

Preparation of a perovskite $\text{La}_{0.2}\text{Sr}_{0.8}\text{CoO}_{3-x}$ membrane on a porous MgO substrate

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Abstract

Crack-free $\text{La}_{0.2}\text{Sr}_{0.8}\text{CoO}_{3-x}$ (LSCO-80) thin films have been fabricated on porous MgO substrates through dip coating followed by sintering. To avoid cracks in the LSCO-80 thin film during sintering caused by the shrinkage mismatch between the film and the substrate, a silver coating on top of the LSCO-80 powder casting layer prior to sintering was found effective. This paper focuses on the control of the porous structure of the MgO substrate, the preparation of sub-micron and narrowly distributed LSCO-80 powder, and the formulation of colloidal suspensions of LSCO-80 powder in an organic medium. The theme of the present work lies in exploiting dip-coating for fabricating a perovskite LSCO- x thin film on asymmetric porous substrates. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Perovskite-type $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-y}$ (LSCO- x) oxide is known to possess mixed conductive (e^-/O^{2-}) character at high temperatures.¹ Because of this unique property, the oxide has a number of important applications, such as being the cathodic material for solid oxide fuel cells² or the membrane material for the electrochemical separation of oxygen.³ In the $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-y}$ oxide system, the substitution of Sr^{2+} for La^{3+} induces oxygen vacancies in the lattice to keep electric neutrality. Such vacancies are responsible for the high temperature diffusion of oxygen anions in the lattice matrix. In this study, $\text{La}_{0.2}\text{Sr}_{0.8}\text{CoO}_{3-y}$ (LSCO-80)⁴ is used for fabricating thin membranes.

In principle, a chemically reactive membrane device consists of a substrate and an overlying membrane.^{5,6} The substrate should be porous in order to allow the membrane to be accessible by the reacting species. Magnesium oxide is one of the candidate substrate materials suitable for supporting LSCO-80 membranes

since it is chemically stable to LSCO- x at high temperatures and has excellent thermal and mechanical properties. In the light of the coating techniques available,^{7,8} dip coating is attractive since it is easy to operate and scale up. The porous structure of the substrate and the composition of the coating suspension are the two main factors that affect the integrity and uniformity of the solid membrane. Usually, the coating solution is composed of colloidal particles of a solid (the membrane material) as the dispersed phase and a solution containing a polymer binder, a deflocculating agent and a defoaming agent as the continuous phase. In this paper LSCO-80 powder was prepared through the combustion of the chelating precursors of the three metal ions (the Pechini method).⁹ This method is normally unsuited for the production of a narrow particle size distribution; here it has been successively modified by using a water-soluble polymer as a combustion additive.

A challenging problem associated with dip coating for the fabrication of ceramic thin membranes is film cracking during sintering. The existence of shrinkage mismatch between the membrane and the substrate during sintering of the coating can account for cracking in the membrane. The problem is worse when the

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substrate has a very different composition from that of the membrane, i.e. an asymmetric substrate. One solution, developed in this study, is to apply a metal covering layer on the powder coating layer to counter the tensile stress existing in the membrane during the sintering of the powder assembly. It was found that this approach could effectively prevent cracks in the LSCO-80 thin film on the MgO substrate.

2. Experimental procedure

2.1. Preparation of LSCO-80 powder via combustion

In a typical procedure for the preparation of LSCO-80 powder, ethylenediaminetetraacetic acid (EDTA, 10.04 g, 34.4 mmol) was introduced with magnetic stirring into 25 ml DI water placed in a 100 ml beaker. Aqueous ammonia solution was then added dropwise to neutralize the EDTA until a clear aqueous solution was obtained. To the resultant solution (pH = 8–9), $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (1.488 g, 3.436 mmol), $\text{Sr}(\text{NO}_3)_2$ (2.91 g, 13.75 mmol) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (5.00 g, 17.18 mmol) were added. Three kinds of chelating complexes formed with the dissolution of the nitrate salts in the solution. A dark-brown solution was obtained, which changed gradually into a highly viscous gel under stirring on a hot plate at about 150–200°C. Following the formation of the highly viscous gel, the temperature of the hot plate was increased to about 400°C to conduct pyrolysis of the gel. After burn out of the organics, a black powder was obtained. The preparation was carried out in a well-ventilated fume hood to prevent gases and ashes from being inhaled. The powder was calcined under airflow (5 l/min) at 900°C for 2 h in a Carbolite furnace. Then, the powder was ground and sieved (opening: 45 μm). The oxide powder was also prepared by using other chelating agents, including water-soluble polymers in some cases, with the purpose of introducing hollowness into the oxide powders.

2.2. Preparation of the LSCO-80 colloidal suspension

A given amount of LSCO-80 powder (15–20% by weight of the suspension) was dispersed into a solution of polyvinylbutyral resin (Butvar-79[®], Monsanto) in a mixture of toluene and methylethylketone (MEK) (v/v = 1/1) to form a suspension. The deflocculating agent (Fish oil, 3–5% by weight of the powder), the plasticizer (dibutyl phthalate, 1–2% by weight of the powder) and the surfactant (Span-80, 1–2% by weight of the powder) were introduced into the suspension subsequently. The suspension was then ball-milled with using zirconia ceramic balls as milling media for three days to break up the agglomeration of the oxide particles. An ink-like colloidal suspension was obtained.

2.3. Preparation of porous disks

In a typical procedure for the preparation of porous disks: MgO fine powder (Aldrich, ~325 mesh) was calcined at 900°C for 2 h before use to avoid over shrinkage. Then a given amount of carbon black powder (4–12% by weight of the powder) was mixed with the MgO powder in the dry state, and the mixture was then introduced into a solution of Butvar-79 (2–3% by weight of the powder) in toluene/MEK (v/v = 1). The resulting slurry was thickened and finally dried by evaporating the solvent under stirring. The dry lump left was crushed by grinding and sieved (opening: 45 μm). About 1 g of the fine powder was subjected to pressing in a pellet-die on a Carter's hydraulic press by using a pressure of 68 atm/cm². The green pellets prepared were thus sintered at 1600°C for 1 h. The sintered MgO disks were polished by grinding paper (Carbimet, grit 600), followed by polishing cloth (Buehler) to make a flat surface. Finally, the surface of the disks was carefully cleaned by ultrasonication in acetone and water subsequently before dip coating.

2.4. Fabrication of LSCO-80 membrane on MgO substrate

A MgO disk was stuck onto a holder with the polished surface up. Then the disk was horizontally dipped into a LSCO-80 colloidal suspension until half of it is inside the suspension. After being held for a few seconds, the disk was raised gradually out of the suspension. The suspension was sucked into the substrate by the capillary force of the pores inside the disk. The coating layer was dried by a hair drier, and another dip coating was followed. A few repetitions of the dipping and drying were carried out to obtain a powder-packed layer of a certain thickness. The obtained coating layer was covered further by a silver layer via dipping in a high purity and well degassed silver paint (SPI). After the silver paint was dried, the disk was first slowly heated up to 400°C at the rate of 0.5°C/min, held for 1 h, then to 1050°C at the rate of 2°C/min, held for another 1 h. Finally a slow cooling rate (2°C/min) is applied. A crack-free and mesoporous LSCO-80 membrane was thus obtained.

2.5. Sample characterizations

The characterizations of samples were performed by the following methods: (1) scanning electron microscopy (SEM), JEOL JSM-5600; (2) energy dispersive X-ray spectroscopy (EDX), Oxford-6587; (3) X-ray diffraction (XRD), Philips X'Pert-MPD XRD; (4) atomic force microscopy (AFM), NanoScope IIIa Multi-ModeTM SPM; (5) particle size analysis, Brookhaven 90 Plus Particle Size Analyser; (6) inductive coupled

Table 1
Composition for formulating various precursor solutions

	Organic components		Nitrate salts/(mmol)
	Ligand/(mmol)	Polymer/(g) ^a	
S ₁	Citric acid (100)		La(III); Sr(II); Co(II) (3.436);(13.75);(17.18)
S ₂	Ethylene glycol + glycine (52 + 172)		As above
S ₃	Ethylenediamine tetraacetic acid (EDTA) (34.4)		As above
S ₄	EDTA (34)	Polyvinylpyrrolidone (PVP) (0.5)	As above
S ₅	EDTA (34)	Polyvinylalcohol (PVA) (0.5)	As above
S ₆	EDzTA(34)	Methocel/(0.5)	As above

^a PVP (\bar{M} = 38,000); PVA (\bar{M} = 15,000); Methocel (Dow chemical).

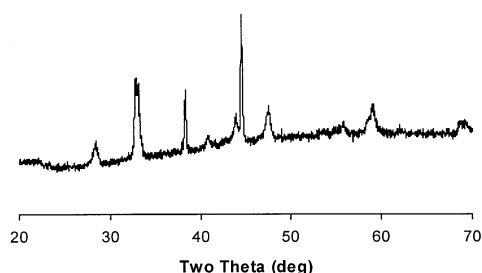


Fig. 1. X-ray diffraction pattern of the LSCO-80 powder (S₅) after calcination at 900°C for 2 h.

plasma analysis, Thermo Jarrell Ash IRIS/AP Duo; (7) mercury porosimetry, Micromeritics AutoPore III.

3. Results and discussion

3.1. Preparation of LSCO-80 powder suitable for formulating a dip coating suspension

A modified Pechini method was developed in this research for the preparation of a narrowly sized LSCO-80 fine powder (Table 1). The powder thus obtained contains both the hexagonal and the cubic phases as

Table 2
ICP analysis of the La_xSr_{1-x}CoO_{3-y} powders based on different precursors ($x=0.2$ according to the stoichiometry of the feed stock)

	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆
La (mol%)	8	8	9	8	8	7
Sr (mol%)	32	34	37	34	32	33
Co (mol%)	42	42	47	40	40	41
La:Sr:Co	0.20: 0.80: 1.05	0.19: 0.81: 1.00	0.20: 0.80: 1.02	0.19: 0.81: 0.95	0.20: 0.80: 1.00	0.18: 0.82: 1.03

shown in the X-ray diffraction spectrum (Fig. 1) the former phase converts continuously to the latter phase with an increase in the calcination temperature [10]. The atomic ratios of the three types of cations in the various batches of LSCO-80 oxide powders resulting from the use of different organic additives are close to the stoichiometry of the metals in the initial aqueous solutions according to ICP analysis (Table 2).

It is known that the combustion behavior of a chelating polymer influences the architecture of the oxide powder obtained via the process [10], and the types of organic components in the chelating polymer determine to a large extent the combustion behavior. Therefore, the particle architecture of the oxide powder can be adjusted by varying the organic ligands employed initially to prepare the precursor solution. Powders obtained by calcinations then comprise coarse particles with very different architectures. Take for example the morphology of four kinds of EDTA-based powders displayed in Fig. 2. When the precursor solution contains only EDTA as the ligand, the resulting coarse particles are light agglomerates of small particles with micron and sub-micron sizes (Fig. 2a). However, when the precursor solution contains EDTA and a polymer as a pore former, the resulting coarse particles are harder agglomerates encompassing lots of internal voids (Fig. 2b–d). When these two sorts of powders were subjected to grinding and ball-milling, the particle size analysis revealed a narrower particle size distribution from the originally coarser powders (Table 3). It is very likely that the three types of polymers actually play a role in facilitating the micro breakage of the coarse particles via implementing the hollow architectures. For comparison, in the case of sample S₃ where no polymer pore former was used, grinding and ball-milling produced bigger average particle sizes and a wider particle size distribution. In conclusion, the presence of a polymer pore former in a chelating precursor is necessary for the post-calcination grinding in order to obtain a fine powder with a narrow particle size distribution.

3.2. Preparation and characterizations of porous MgO substrates

As the cobalt oxide in the LSCO- x composition reacts with Al₂O₃ at high temperatures, MgO was employed as

Table 3
Particle size analysis of the LSCO-80 powders^a

	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆
Mean particle size (nm)	236	295	236	282 ^b	219	302
Polydispersity ^c	0.169	0.181	0.133	0.005	0.005	0.005

^a The samples were collected from suspensions after ball-milling for one week.

^b The power was gathered from the upper portion of the suspension by a sedimentation process.

^c The value is related to the width of half-height of the distribution curve.

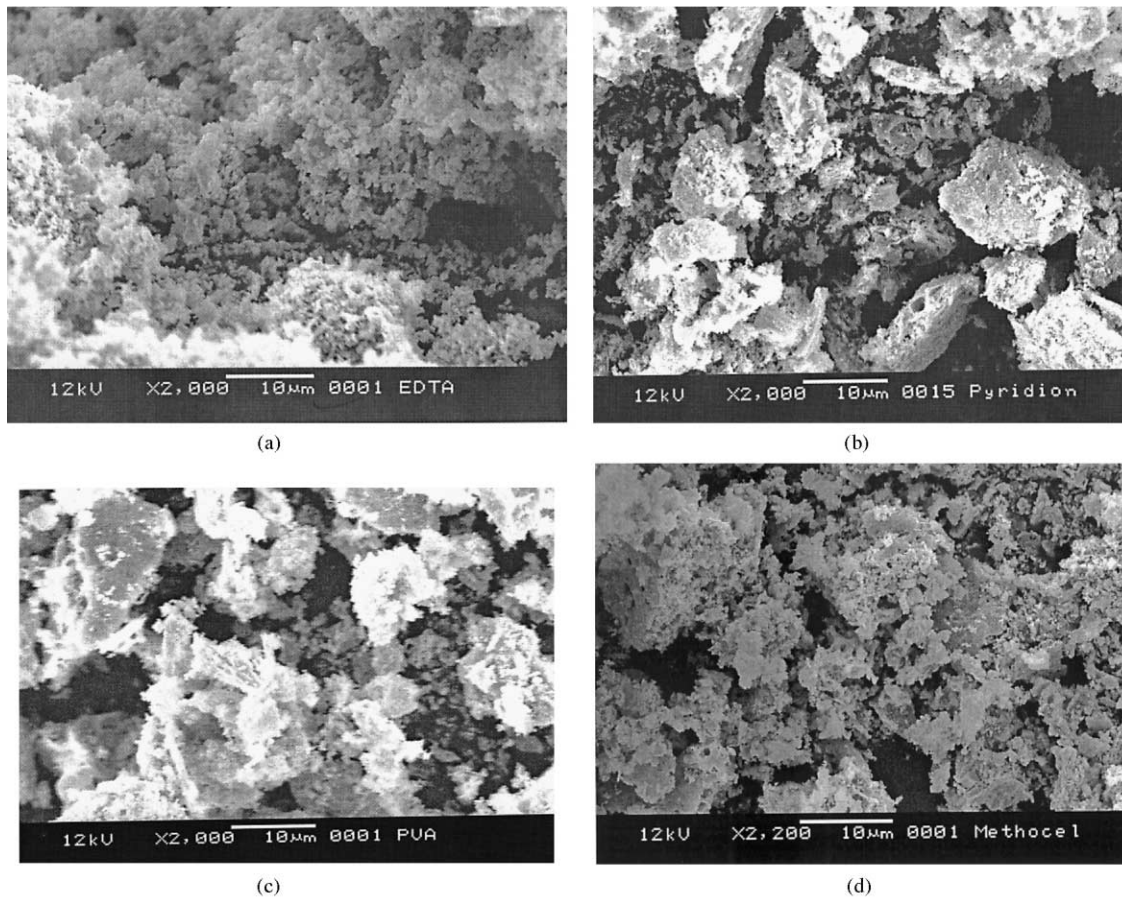


Fig. 2. SEM micrographs of the calcined LSCO-80 powders made from using (a) DETA; (b) EDTA plus PVP; (c) EDTA plus PVA; and (d) EDTA plus Methocel as the additive in their precursors (see Table 1 for abbreviations).

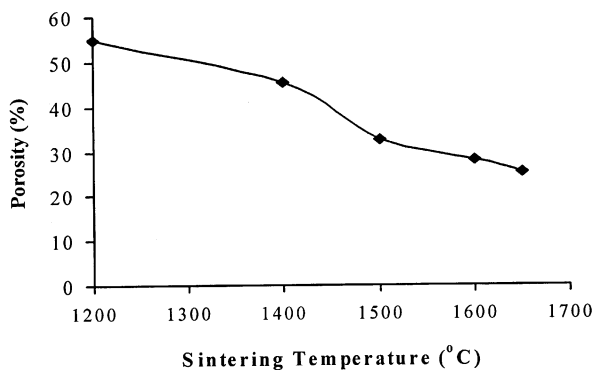


Fig. 3. Sintering profile of MgO disk with using 4%-carbon black as pore former.

the substrate for supporting the LSCO-80 film. To prepare a porous MgO matrix, carbon black with nano particle sizes was used as the pore former. Fig. 3 displays the sintering behaviour of MgO sample containing 4 wt.% of carbon black. It is found that a sintering temperature of 1600°C ensures both the mechanical strength and the necessary porosity. Table 4 shows the change of porosity and the most abundant pore size of sintered MgO disks with different amounts of carbon black in their green bodies. The pore-size distribution also broadens with increase in the carbon black content due to the agglomeration of carbon particles (Fig. 4); SEM micrographs of the surface of the sintered MgO disks, however, reveal little difference in their porous

Table 4
Parameters of the porous structure of the sintered MgO substrates^a

	4% Carbon black	8% Carbon black	12 Carbon black
Porosity	28%	37%	44%
Most abundant pore size (μm) ^b	0.7	1.1	2.4

^a After being sintered at 1600°C for 2 h.

^b The values are taken from Fig. 5.

structures (Fig. 5). This suggests that the surface layer of MgO undergoes a larger degree of sintering than the bulk phase. The MgO disk suffered from warping when the initial content of carbon black was raised to 16%. Therefore, a carbon content of less than 12% is selected as a suitable level.

To use the MgO disks as the substrate for dip coating, the dense surface layer must be removed by lapping to allow the exposure of the porous structure to the dip

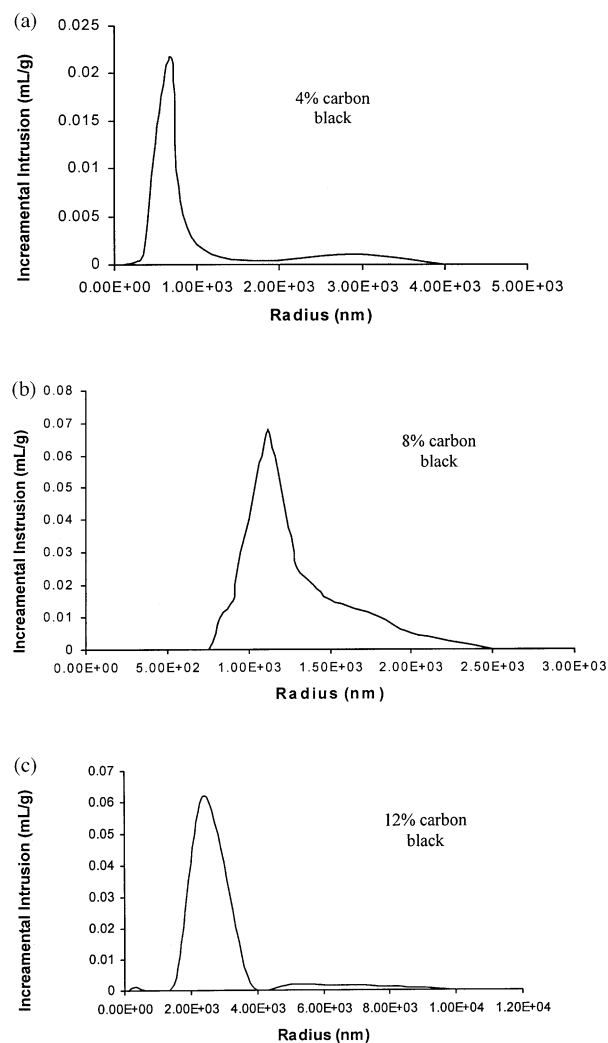


Fig. 4. Pore size distributions of MgO disks based on using various amount of carbon black as the pore former.

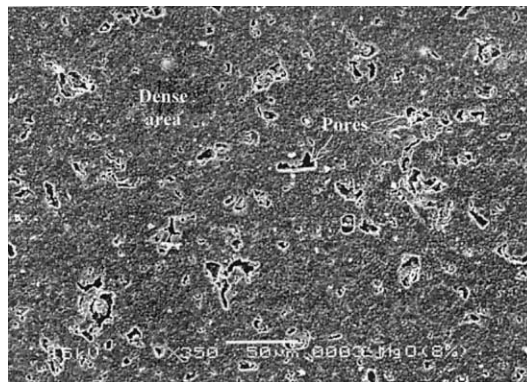


Fig. 5. The surface of MgO disk made by using 8%-C as pore former.

coating suspension. In the following section, the MgO disk based on using 8% of carbon black as pore former was employed since it combines the high porosity and small average pore size desirable for developing a thin ceramic film. The significance of the small pore size requirement is linked to the small particle size requirement for formulating a dip coating solution. As the LSCO-80 powders prepared in this work have particle sizes below sub-micrometer, large pores on the substrate would only retain, like a sieve, the coarse particles. Consequently, as the powder-packed layer is subjected to sintering, the resulting film would have a looser structure than those films developed on a surface with small pore sizes. Two LSCO-80 films formed on 4%-C disk and 12%-C disk respectively reveal different morphologies consistent with this argument as shown in Fig. 6.

3.3. Formulating a colloidal suspension for growing LSCO-80 film on a porous MgO substrate

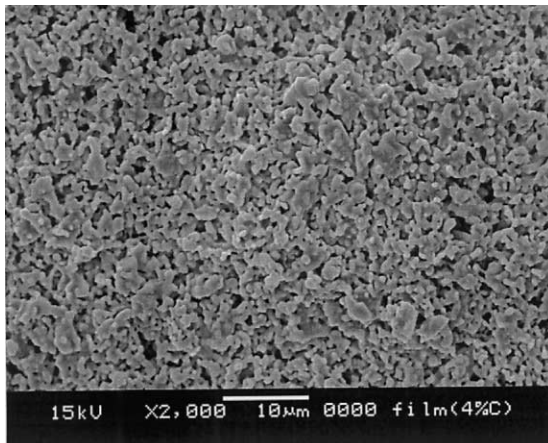
To formulate a LSCO-80 colloidal suspension, the powder of S₅ batch (Table 1) was chosen by virtue of its small particle size and its precise stoichiometry. In addition, polyvinylbutyral (Butvar-79[®], Monsanto) was employed as the binder. It was found that a binary solvent consisting of toluene and MEK is effective for dissolving Butvar-79 to yield polymer solutions with viscosity in the required range as shown in Fig. 7. Fig. 8 provides an overview of the influence of the dosage of Butvar-79 polymer on the viscosity of the solution in the binary solvent ($v/v=1/1$) and on the viscosity of the corresponding suspension with a fixed solid content. There is a finite and relatively constant drop when the powder is added to the polymer solutions.

It was found experimentally that when the viscosity of the suspension falls in the range between 70 to 80 cp it is suitable to achieve an even powder casting layer. Accordingly, a solution containing the binary solvent ($v/v=1/1$) and 2% of Butvar-79 with a viscosity of 79 cp (Fig. 8) is pertinent as medium for the LSCO-80 powder because the powder will itself reduce the visc-

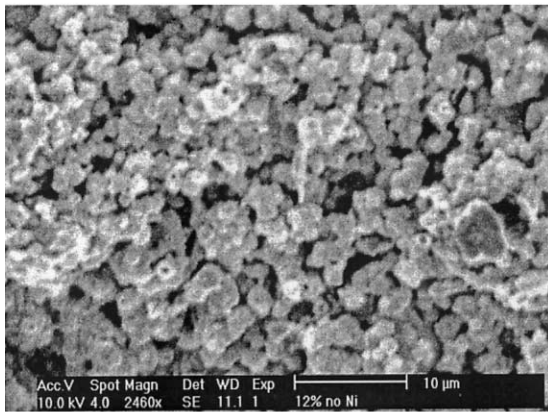
osity to a certain extent. Based on using this dispersing medium, the effect of solid content on the viscosity of suspension has been investigated (curve b, Fig. 9). Technically, the higher the solid content of the suspension the greater will be the packing density in the powder-packed layer. To confirm this, the air permeation flux of LSCO-80/MgO membranes developed from suspensions with different solid contents was measured against pressure as shown in Fig. 10. The membrane based on the suspension with 20% solid content exhibits the lowest air flux. It was also observed according to the SEM micrograph that the thickness of the sintered LSCO-80 films increases with increase in solid content of suspension, for instance, the one from the suspension with 20% solid content having a thickness of about 20 μm (Fig. 11).

3.4. The role of a silver covering layer in preventing cracks of LSCO-80 film on porous MgO substrate

When the LSCO-80 powder-packed layer on the MgO disk is subjected to sintering at 1050°C, large shrinkage of the layer against nil shrinkage of the substrate causes



(a)



(b)

Fig. 6. Morphologies of LSCO-80 films formed on (a) 4%-C MgO disk and (b) 12%-C MgO disk.

tensile stresses in the membrane, which always lead to cracks throughout the membrane as shown in Fig. 12a. To avoid the cracks, a silver metal coating on the LSCO-80 powder-packing layer was found to be effective. Fig. 12b displays a crack-free LSCO-80 membrane obtained after sintering. The Ag coating is believed to play a role in absorbing the stress in the LSCO-80 layer; this function is associated with its high melting point (at

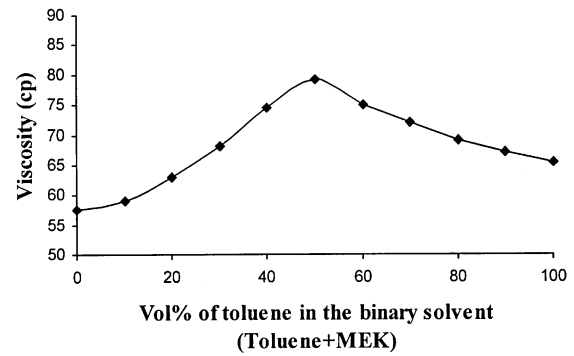


Fig. 7. Viscosity of the solutions of Butva-79 (2 wt.%) in the mixtures of toluene and MEK.

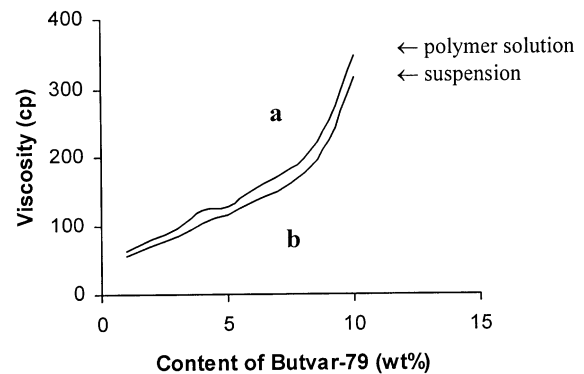


Fig. 8. A change in the viscosity of (a) the Butva-79 solution in the binary solvent of toluene and MEK ($v/v=1$) with an increase in the concentration of the polymer; (b) the suspension formulated by dispersing the LSCO-80 powder (S_5 , 20 wt.%) in the above polymer solutions.

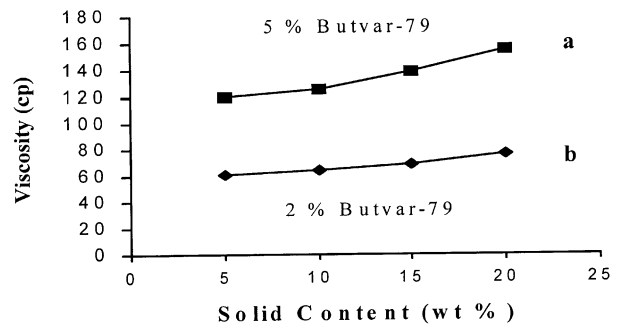


Fig. 9. A change of the viscosity in the suspension of the LSCO-80 powder (S_5) in the polymer solution of 2 wt.% of Butva-79 in toluene/MEK ($v/v=1$) with an increase in the content of S_5 powder.

960°C) that is rather close to the sintering temperature used and with its chemical stability to LSCO-*x* materials at high temperatures. As the Ag no long has mechanical property after it melts, it is logic to know the sintering extent of the LSCO-80 membrane achieved by this temperature point as well as the whole sintering profile. Experimentally, the shrinkage of the LSCO-80 membrane cannot be measured directly. It is, therefore, suitable to use LSCO-80 disks made by slip-casting method for simulating the sintering process of membrane. The sintering profile (Fig. 13) shows that by the melting point of Ag (960°C), the disk has fulfilled about 66% of the consolidation that can be obtained at 1050°C. According to this analogy, the Ag metallic skin is able to absorb the stress generated by 2/3 of the total shrinkage. It is reasonable to consider that the Ag shrinks more than the LSCO-80 layer underneath before it melts. As a result, the compressive force acting on the LSCO-80 layer can offset the tensile force

imposed by the MgO disk. Moreover, since the sintering extent at different loci of LSCO-80 layer is uneven because of its powder packing structure, the Ag metallic skin can also buffer the stress produced due to uneven shrinking. On the other hand, although the continuous sintering of LSCO-80 layer in the temperature range beyond the melting point of Ag accounts for about 1/3 of shrinkage and the Ag melt does not have an effect on removing the stress generated in this process, it is likely that the stress buildup is still below the level the material

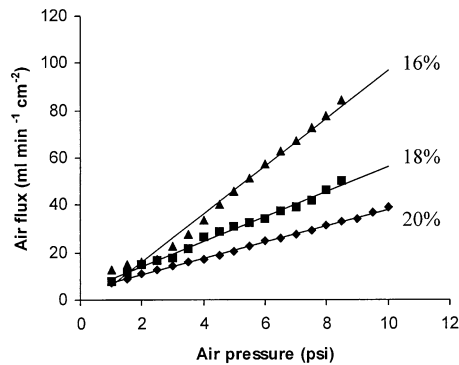


Fig. 10. Air permeation test of the LSCO-80 films fabricated on 8%-C MgO substrate (thickness = 2.5 mm) by using dip-coating suspensions with various contents of S₅ powder. Each coating layer was developed by 10 coatings and followed by sintering at 1050°C for 1 h.

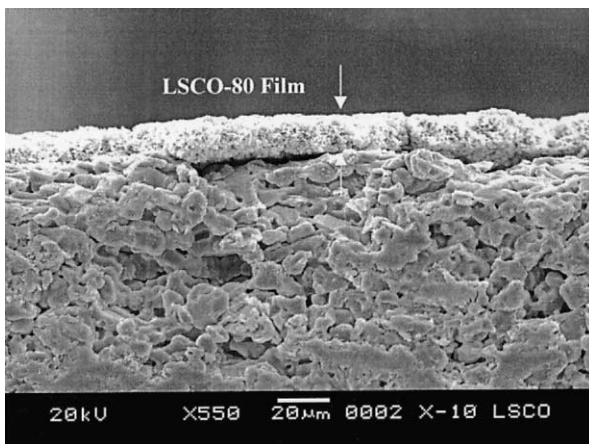
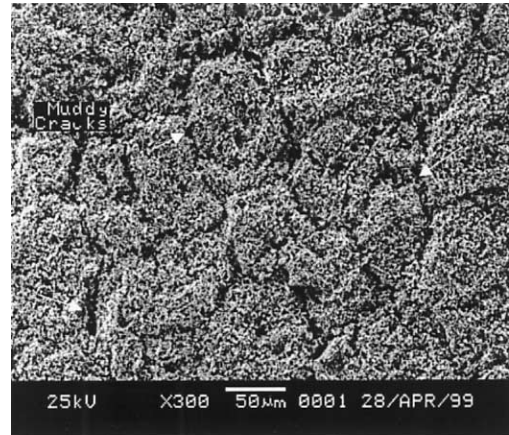
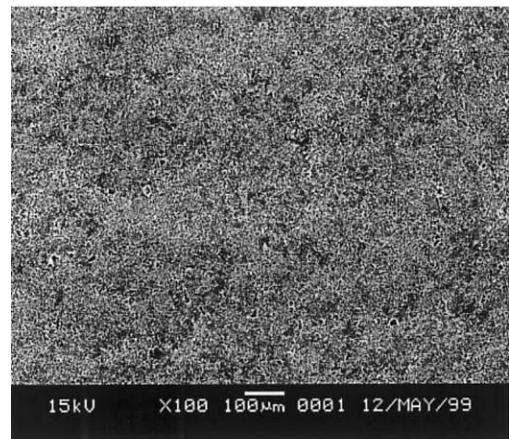


Fig. 11. A cross-section display of the membrane consisting of LSCO-80 membrane/8%-C MgO disk.



(a)



(b)

Fig. 12. (a) The LSCO-80 membrane prepared in the absence of Ag coating; (b) the LSCO-80 membrane prepared in the presence of Ag coating.

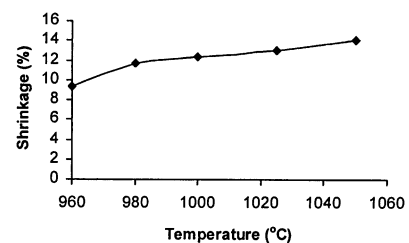
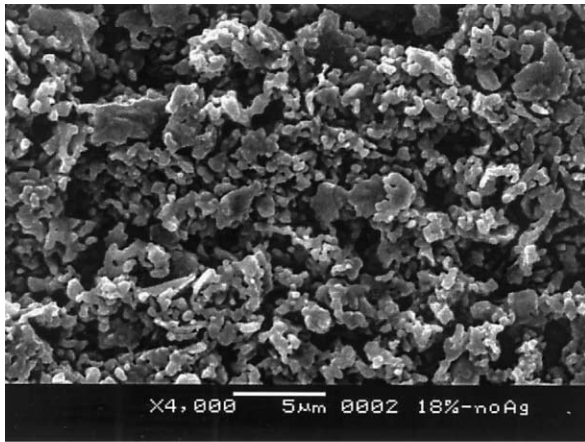
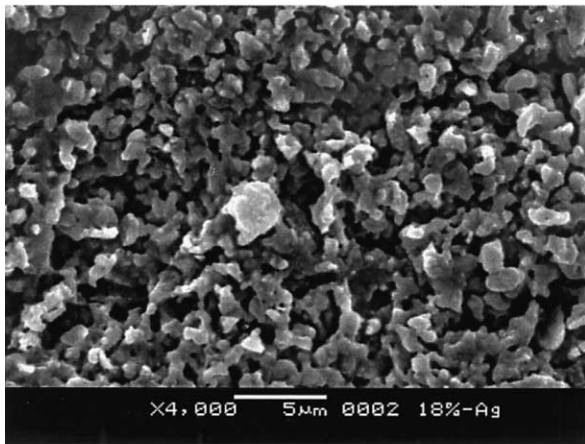


Fig. 13. The sintering profile of LSCO-80 disks (each disk providing one shrinkage value).



(a)



(b)

Fig. 14. (a) An amplified view of the film shown in Fig. 12a; and (b) in Fig. 12b.

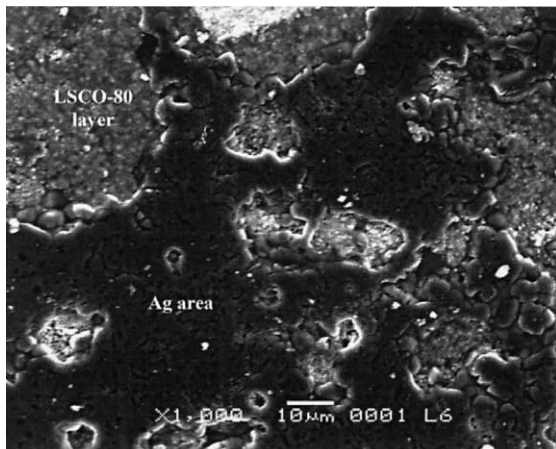


Fig. 15. The morphology of silver at the surface of the sintered LSCO-80 membrane.

cannot endure by virtue of the stress-removing effect of Ag in the course before it melts. This interpretation is also supported by the two different types of microstructures of the respecting membranes in Fig. 14. In the

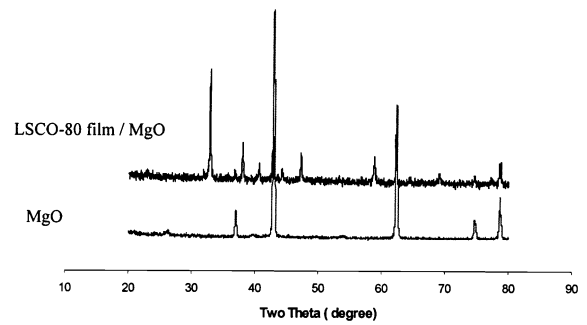


Fig. 16. X-ray diffraction of the perovskite LSCO-80 membrane on MgO.

absence of silver, the shrinking of the packed LSCO-80 powders leads to a large number of disconnection domains that constitute fractures of the membrane. On the contrary, the shrinking did not cause as many disconnection loci as before in the presence of silver.

It is possible that the thermal mismatch between the sintered membrane and the substrate that occurs in the course of cooling will also lead to cracking if the overlying Ag layer is absent. Fig. 15 shows the microstructure of the surface of a sintered membrane; the shape of the condensed Ag domains records their state when melted. Most of the silver melt retained on the surface with forming irregular domains. The Ag domains and LSCO-80 layer were identified by the EDS analysis. Hence, it can be expected that the Ag can resume its effect on absorbing stress from the sintered membrane as soon as it condenses. The silver domains left on the LSCO-80 membrane after sintering can be removed readily by immersing the disk into a potassium cyanide solution in ethanol for a few minutes. The XRD of the resultant LSCO-80 membrane/MgO-disk shows the perovskite structure of LSCO- x (Fig. 16). In summary, the silver coating plays a key role in diminishing the micro-cracks in the LSCO-80 membrane underneath before it melts and after it condenses.

4. Conclusion

The perovskite type $\text{La}_{0.2}\text{Sr}_{0.8}\text{CoO}_{3-y}$ (LSCO-80) thin film has been fabricated on a porous MgO substrate by means of a dip coating technique. The paper conducts a systematic investigation into the processing parameters that include the porous structure of the MgO substrates and the solid content as well as the viscosity of the LSCO-80 colloidal suspensions in an organic medium. The exploration attempts to achieve a highly packed LSCO-80 powder layer on the MgO substrate, which is a prerequisite for fabricating a dense LSCO-80 film via sintering. The study also modified the Pechini method by introducing a water-soluble polymer into the pre-

cursor aqueous solution. Smaller particle sizes and a narrower particle size distribution are the result of the presence of the polymer during the combustion of the chelating precursor. More importantly in this work, an approach called metal (silver in this case) topping has proved feasible for overcoming the film cracking problem that is due to the shrinkage mismatch occurring when the LSCO-80 powder casting layer is sintered on the MgO substrate.

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