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Porosity Control of LSM/YSZ Cathode Coating Deposited by Electrospraying

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The deposition of a composite electrode, which consisted of a mixture of a solid electrolyte (YSZ) and an electrocatalytic material (LSM), on an YSZ substrate was studied using the electrostatic spray deposition (ESD) technique. Films with various morphologies were obtained. The surface morphology was strongly influenced by the deposition temperature, precursor solution flow rate, and nozzle to substrate distance as a function of the nature of precursor solution. Processes involved in the porous film formation were discussed. Powder X-ray diffraction analysis showed that only the LSM hexagonal phase and the cubic YSZ phase were formed in the LSM/YSZ composite cathode after thermal treatment at 800 °C.

Introduction

Main issues in solid oxide fuel cells (SOFCs) development are recently focused on cost reduction and improvement of durability in long-term operation. In this context, SOFCs will be operated at reduced temperature from the traditional 1000 to 800 °C. Consequently, detrimental chemical reactions between the electrode materials and electrolyte will be avoided. A decrease in the operating temperature can be achieved by improving the electrode performance, that is, reducing the electrode overpotentials especially at the cathode. In general, two research directions are suggested in the literature: (i) optimizing the microstructure of the electrochemically active layers,[1] and (ii) a replacement of pure electronic conductor cathode by mixed ionic electronic conductor (MIEC).[2,3]

Composite cathodes consisting of a mixture of strontium-doped lanthanum manganite (LSM) and the electrolyte materials such as yttria-stabilized zirconia (YSZ) or gadolinia-doped ceria (GDC) are regarded as promising cathodes for the intermediate temperature solid oxide fuel cells. Steele et al.[4] concluded that composite electrodes not only provide very effective electronic and ionic pathways to electrode/electrolyte interfaces, but also enhance the injection of mobile charged oxygen surface species into the YSZ electrolyte. Addition of YSZ to the LSM cathode improved the adhesion of the electrode onto the YSZ substrate and significantly enlarged the triple phase boundary (TPB) area, where the gas, the electrode, and the electrolyte are in contact.[3] The enlargement of the TPB area has led to a pronounced improvement in electrochemical performance of the LSM/YSZ composite cathode. Also, the composite cathodes consisting of the GDC and the LSM have better electrochemical performance than the cathode consisting of LSM alone.[5] Perry Murray et al.[6] have compared the electrochemical performance of the pure LSM and composite LSM/GDC cathode. The results have shown that the addition of GDC to LSM yielded 7 times lower interfacial resistance as compared to LSM. Hayashi et al.[7] also have observed low cathodic overpotential in the case of adding YSZ to LSM. Jorgensen et al.[8] have reported that composite LSM/YSZ cathodes under 0 dc polarization showed little or no degradation.

The chemical reaction between the LSM and the YSZ can cause a degradation of the composite cathode. A-deficient perovskites or B-site hyperstoichiometric perovskites seem to be favorable candidates due to their decreased tendency to form insulating zirconates such as $La_2Zr_2O_7$, $SrZrO_3$ at the YSZ/LSM interfaces. Therefore, in this work, we have selected the $(La_{0.85}Sr_{0.15})_{0.95}MnO_{3-\delta}$ composition as previously reported.[9] The composite cathodes consisting of 40% YSZ and 60% LSM were chosen, because the addition to the cathode of up to 40% YSZ improved its performance as has been shown by Østergård et al.[2] and Deseure et al.[10]

The electrostatic spray deposition (ESD) technique provides the potential to produce a large variety of ceramic thin films. In the ESD technique, a precursor solution is atomized into charged droplets by an electrohydrodynamic force. As

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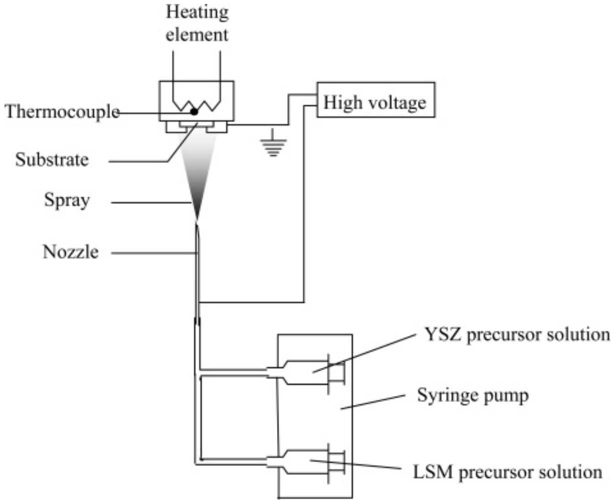

Figure 1. Experimental setup.

compared to the other spray deposition techniques, ESD is particularly advantageous in tailoring the film morphology. Depending on deposition conditions, films of different surface morphologies, ranging from dense to very porous, were obtained by ESD.[11] Additionally, the technique offers the advantages of simple and cheap equipment, ease of up-scaling, wide choice of precursors, high deposition efficiency, easy composition control, and ambient atmosphere operation.

The aim of the present work is to prepare composite LSM/YSZ films with different morphologies using the ESD technique. The influence of the process parameters on the film porosity will be studied to find the process parameter window (temperature, flow rate, or distance) for the deposition of a controlled microstructure.

Experimental Section

The LSM/YSZ cathodes were prepared using a vertical ESD setup shown in Figure 1. The ESD technique involves atomization of precursor solution to an aerosol, which is then directed by an electric field to heated substrate, where a film is formed. To feed two separate precursor solutions simultaneously, the configuration with two separated feed-pipes and syringes was used. The two feed-pipes were connected at the nozzle. The two syringes containing precursor solutions were pushed at the same velocity. So, in all experiments, both LSM and YSZ precursor solutions were delivered to the nozzle at the same flow rate.

LSM/YSZ composite films were deposited on a hot-pressed polycrystalline YSZ substrate. Disks of homemade YSZ were 20 mm in diameter and 1 mm in thickness.

The precursor solution for LSM consisted of lanthanum nitrate, $La(NO_3)_3 \cdot 6H_2O$, 99% (Fluka), strontium chloride, $SrCl_2 \cdot 6H_2O$, 99% (Aldrich), and manganese nitrate, $Mn(NO_3)_2 \cdot 4H_2O$, 98% (Aldrich), dissolved in the 33 vol % of ethanol, C_2H_5OH, 99.9% (Prolabo), and 67 vol % of diethylene glycol monobutyl ether (butyl carbitol), $CH_3(CH_2)_3OCH_2CH_2OCH_2CH_2OH$, 99+% (Acros Organics). The precursor solution was prepared according to the stoichiometry of the required film $La_{0.8075}Sr_{0.1425}MnO_{3-\delta}$. The total concentration of the salts in the solution was 0.024 mol/L.

The YSZ precursor solutions were prepared according to the stoichiometry of the required film $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$. Yttrium chloride $YCl_3 \cdot 6H_2O$ (Alfa Aesar) and either Zr acetylacetonate $Zr(C_5H_7O_2)_4$ (Fluka Chemie) or zirconyl nitrate hydrate $ZrO(NO_3)_2 \cdot$aq (Fluka Chemie) were dissolved in two different solvent mixtures. A solvent mixture contained 67 vol % of butyl carbitol and 33 vol % of either ethanol or water. The total concentration of the salts in this solution was 0.016 mol/L. Two different precursor solutions were prepared. One was Zr acetylacetonate dissolved in ethanol, denoted as YSZ1. A second was zirconyl nitrate dissolved in water, denoted as YSZ2. Each of the solutions contained yttrium chloride and 67 vol % of butyl carbitol.

The deposition time was 1 h. The flow rate of precursor solution was varied from 0.33 to 1.17 mL/h using a Sage M361 syringe pump. The precursor solution was atomized using a positive high voltage from 6 to 10 kV. The deposition temperature ranged from 300 to 375 °C. The nozzle-to-substrate distance varied from 27 to 47 mm.

Surface morphologies were analyzed using scanning electron microscopy (SEM) (LEO 400).

Samples were postannealed at a heating rate of 2 °C/min in air for 1 h at 800 °C to investigate the influence of thermal treatment on the morphology and on the reactivity products.

X-ray powder diffraction was carried out using a Siemens D500 $\theta/2\theta$ diffractometer in the Bragg Brentano geometry from 25° to 95° in 2θ (0.04° in 2θ step, 8 s as a counting time) with Fe Kα radiation ($\lambda = 0.1936$ nm). Phases were identified using DIFFRAC-AT software systems (Socabim, Paris).

Results and Discussion

Porosity Control by the Deposition Temperature. In this study, we have used only one precursor solution for LSM and two different YSZ precursor solutions for the deposition of the LSM/YSZ composite layer. The effect of the deposition temperature on the composite layer porosity will be discussed for the different YSZ precursor solutions.

Figure 2 shows different surface morphologies of composite LSM/YSZ films deposited from precursor solutions LSM and YSZ1 (Zr acetylacetonate in ethanol) at different temperatures ranging from 300 to 375 °C. At 300 °C, the film is porous but cracked as shown in Figure 2a. Indeed, a large volume change occurred during the drying process of a large quantity of liquid on the substrate at the lowest deposition temperature. Therefore, the stresses have been developed and caused the film cracking. Porous films are obtained at higher temperatures, that is, 325 °C (Figure 2b) and 350 °C (Figure 2c). At higher temperature, the arriving droplets contain less solvent. Therefore, during the drying step, a smaller volume change occurs, and consequently stresses disappeared leading to crack-free films. The porous microstructure (Figure 2a,b,c) can be the consequence of simultaneous boiling and drying of precursor solution, which is possible when substrate surface temperature is close to the boiling point of the solvent.[12] It is the case with butyl carbitol, which presents a 230 °C boiling point. Finally, at the highest deposition temperature (Figure 2d), the film is dense with some particles on the surface. Faster evaporation of solvent at 375 °C leads to a smaller amount of liquid carried by droplets to the substrate. Therefore, simultaneous boiling and drying is not possible anymore due to the

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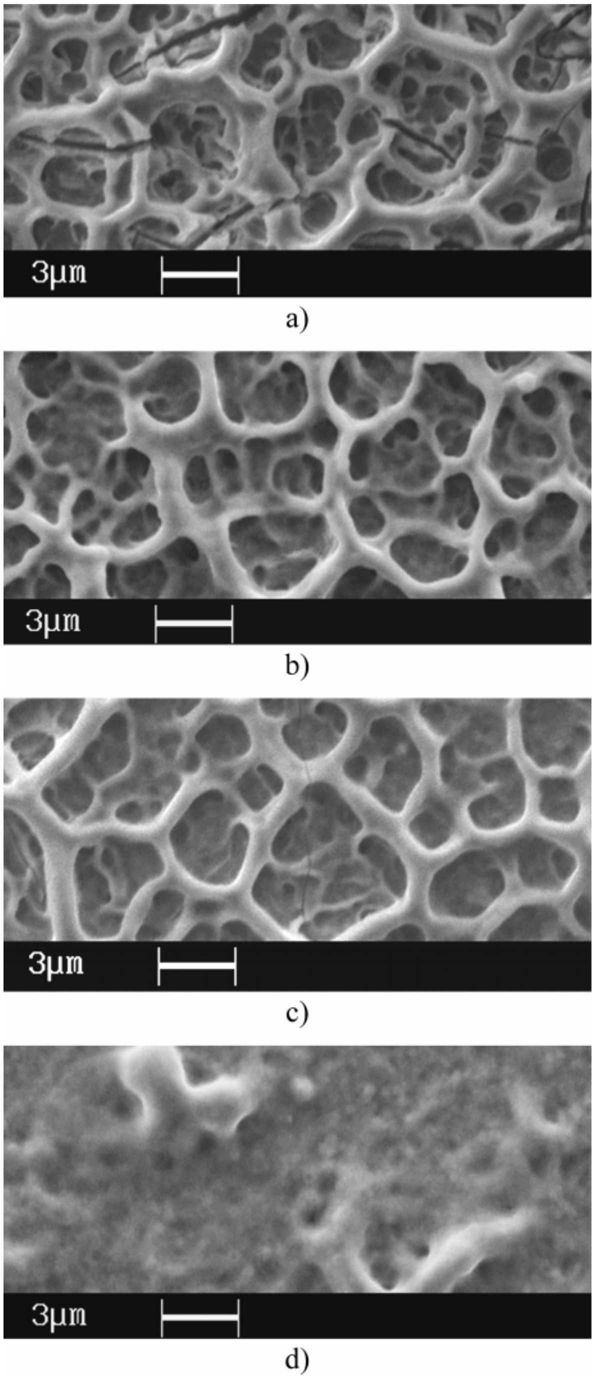

Figure 2. Influence of deposition temperature on the morphology of LSM/YSZ coatings: (a) 300 °C, (b) 325 °C, (c) 350 °C, and (d) 375 °C. Precursor solutions: LSM and YSZ1. Solution flow rate: 0.50 mL/h. Deposition time: 1 h. Nozzle to substrate distance: 27 mm.

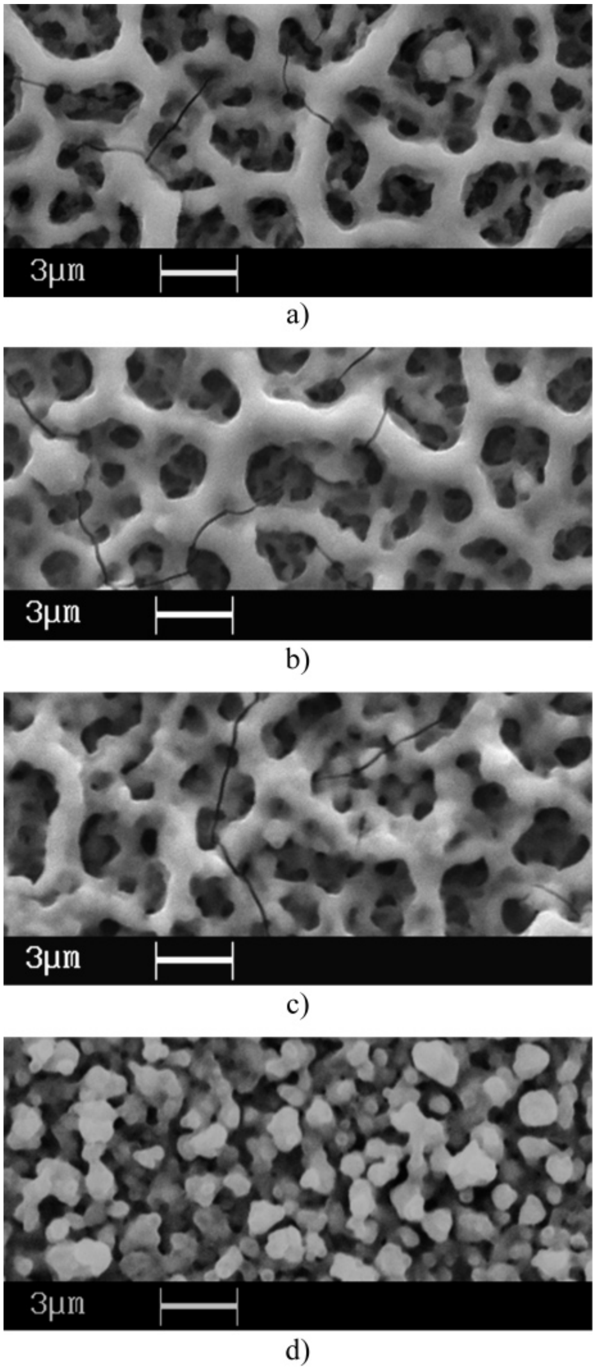

Figure 3. Influence of deposition temperature on the morphology of LSM/YSZ coatings: (a) 300 °C, (b) 325 °C, (c) 350 °C, and (d) 375 °C. Precursor solutions: LSM and YSZ2. Solution flow rate: 0.50 mL/h. Deposition time: 1 h. Nozzle to substrate distance: 27 mm.

deficiency of liquid for boiling. Consequently, dense film was formed.

Figure 3 shows different surface morphologies of composite LSM/YSZ films deposited using precursor solutions LSM and YSZ2 (zirconyl nitrate in water) at different temperatures ranging from 300 to 375 °C. All films were porous in the temperature range. The microstructure obtained at 300, 325, and 350 °C (Figure 3a,b,c) can be the consequence of simultaneous boiling and drying of precursor solution. At 375 °C (see Figure 3d), a different type of porous microstructure was obtained surprisingly at only 25 °C above. The agglomeration of interconnected particles was formed instead of the net-like structure. At 375 °C, the arriving droplets do not contain enough solvent for the formation of liquid film. The droplets do not spread rapidly; they just stick to the previously arrived particles or to the substrate surface. So, the spreading step is different for Zracac in ethanol and zirconyl nitrate in water at the same experimental conditions.

The film obtained using the YSZ2 precursor solution containing water and zirconyl nitrate (Figure 3a) has less cracks and is more three-dimensionally porous as compared to the one that was deposited by spraying the YSZ1 precursor solution containing ethanol and Zracac (Figure 2a). It is difficult to give a clear interpretation of these experimental

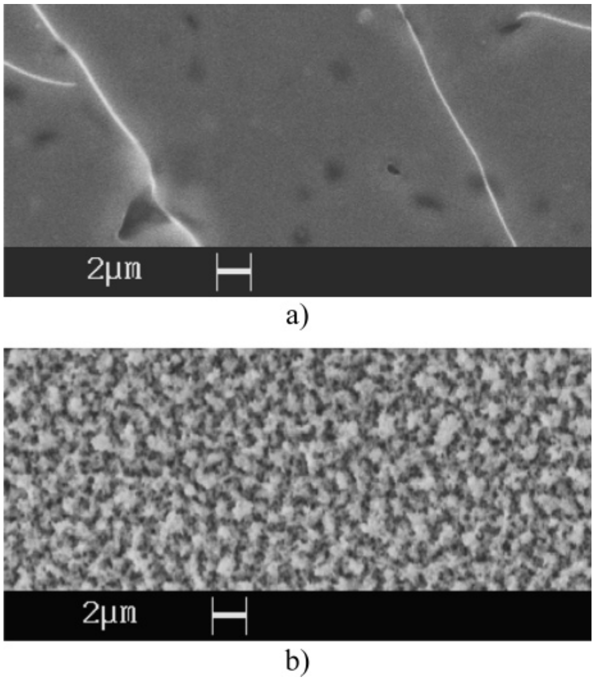

Figure 4. Influence of the zirconium salt nature on the morphology of YSZ coatings: (a) Zracac, (b) zirconyl nitrate. Solvent: 33 vol % ethanol + 67 vol % butyl carbitol. Precursor solution flow rate: 0.5 mL/h. Deposition temperature: 300 °C. Deposition time: 1 h. Nozzle to substrate distance: 27 mm.

results. A possible explanation can be the effect of zirconium salt nature. Figure 4 demonstrates the effect of the zirconium salt nature on the film morphology. Dense, cracked YSZ film was obtained in the case of Zracac (Figure 4a). In contrast, porous and crack-free YSZ film was deposited when the zirconyl nitrate was used as precursor (Figure 4b). Therefore, the LSM/YSZ film is cracked (Figure 2a) when deposited at 300 °C by spraying the YSZ1 (containing Zracac) and LSM precursor solutions. Zirconyl nitrate promotes the growth of a porous layer as demonstrated in Figure 4b. Consequently, the LSM/YSZ film was less cracked and more homogeneously porous when the YSZ2 (containing zirconyl nitrate) and LSM precursor solutions were used for deposition (Figure 3a).

Usually at 375 °C, droplets arriving to substrate contain mostly precursor salts and butyl carbitol solvent (67 vol %), because ethanol or water evaporates much faster as compared to the butyl carbitol (boiling point 230 °C). Furthermore, Zracac is better soluble in butyl carbitol than zirconyl nitrate. Therefore, the precipitation in the YSZ2 droplets occurred, whereas still liquid droplets arrived to the substrate in the case of YSZ1. This could lead to the formation of dense film for YSZ1 and agglomeration of interconnected particles for YSZ2.

Porosity Control by Flow Rate. We have demonstrated that the deposition temperature plays an important role in the formation of a porous film. Furthermore, the other spray parameters such as the flow rate of precursor solution and the nozzle to substrate distance can influence the film morphology. For instance, the flow rate of a precursor solution can influence the porosity of a film, because it controls the amount of solution deposited on the substrate. In the following, we have studied the influence of the flow rate using the precursor solutions LSM/YSZ1 and LSM/YSZ2, respectively.

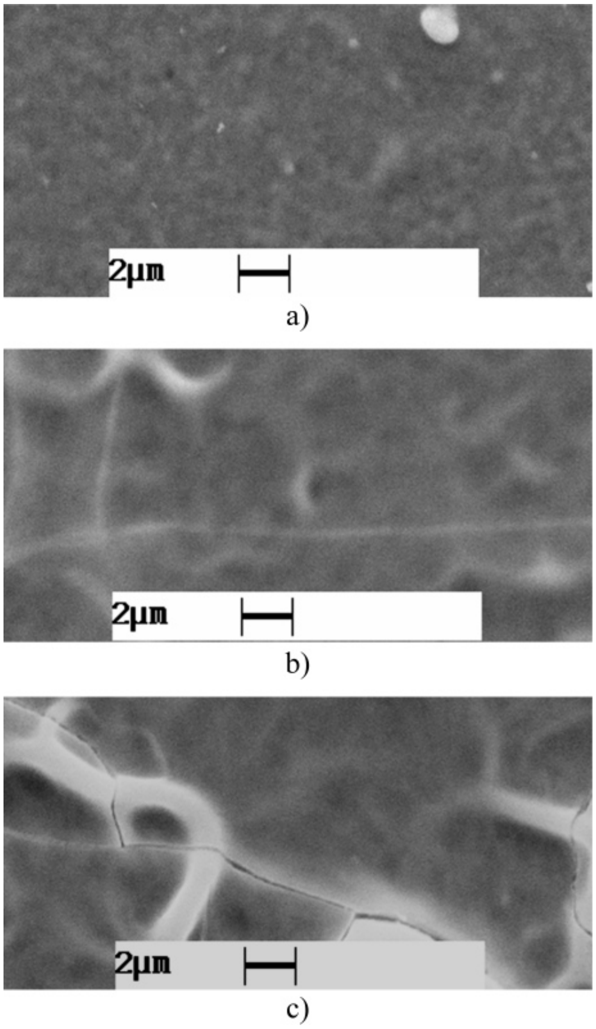

Figure 5. Influence of precursor solution flow rate on the morphology of LSM/YSZ coatings: (a) 0.50 mL/h, (b) 0.67 mL/h, and (c) 1.17 mL/h. Precursor solutions: LSM and YSZ1. Deposition temperature: 300 °C. Deposition time: 1 h. Nozzle to substrate distance: 37 mm.

Figure 5 shows surface morphologies of composite LSM/YSZ films deposited by spraying the precursor solution LSM and YSZ1 at three different flow rates: 0.50, 0.67, and 1.17 mL/h. The films are not porous at all flow rates. Dense, smooth film was obtained at the flow rate of 0.50 mL/h (see Figure 5a). The liquid layer on the substrate was not present at this low flow rate, because not enough solution was deposited on the substrate. Consequently, boiling of a layer was not possible. Therefore, dense coating was obtained.

At higher flow rates of 0.67 and 1.17 mL/h (see Figure 5b and c), netlike structure occurs on the film surface, but film morphology still remains dense. Additionally, some small cracks appeared due to the stresses originating from the too fast drying.

Completely different morphologies at the same experimental conditions were obtained in the case of spraying the LSM and YSZ2 precursor solutions. Figure 6 shows the resulting surface morphologies of composite LSM/YSZ films deposited at different precursor solution flow rates ranging from 0.50 to 1.17 mL/h. In contrast to the YSZ1 precursor solution, the deposited films were porous at all flow rates.

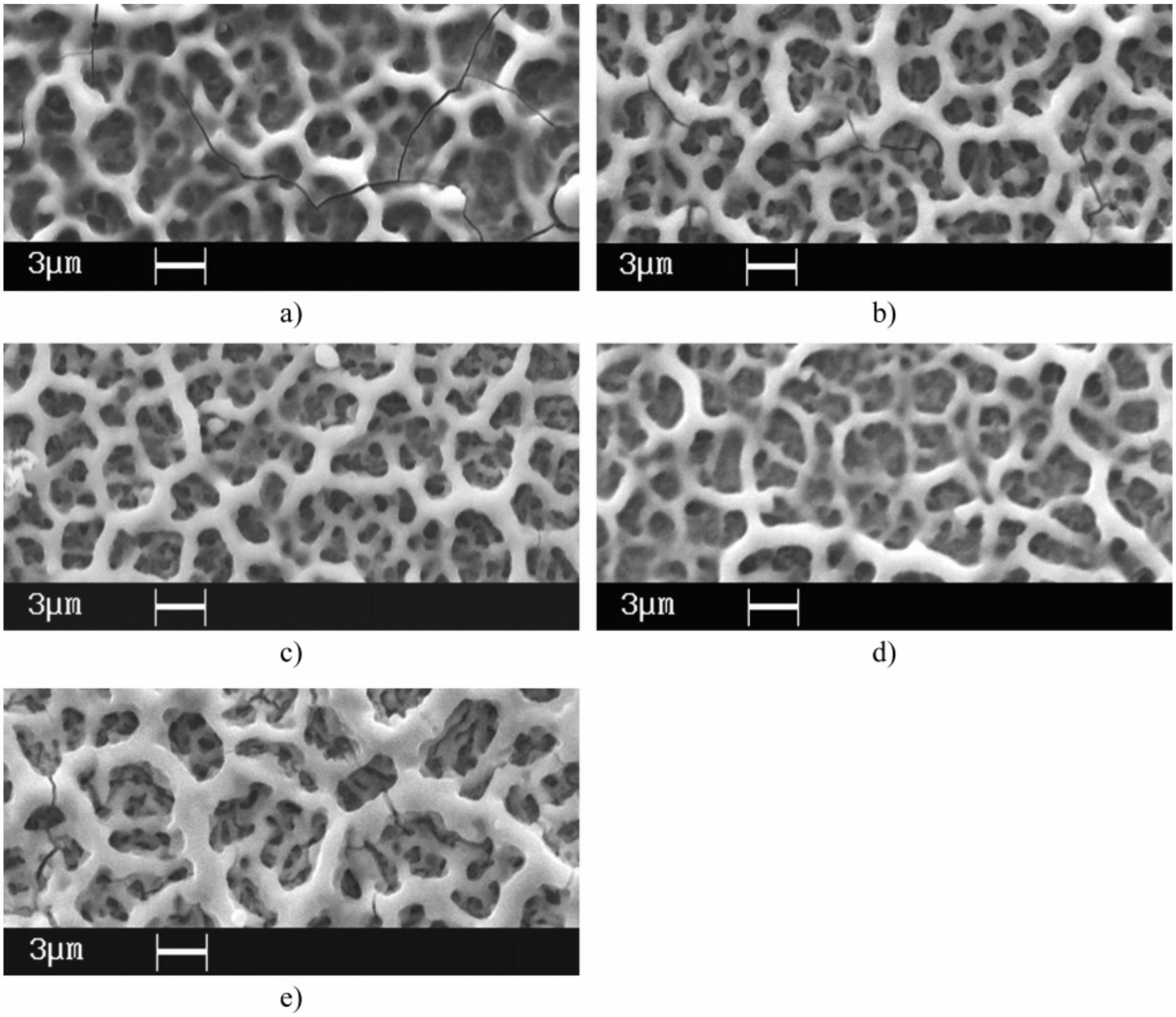

Figure 6. Influence of precursor solution flow rate on the morphology of LSM/YSZ coatings: (a) 0.33 mL/h, (b) 0.50 mL/h, (c) 0.67 mL/h, (d) 0.86 mL/h, and (e) 1.17 mL/h. Precursor solutions: LSM and YSZ2. Deposition temperature: 300 °C. Deposition time: 1 h. Nozzle to substrate distance: 37 mm.

At the lowest flow rate (see Figure 6a), the surface morphology seems to be slightly denser as compared to that of films deposited at higher flow rates. The most “three-dimensional” network (see Figure 6e) was obtained at the highest flow rate with the appearance of a few cracks as in the case of YSZ1 (Figure 5c). It can be concluded that films deposited by spraying a precursor solution that contains the Zracac have a tendency to be dense. In contrast, when zirconyl nitrate-containing solutions are sprayed, films tend to be more porous.

So, it was observed that the type of precursor salt and solvent could change the film growth mechanism as in the case of varying the deposition temperature.

Porosity Control by the Nozzle to Substrate Distance. The amount of precursor solution arriving onto the substrate is also controlled by the nozzle to substrate distance. The shorter the distance is, the larger amount of precursor solution is deposited on the substrate. Therefore, we could expect to control the film porosity by changing the nozzle to substrate distance, in the same way as the influence of flow rate in terms of quantity of precursor solution arriving on the substrate. Here also, two YSZ precursor solutions will be compared.

Figure 7 shows surface morphologies of composite LSM/YSZ films obtained by spraying the LSM and YSZ1 precursor solutions at different nozzle to substrate distances ranging from 27 to 47 mm. At longer distances of 47 and 37 mm (see Figure 7a and b), dense and smooth films were deposited due to the absence of a boiling liquid layer during the deposition. The continuous liquid layer was not formed, because a smaller quantity of droplets has reached the substrate and the arrived droplets contain less solvent due to longer time for transportation from the nozzle to the substrate. The condition for simultaneous boiling and drying of liquid layer on the substrate was obtained when the nozzle to substrate distance ranged from 34 to 27 mm (see Figure 7c−f). The film morphology starts to change from dense to porous at 34 mm distance (see Figure 7c) where reticular network was observed on the dense film surface. Some films present a few small cracks (see Figure 7c,d) due to the stresses, which resulted from a too large volume change during the drying of liquid layer. Furthermore, a crack-free porous layer has been obtained for an intermediate distance (29 mm, see Figure 7e). In this case, the propagation of cracks was reduced by a porous microstructure of the layer. More and larger cracks appear again when the nozzle to

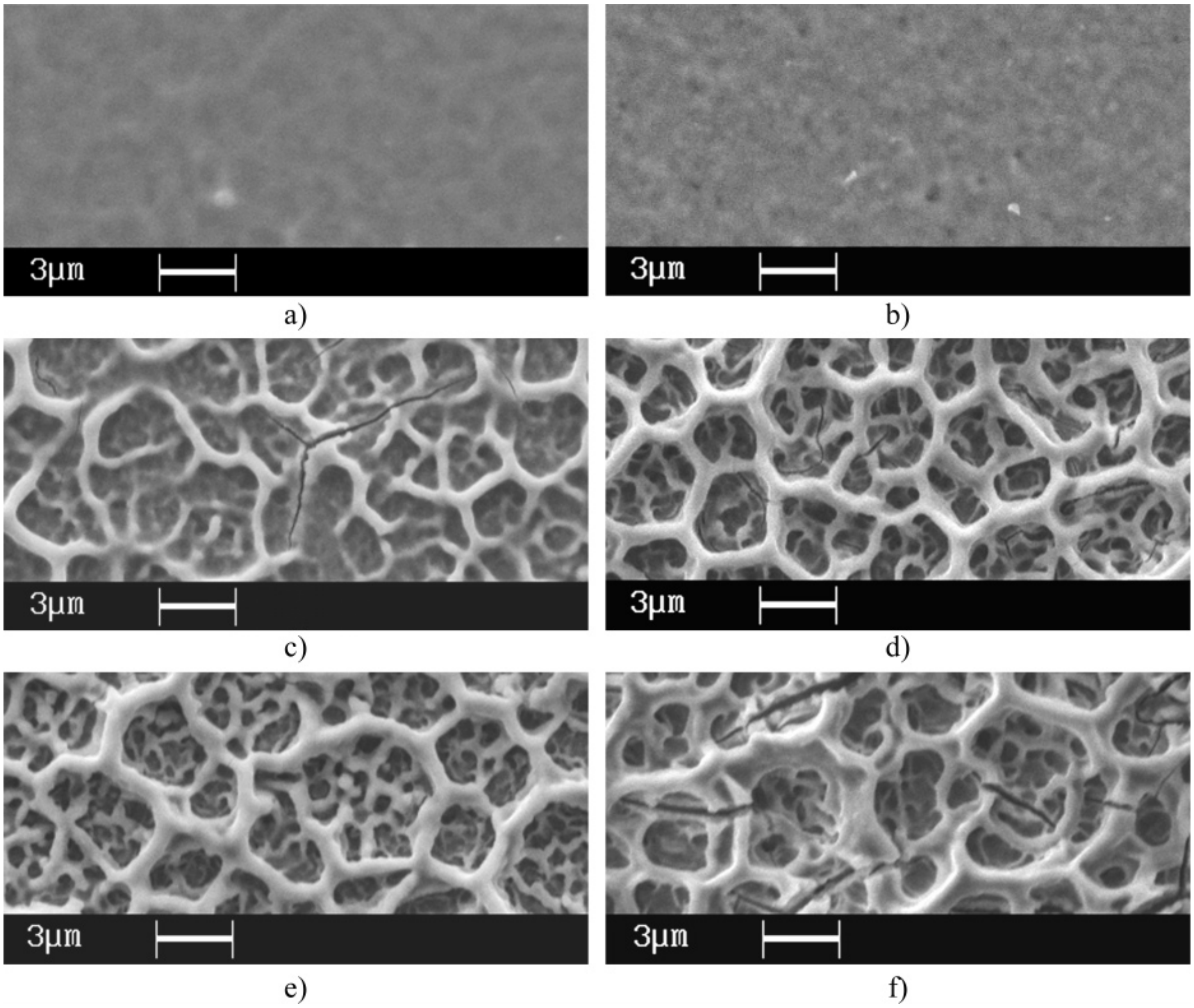

Figure 7. Influence of nozzle to substrate distance on the morphology of LSM/YSZ coatings: (a) 47 mm, (b) 37 mm, (c) 34 mm, (d) 32 mm, (e) 29 mm, and (f) 27 mm. Precursor solutions: LSM and YSZ1. Deposition temperature: 300 °C. Solution flow rate: 0.5 mL/h. Deposition time: 1 h.

substrate distance is shortened (see Figure 7f). Indeed, a thicker liquid layer is now present and leads to larger stresses during drying.

The influence of nozzle to substrate distance on the surface morphology of composite LSM/YSZ films obtained using the LSM and YSZ2 precursor solutions is shown in Figure 8. A larger process parameter window for deposition of porous film was obtained in this case as compared to the YSZ1 precursor solution. In the case of the YSZ2 precursor solution, all of the coatings were porous for nozzle to substrate distances ranging from 27 to 47 mm. The difference can be explained by the type of zirconium salt and its solubility in butyl carbitol as discussed previously in Figure 4.

So, we have found a behavior similar to that when the flow rate was increased. To deposit LSM/YSZ composite with graded porosity in the future, it will be more suitable to change the nozzle to substrate distance than the flow rate of the precursor solution with our setup.

Influence of Thermal Treatment on Composite Coatings. Figure 9 shows XRD patterns of LSM/YSZ films thermally treated for 1 h in air at 800 °C. The XRD patterns of the films consisted only of YSZ and LSM phases. The presence of any other phases was not detected. It is necessary to obtain a crystalline mixture of LSM and YSZ phases without any secondary phases to be applied as a reduced temperature SOFC cathode.

Furthermore, we have checked that the porous morphology of the cathode films does not change significantly during the thermal treatment at 800 °C and for long-term SOFC operation.

The above results indicate that the deposited LSM/YSZ films can be used as cathodes for SOFC. Further electrical and electrocatalytic characterizations are in progress to investigate the role of the film morphology on the performance of the LSM/YSZ composite cathode. Low interface polarization losses due to the homogeneous in-situ formation of the layer and large electrochemically active surface areas resulting from the highly porous film morphology are expected to lead to the significant improvement in characteristics of the deposited LSM/YSZ cathode. To the best of our knowledge, thin composite films of such porous morphology with micrometer pore sizes can be deposited by ESD technique only. Moreover, we have demonstrated that the film morphology can be easily controlled by changing the process parameters such as deposition temperature, nozzle to substrate distance, and precursor solution flow rate. Easy control of the film morphology is the main advantage of ESD as compared to the conventional spray deposition techniques.

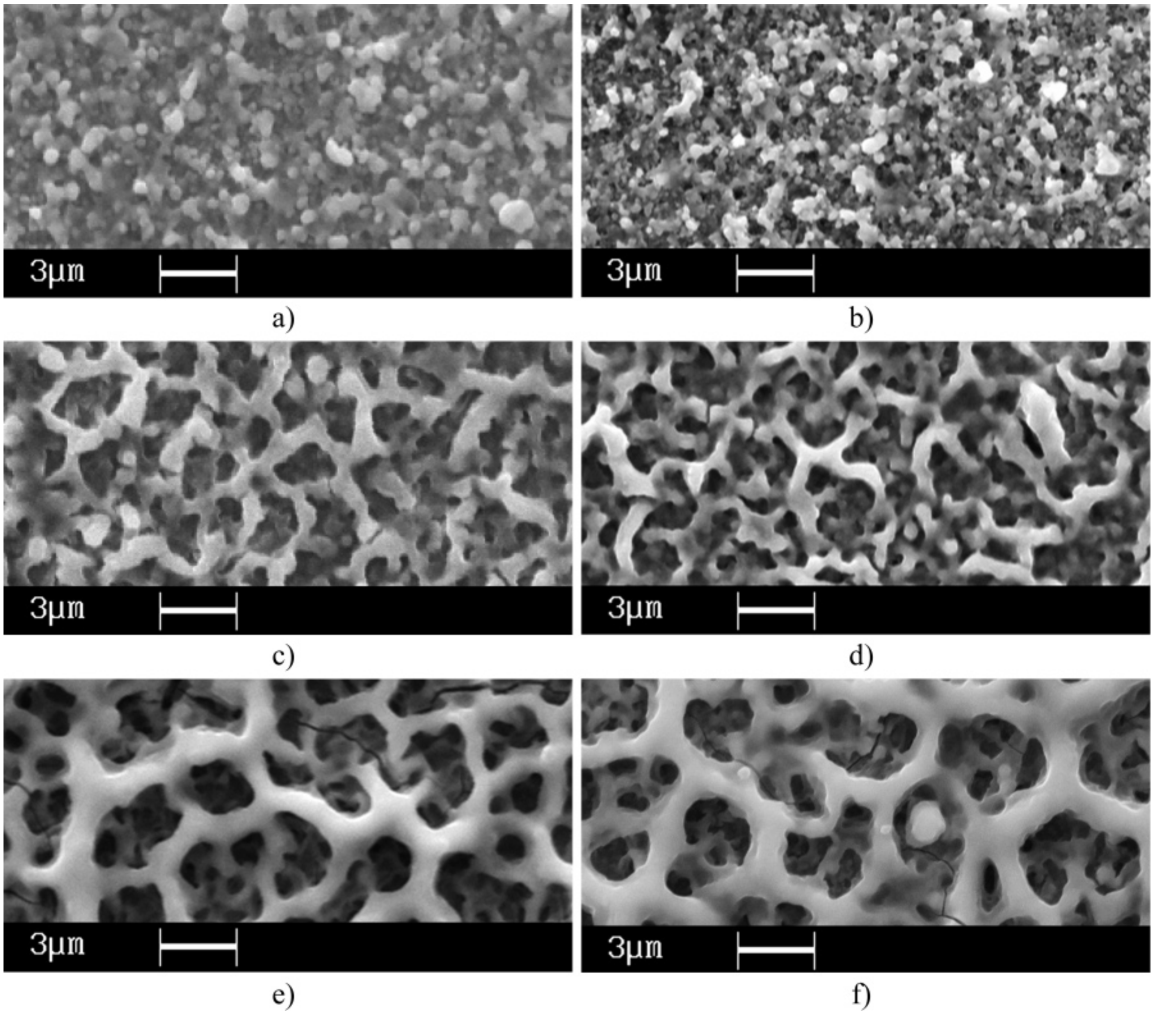

Figure 8. Influence of nozzle to substrate distance on the morphology of LSM/YSZ coatings: (a) 47 mm, (b) 44.5 mm, (c) 42 mm, (d) 39.5 mm, (e) 37 mm, and (f) 27 mm. Precursor solutions: LSM and YSZ2. Deposition temperature: 300 °C. Solution flow rate: 0.5 mL/h. Deposition time: 1 h.

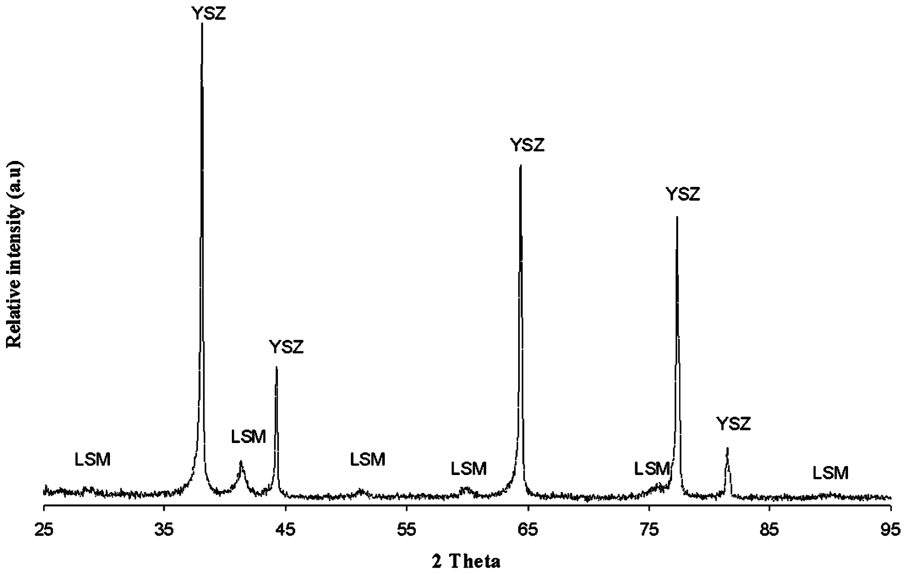

Figure 9. XRD patterns of LSM/YSZ films heat-treated for 1 h in air at 800 °C.

Conclusion

In this study, we have investigated the influence of ESD deposition parameters such as the deposition temperature, the flow rate of a precursor solution, and the nozzle to substrate distance on the morphology of LSM/YSZ films. Furthermore, it was observed that the nature of the precursor solution plays an important role. The largest domain of porosity was obtained using the LSM/YSZ2 precursor solution (zirconyl nitrate in water and butyl carbitol mixture). This was the case for all of the process parameters (deposition temperature, flow rate of a precursor solution, the nozzle to substrate distance). The films deposited using the LSM and YSZ1 precursor solutions (Zracac in ethanol and butyl carbitol mixture) were porous only for some particular sets of process parameters. Therefore, the LSM/YSZ2 precursor solution will be chosen for the deposition of LSM/YSZ cathode with graded porosity in the future. Furthermore, it was found that the solution flow rate influence was quite similar to the nozzle to substrate distance on the control of coating porosity. Finally, the nozzle to substrate distance and the deposition temperature allow easier control of the film porosity from a technical point of view as compared to the control by the solution flow rate. It follows that the most suitable way to prepare the porous LSM/YSZ films with graded porosity is to spray the LSM and YSZ2 precursor solution and control either the deposition temperature or the nozzle to substrate distance. Only the LSM and YSZ phases in the LSM/YSZ composite coatings were detected after annealing at 800 °C by XRD. All coatings were free of cracks after the thermal treatment.

This work has allowed us to extract the main ESD parameters that have an impact on the porosity control of LSM/YSZ composite. The preparation of these composite cathodes using ESD with graded porosity is in progress.

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