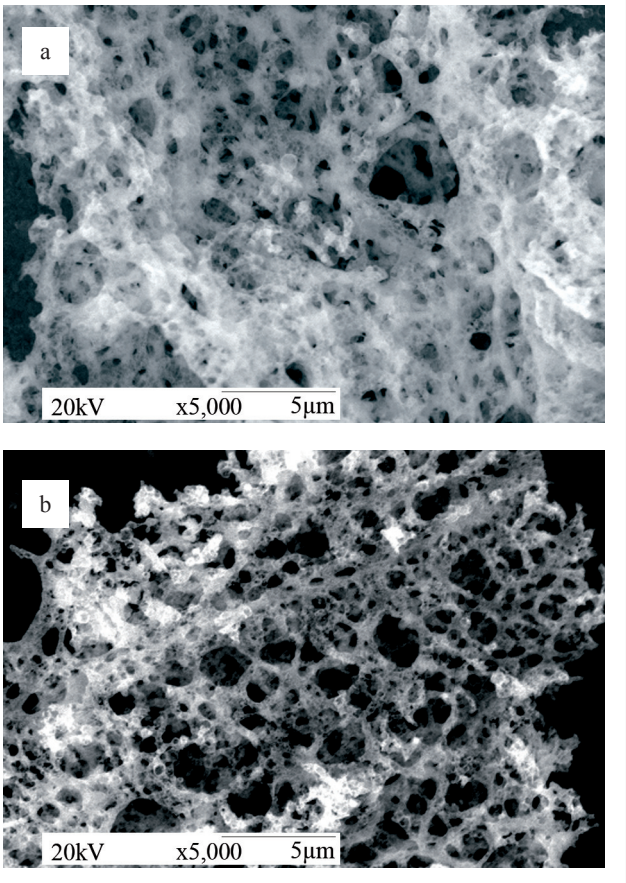

Figure 2. SEM micrographs with magnification of 5000x. (a) As-obtained powder, (b) After calcination.

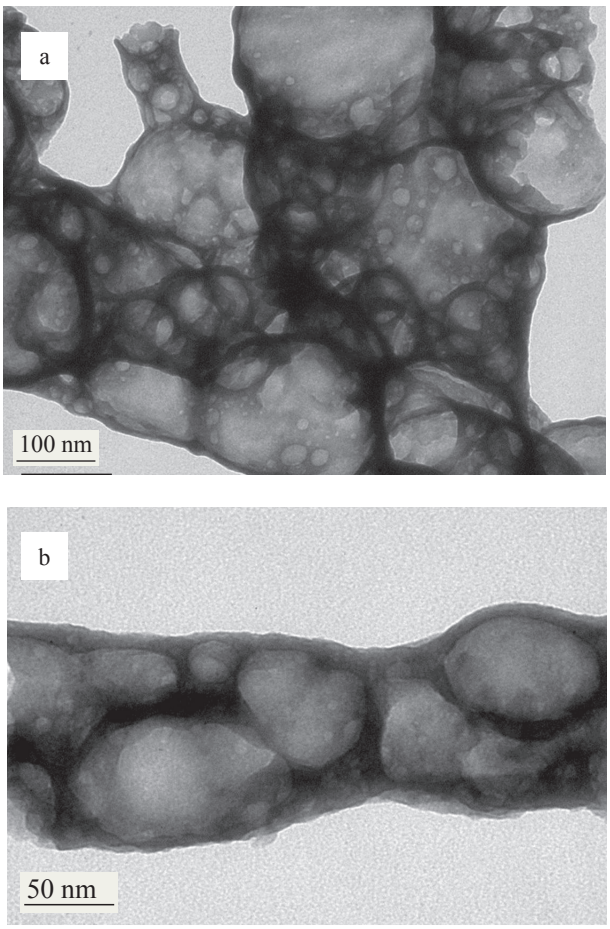

Figure 3. TEM micrographs of the as-obtained LSM powder.

In the Fig. 4 is the sintering curve of the ceramic bodies produced with the as-obtained powder. At higher temperatures higher densities were achieved and at 1050ºC a 31% open porosity was reached and, therefore, SEM micrographs were taken from this sample.

Top and cross-section micrographs of the sintered sample can be visualized in Fig. 5. The resulting microstructure has aggregates smaller than 1 µm and porosity evenly distributed throughout the bulk. In the cross-sectional micrograph it is possible to see that and interconnected

porosity courses the whole body, which is indispensable for the correct functioning of the cathode.

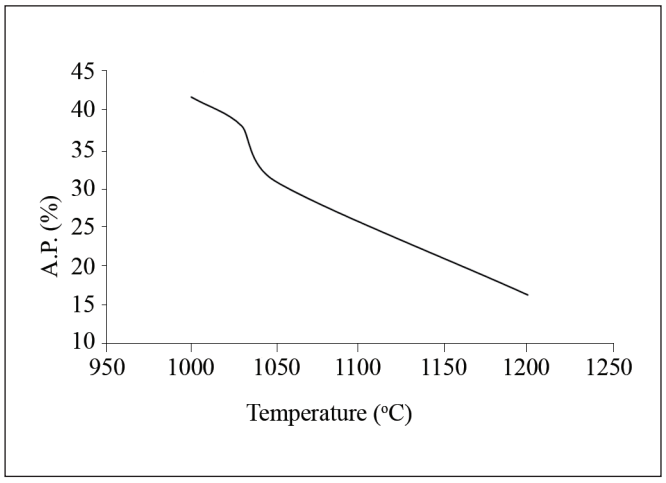

Figure 4. LSM sintering curve from the as-obtained powders.

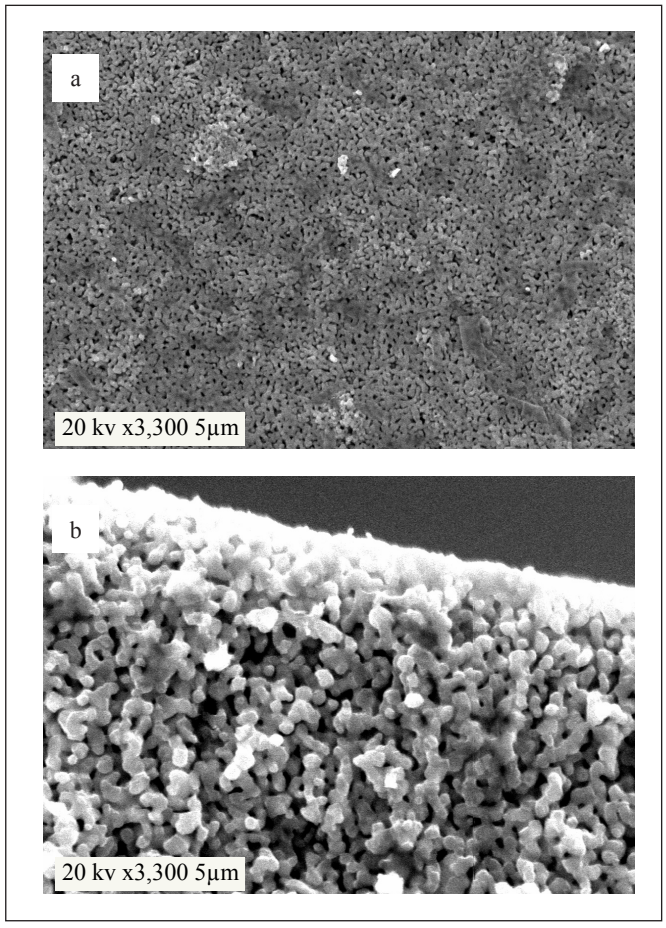

Figure 5. SEM micrographs of LSM sintered at 1050ºC. (a) Surface, (b) Cross-section.

Conclusions

Combustion synthesis has great potential in the obtaining of SOFC's cathodes, not only due to powders' purity, but also because of its morphological characteristics. Besides, the use of sucrose led to a specific surface area of 45 m²/g and through SEM and TEM micrographs it was observed a very porous powder and the formation of nanometric bubbles. When sintered at 1050ºC the LSM body presented an open porosity of 31%, within the limits for the desired application. SEM micrographs revealed a highly porous sintered body with an interconnected porosity, possibly as a feature of the starting combustion synthesized powder.

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