

Effect of a zirconia interlayer on the morphological properties of LaSrMnO₃-4YSZ composite films obtained by spin coating

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In this study, a chemical route was adopted to obtain strontium-doped lanthanum manganite (LaSrMnO₃ or LSM) powders in order to prepare LaSrMnO₃-4YSZ (4 mol% Y₂O₃) composite films by the suspension spin coating method onto 4YSZ and 8YSZ/8YSZ-NiO substrates with or without the application of a zirconia interlayer in the film/substrate interface. The multilayers were sintered at 1150 °C for 6 h and the effect of the interlayer on the morphological properties of the films has been investigated by scanning electron microscopy. The results show that in the less roughn substrates the application of the interlayer (~500 nm) not only improved the adhesion in the film/substrate interface, but also avoided new coating failures. All the films were porous, crack-free and with a thickness below 30 µm, desirable features for application as SOFC cathodes.

Key words: Composite cathodes, interlayer, microstructure, spin coating, SOFC.

Introduction

Strontium-doped lanthanum manganite (La_{1-x}Sr_xMnO₃ or LSM) has been considered one of the most promising cathode materials in solid oxide fuel cells (SOFCs) because of its excellent electrochemical performance, thermal and chemical stability and relatively good compatibility with a yttria-stabilized zirconia (YSZ) electrolyte. On the other hand, LSM is limited at reduced temperatures as a result of its low oxygen ion conductivity and high activation energy for oxygen dissociation. It is found that the addition of an electrolyte component to the LSM in the formation of the composite cathodes enhances electrochemical performance of the cathode. This is attributed to the extension of the three-phase boundary (TPB) areas from the electrolyte/cathode interface deep into the bulk cathode. The main problem of mixing LSM with YSZ is the formation of La₂Zr₂O₇ and SrZrO₃ compounds, which have conductivities lower than those of LSM and YSZ. These undesirable compounds are formed due to lanthanum and strontium atomic diffusion in the structure of zirconia, thereby negatively affecting the cell efficiency [1-5].

Several studies have reported the use of an interlayer between cathode and electrolyte materials in order to decrease the formation of these undesirable compounds [6-10], but we have no knowledge of reports which have

focused on the application of an interlayer in order to improve the adhesion in the cathode/electrolyte interface. There are many methods which can be used to deposit ceramic coatings such as dip-coating, screen printing, tape casting, plasma spraying and spin coating. We have selected the spin coating method due its short process time (only a few seconds per coating) and high uniformity over the surface. This process has been developed to fabricate porous cathodes and thin electrolyte layers with controlled microstructures for SOFC applications [11-12].

In this study, LSM-YSZ composite cathodes films were prepared by spin coating from ceramic suspensions consisting of LSM (50 wt.%), 4YSZ (50 wt.%), ethanol and a pore former onto two types of substrates: 8YSZ-NiO supported 8YSZ films (8YSZ/8YSZ-NiO) and 4YSZ pellets. The main aim of this study is focused on the influence of a zirconia interlayer (obtained in the film/substrate interface) on the morphological properties of the LSM-YSZ films.

Experimental

The polymeric precursor method was used to synthesize strontium-doped lanthanum manganite (La_{0.85}Sr_{0.15}MnO₃, LSM 15 and La_{0.78}Sr_{0.22}MnO₃, LSM 22) powders for fabrication of composite cathodes after mixture with commercially available 4YSZ powder (4% mol yttria-stabilized zirconia - Tosoh Corporation, Japan). Details of the LSM preparation method are described in our previous report [13]. The precursor powders of LSM phases were calcined at 700 °C for 2 h in air atmosphere at a heating rate of 3 K·minute⁻¹. Powder X-ray diffraction (XRD)

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data were obtained using a Shimadzu 7000 diffractometer with Cu K α radiation. Intensities were obtained in the 2θ range between 20° and 80° with a step size of 0.02° and a measuring time of 6 s at each step. The crystallite size was calculated through Rietveld XRD data refinement with the program BDWS-9807. The FWHM corrections were made with lanthanum-hexaborate (LaB₆). Particle size distribution analyses were performed by laser scattering (Cilas 1064 granulometer). The 4YSZ powder was compressed into pellets (15 mm in diameter) under a uniaxial pressure of 74 MPa. The pellets were sintered in air at 1500°C for 4 h to increase their mechanical strength for application as substrates in the films deposition step.

LSM and 4YSZ powders were mixed in a weight ratio of 1 : 1 and the mixture was ball-milled for 2 h in ethanol to form the LSM-4YSZ composite cathodes. The powders were dried and sieved through 100 mesh. As a pore former, 12.5 wt.% of ethyl cellulose was added to the mixture, which was subsequently ball-milled for other 24 h to form ceramic suspensions. The solvent was ethanol and the liquid/solid volume ratio was 14. LSM 15/4YSZ and LSM 22/4YSZ composite cathodes films were prepared onto 4YSZ (sintered in the laboratory) and 8YSZ/8YSZ-NiO (Forschungszentrum Jülich-FZJ, Germany) substrates by a suspension spin coating method (KW-4A spin-coater, Chemat Technology) at a rotation speed of 3000 rpm for 30 seconds. This process was repeated for 20 times to achieve the required film thickness. To avoid cracks or pores induced by evaporation of the organics during the sintering, the multilayers were heated at 400°C for 2 h with a heating rate of $2\text{ K}\cdot\text{minute}^{-1}$ in an air atmosphere.

The surface roughness of the substrates was measured by digital equipment from Taylor Hobson, model Surtronic 25. The effect of a zirconia interlayer (Fig. 1) prepared by spin coating of the polymeric resin in the film/substrate interface has been investigated. Finally, the composite films (with or without interlayer) obtained onto different substrates were sintered at 1150°C for 6 h and studied using scanning electron microscopy (SEM, Shimadzu

SSX-550 at 25 kV).

Results and Discussion

As shown in Fig. 2, LSM 15 and LSM 22 powders calcined at 700°C for 2 h possess the perovskite structure of the strontium-doped lanthanum manganite. The crystal structures obtained are rhombohedral with space group $R\bar{3}c$, in accord with the literature [14-15] and the average crystallite size for both powders was $\sim 20\text{ nm}$. These results were confirmed by Rietveld calculations. It should be mentioned that the LSM powder, which was prepared by the polymeric precursor method, has such a small crystallite size and high surface energy that it typically forms aggregates [16].

A secondary phase was found and identified as La₂O₃ in both compositions, LSM 15 and LSM 22, which were quantified, as 3.06 mol% and 1.71 mol%, respectively. This phase is formed due to the decomposition of (LaO)₂CO₃, proceeding from the incomplete complexation of the ions La³⁺. One way to avoid the crystallization of secondary phases is changing some synthesis parameters. It is necessary to obtain a better metallic cations complexation at the citrate formation step, increasing the time for La³⁺ complexation, for example.

In order to further investigate the agglomerate property of the LSM 15, LSM 22 and 4YSZ powders, their particle size distributions were measured and the comparative result was shown in Fig. 3. The LSM powders presented similar particles/agglomerates size distribution range. The average particle/agglomerate sizes were 1.09 and $1.63\text{ }\mu\text{m}$ and the average sizes at 50% (d_{50}) were 0.98 and $1.59\text{ }\mu\text{m}$, respectively for LSM 15 and LSM 22. The LSM 22 powder presents slightly higher degree of agglomeration. The small average size and d_{50} difference is due to the non occurrence of a statistic al normal distribution of the particle/agglomerate size curves. Upon comparison of the particle size distribution data with the XRD results, it

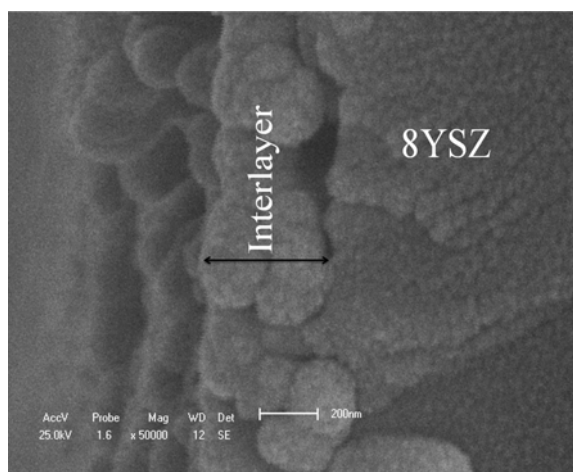


Fig. 1. SEM micrograph of the zirconia interlayer.

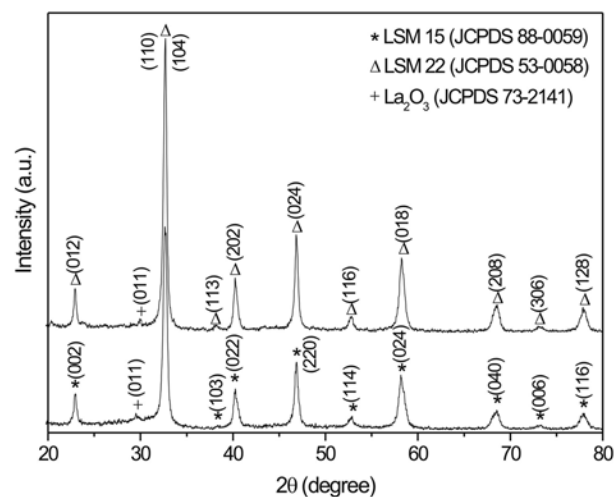


Fig. 2. XRD patterns of the LSM 15 and LSM 22 powders calcined at 700°C for 2 h.

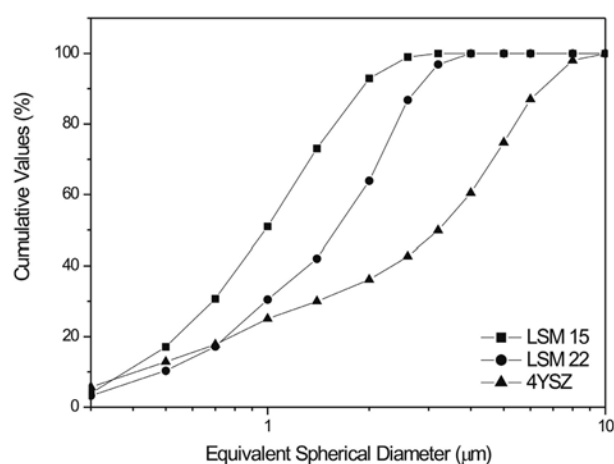


Fig. 3. Particle size distribution curves of the powders.

could be concluded that each particle of the LSM powders is still an agglomerate of finer primary particles rather than a single-crystalline particle. The 4YSZ powder showed a particle size distribution range with an average size at 50% (d_{50}) of 3.21 μm . Such granulometries are adequate for the preparation of LSM-YSZ composite cathodes obtained by deposition of ceramic suspensions.

SEM micrographs of the pore structures of the films deposited onto different substrates are shown in Fig. 4. The surface porosity of these films was calculated using image processor software (Image-Pro Plus), finding the values of 18.2, 11.8, 11.3 and 20.5%, to the samples (a), (b), (c) and (d), respectively. It was observed that the type of substrate has an influence on the film porosity. On the films deposited onto the same substrate, it was notable that the microstructures with the most homogeneous fine particle distributions developed more porosity, on the other hand, the less porous films were those with more particle agglomeration. The average pore diameter was also calculated by image analyses, being found to be between 219 and 294 nm. The surface microstructures more adequate for application as composite cathode for solid oxide fuel cell show a small particle size, high porosity and high specific surface areas, allowing fast oxygen diffusion through the cathode [17]. The reduction in sintering temperature to 900-1000 $^{\circ}\text{C}$ could result in microstructures with more fine particles and a higher porosity, due to the lower densification of the films.

Fig. 5 shows SEM micrographs of the film/substrate interface of LSM-YSZ composites films deposited onto 8YSZ/8YSZ-NiO (with a zirconia interlayer) and 4YSZ (without a zirconia interlayer) substrates. The surface roughness found for the 8YSZ/8YSZ-NiO and YSZ substrates were 356 and 522 nm, respectively. It was observed that for the less rough substrate the application of a zirconia interlayer can avoid new coating failures. Although, a higher roughness of the 4YSZ substrate made possible a higher adhesion in the film/substrate interface and attainment of composite films free of imperfections

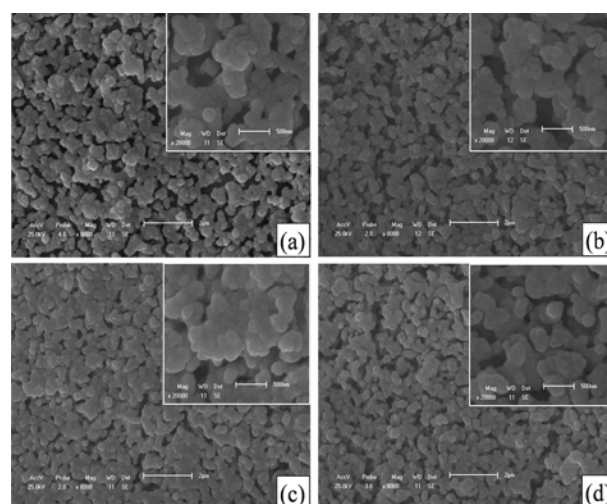


Fig. 4. SEM micrographs of the pore structures of the films deposited onto 8YSZ/8YSZ-NiO (with an interlayer): (a) LSM 15-4YSZ film and (b) LSM 22-4YSZ film; and onto 4YSZ (without an interlayer): (c) LSM 15-4YSZ film and (d) LSM 22-4YSZ film.

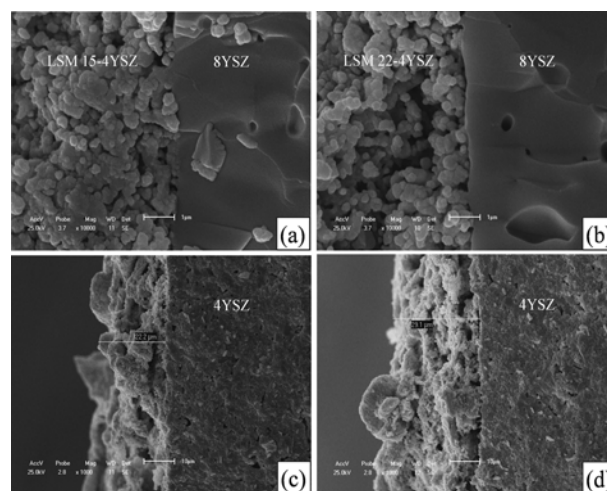


Fig. 5. SEM micrographs of the film/substrate interface: (a) LSM 15/4YSZ film and (b) LSM 22/4YSZ film, both onto 8YSZ/8YSZ-NiO (with an interlayer); (c) LSM 15/4YSZ film and (d) LSM 22/4YSZ film, both onto 4YSZ (without an interlayer).

on the surface without the use of a coating. SEM images display that the application of the interlayer (Fig. 1) improves the adhesion in the film/substrate interface (Fig. 5(a)-(b)), while Fig. 5(d) illustrates the lower adhesion of the film while the zirconia interlayer is not used. Independent of the type of substrate used were attained composite films were attained with thickness varying between 19 and 29 μm . Specialized literature reports that this is the ideal thicknesses for a LSM-YSZ film to act as a functional cathode layer in a SOFC, in not having significant changes in its electro catalysts activity to O_2 reduction.

Conclusions

LSM powders obtained by the polymeric precursor method

and commercial 4YSZ powders have been successfully used to prepare LSM-4YSZ composite films by a suspension spin coating method. Particle size distribution analyses showed that the granulometries of the starting powders were adequate to prepare of ceramic suspensions for film depositions. The porosity of films is influenced by the type of substrate used, higher values being observed in the microstructures with a more homogeneous fine particle distribution. The application of a zirconia interlayer has been shown to be an efficient alternative to improve adhesion in the film/substrate interface. A film with a higher potential for application as a composite cathode for a SOFC was attained by deposition of a ceramic suspension LSM15-4YSZ onto 8YSZ/8YSZ-NiO, this film had the porosity, thickness and adhesion adequate for a good electro catalysts activity to O_2 reduction.

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