

Preparation of $\text{La}_{1-z}\text{Sr}_z\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-x}$ thin films, membranes, and coatings on dense and porous substrates

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A modified Pechini process has been successfully developed for preparation of thin films of $\text{La}_{1-z}\text{Sr}_z\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-x}$ (LSCF) on both dense and porous substrates. Results indicate that the most important processing parameter is the ratio of the polymerization/complexation agent to metal ions. Ceramic films derived from solutions with a relatively low ratio of citric acid to metal ions are usually cracked, while films derived from solutions with a relatively high ratio are crack-free and uniform. The use of ethylenediamine as an additional chelating agent further improves film quality, especially the adhesion and uniformity of the films. A single coating of solution typically yields a ceramic film of thickness about $0.4 \mu\text{m}$, and thicker films can be prepared by application of successive coatings. For deposition of thin-film membranes on a porous substrate, however, it is necessary to modify the surface of the porous substrate in order to prevent solution from infiltrating into the pores due to capillary force, and to prevent oxide films from cracking due to surface roughness. The application of an intermediate polymer film to the surfaces of porous substrates has effectively overcome the problems and has resulted in uniform, nonporous membranes of LSCF on porous substrates. Successful deposition of thin-film ceramic membranes on porous substrates is important to fabrication of various ionic and micro-ionic devices based on ceramic thin films.

I. INTRODUCTION

Ionic and mixed-conducting ceramics have been widely used in a variety of solid-state ionic devices, such as rechargeable batteries for energy storage, fuel cells for energy conversion, and chemical sensors for monitoring and control of combustion. These materials have also been successfully used in various electrochemical systems or processes for removal of NO_x and H_2S , for gas separation, and for electrosynthesis such as methane conversion.

Perovskite $\text{La}_{1-z}\text{Sr}_z\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-x}$ (LSCF) mixed conductors have attracted much attention due to their high ambipolar conductivity and excellent catalytic activities for oxygen reduction and evolution. In order for an electrochemically functional ceramic film to be accessible to electroactive species, such as gases or ions, the film has to be deposited on a porous substrate, through which electroactive species must transport freely. Electrochemical vapor deposition (EVD) has shown some success in thin-film deposition on porous substrates.¹ However, EVD is applicable only to materials which exhibit sufficiently high ambipolar conductivity, and the processing temperature is typically very high. Accordingly, EVD is difficult to control and is an expensive approach.

Sol-gel techniques have been successfully used to prepare ceramic thin film coatings on dense

substrates for various applications, such as optical waveguides,² ferroelectric ceramics,³ superconductors,⁴ protective coatings,⁵ and so forth. According to the precursors used or gelation mechanism involved, the sol-gel process is typically classified into two categories: alkoxide method and colloidal method.⁶

The Pechini process,⁷ a solution mixing technique, has also been used for preparation of ceramic powder^{8,9} and thin films.¹⁰⁻¹³ In the Pechini process, as described in the original patent,⁷ an alpha hydroxycarboxylic acid, such as citric acid, is used to chelate with various cation precursors by forming a polybasic acid. In the presence of a polyhydroxy alcohol, such as ethylene glycol, these chelates will react with the alcohol to form organic esters and water by-products. When the mixture is heated, polyesterification occurs in the liquid solution and results in a homogeneous sol, in which metal ions are uniformly distributed throughout the organic matrix. When the sol is further heated to remove the excess solvents, an intermediate rigid resin will be formed. Because of the high viscosity of the resin and the strong coordination interactions associated with the complex, metal ions are "frozen" in the solid polymeric network and remain homogeneously distributed. The solid resin is then heated to elevated temperatures to remove organic residuals. The metal precursors are chemically combined to form the desired stoichiometric compounds during

the pyrolysis. The solution chemistry and reactions occurring in the Pechini process can be schematically illustrated in Fig. 1.

The Pechini process offers several advantages for processing of mixed-conductive ceramics, as compared to other thin films deposition techniques such as sputtering, evaporation, and chemical or electrochemical vapor deposition. The Pechini process provides a direct and precise control of stoichiometry of complex materials systems. It also makes possible uniform mixing of multicomponents on a molecular scale. The processing temperature can be considerably reduced, which can be critical to thin-film deposition on porous substrates. The sol prepared in this process has high stability during storage, since the polymerization or gelation process depends primarily on treatment temperature. Finally, the Pechini process is cost-effective since it usually uses inexpensive precursors and involves less equipment.

To date, there has been little success in using solution coating techniques to prepare thin-film membranes on porous substrates.¹⁰⁻¹³ The major challenge in the preparation of ceramic thin-film membranes on porous substrates using the sol-gel approach is the infiltration of sol into the porous substrate by capillary force. This would lead to discontinuities in the thin films such as holes and cracks and to reduction in porosity of the porous substrates. The latter could limit the mass transport of electroactive species through the porous substrates and hence hinder the performance of solid-state electrochemical devices based on thin films.

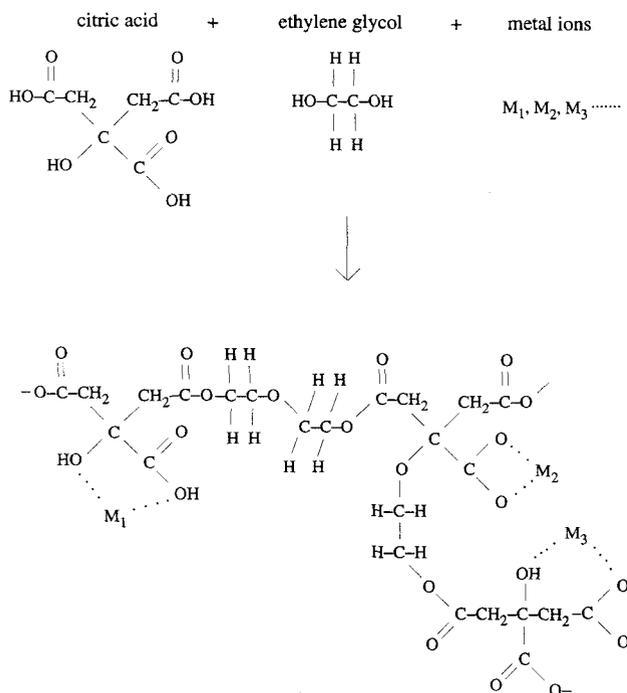


FIG. 1. A schematic showing the solution chemistry and reactions involved in the Pechini process.

In this study, a modified Pechini process is developed to prepare LSCF thin films on both dense and porous substrates. Several important processing parameters, such as sol composition, chelating agents, and dilution media, are examined to optimize the quality of ceramic thin films derived from solutions. Successful deposition of thin-film membranes of mixed-conducting ceramics on porous substrates establishes the technical basis for processing and fabrication of various ionic devices and electrochemical systems based on ceramic thin films, such as solid oxide fuel cells, chemical sensors, and systems for oxygen separation and electrosynthesis.

II. EXPERIMENTAL

A. Preparation of LSCF solution

Precursors used for LSCF were metal nitrates $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. Ethylene glycol and citric acid were used as polymerization/complexation agents for the process. Ethylenediamine was used as an additional chelating agent. Acetic acid, formic acid, and methanol were used as dilution media. All of the chemicals were obtained from Alfa or Aldrich companies. The procedure for preparation of the LSCF sol solution is as follows. First, a measured amount of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in de-ionized water at 60°C . Then, a stoichiometric amount of $\text{Sr}(\text{NO}_3)_2$ was introduced to the solution under stirring. When the Sr precursor is completely dissolved in the solution, controlled amounts of citric acid and ethylene glycol were added (the amounts of citric acid and ethylene glycol were determined by the ratio of citric acid to metal cations and the ratio of citric acid to ethylene glycol). When the solution became clear, stoichiometric amounts of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were subsequently added to the solution. Complete dissolution of the salts would result in a clear, red-brown solution. These procedures are outlined in the flow chart (Fig. 2). In most cases, the stoichiometry of the solutions was controlled to form ceramic LSCF with a composition of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$.

Thin films of prepared solutions were deposited on dense and porous substrates by dip coating. Slides of Pyrex glass and silica, silicon wafers, and gold-coated silicon wafers were used as dense substrates. Porous ANOPORETM Al_2O_3 membranes (from Whatman) were used as porous substrates to support thin films of LSCF. The porous Al_2O_3 substrates have precisely controlled, honeycomb-like channels with an average pore diameter of about $0.2 \mu\text{m}$.

B. Preparation of porous substrates

Before deposition of the LSCF solution films, porous Al_2O_3 substrates were coated with a protective SiO_2

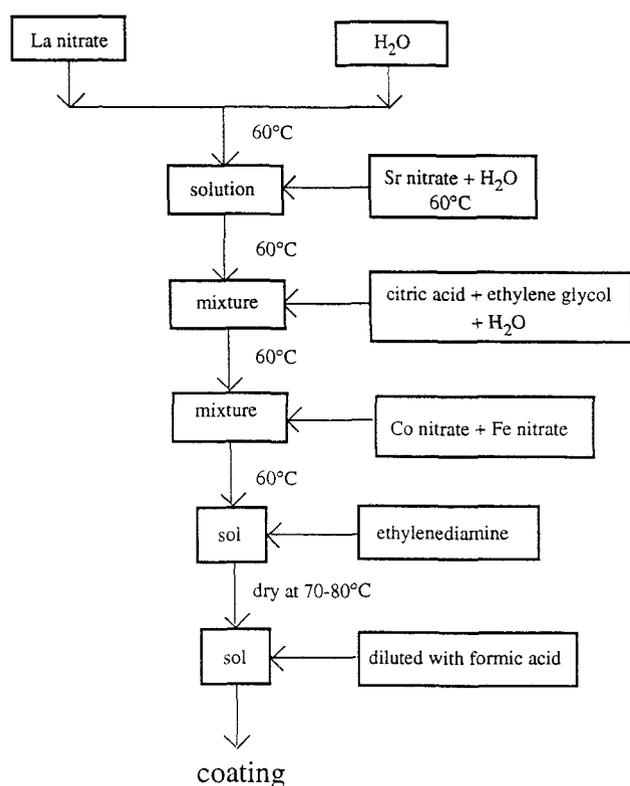


FIG. 2. A flow chart illustrating the processing procedure for the preparation of LSCF solution.

coating to minimize or eliminate reactions between Al_2O_3 and the acidic LSCF solution.¹⁴ This reaction could alter considerably or even destroy the porous structures of the substrates. Tetraethoxysilane (TEOS), $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$, was used as the precursor for the SiO_2 coatings. The sol solution for SiO_2 coatings was prepared as follows. TEOS was diluted with ethanol and small amount of de-ionized water. The pH of the solution was adjusted to about 1.6 by addition of 1 M HNO_3 . After stirring at 60 °C for 1 h, the sol solution is ready for use. Porous Al_2O_3 substrates were dip-coated in the SiO_2 sol and subsequently dried in an oven at 60 °C for 24 h before annealing at 600 °C to retain SiO_2 coatings.

C. Surface modification of porous substrates

In order to prevent LSCF sol from infiltrating into the pores of a porous substrate, an intermediate polymer film without metal cations was prepared on the surface of the porous substrate before deposition of LSCF sol. A suitable polymer film for this purpose should have good wettability to the porous substrate and to the LSCF sol solution. In addition, the polymer should be readily removed during pyrolysis. The polymer film used in this study was produced as follows.¹⁴ First, citric acid was dissolved in ethylene glycol. The molar ratio of ethylene glycol to citric acid was varied from 1 to

6. The resultant mixture was then heated to 80 °C to promote polyesterification and resin formation. When the mixture became viscous, the solution was ready for coating. Porous Al_2O_3 substrates dip-coated with the polymer solution were then subjected to drying at 80 °C in an oven for 3 h. The resulting polymer film was further heat-treated at 200 °C for 5 min to promote partial curation of the polymer film. Finally, the coated substrates were kept at 80 °C for 3–5 h before an LSCF sol film was deposited on the top of the polymer film. The heat treatment at 200 °C is necessary to increase the adhesion of the polymer film to the substrate and to avoid dissolution of the polymer film by the LSCF sol solution during coating and subsequent processing. On the other hand, it was observed that extended heat treatment at 200 °C caused hardening of the polymer film and decreased the wettability of the polymer film to the LSCF sol.

D. Organic burning-off and sintering

All of the thin film coatings were heat-treated in air in a tube furnace. Unless stated otherwise, the firing temperature profile was as follows: the heating rate was 0.5 °C/min from room temperature to 450 °C and 1 °C/min above 450 °C, and the samples were then held isothermally at the final heat-treatment temperature for 1 h.

E. Characterization

The thermal evolution of the solid resin (or gel) was followed using a Perkin-Elmer thermogravimetric analyzer (TGA). The microscopic features of the derived thin-film coatings and membranes were characterized using a Hitachi S-800 field emission SEM and Phillips PW 1800 automatic powder diffractometer. Impedance of solid-state electrochemical cells with LSCF coatings were measured using Solartron 1255 and 1286 interfaced with a computer through Z-Plot.

III. RESULTS

A. Characteristics of LSCF sol solution

Important process parameters investigated in the study include the ratio of citric acid to total metal cations (this ratio is referred to as *C* ratio hereafter), the ratio of citric acid to ethylene glycol, the pH of the solution, the dilution medium, and the type and amount of chelators. It was found that the pH of the solution should be kept at about 2. At higher pH, iron precursors (salts) were converted to iron hydroxide, leading to precipitation of the hydroxide because of its low solubility in the solution. The use of ethylenediamine followed by drying treatment seemed to improve the adhesion of the sol on dense substrates, such as SiO_2 slides. Acetic acid

and formic acid seemed to be good dilution media for the system. These two acids had relatively high vapor pressures so that they facilitated the adhesion of the thin-film coatings to the substrate. The use of methanol as a dilution medium, however, seemed to weaken film adhesion on the substrates and introduced cracks in the derived films.

B. Thermal evolution

Figure 3 shows the thermal evolution of two dried gels in bulk form characterized using TGA. It can be seen that for the gel with $C = 3.75$, most of the weight loss occurred below 420°C . The change of weight is continuous and significant at temperatures from 240 to 420°C , and above 420°C , the weight loss is not observable. For the gel with $C = 1$, however, the pyrolysis initiated and completed at lower temperatures. In addition, spalling of oxide films from substrates was observed when the cooling rate was too fast. This is probably due to the large difference in thermal expansion coefficients between the films and the substrates. Therefore, it is necessary to control the cooling rate during thermal treatment of thin films. The acceptable cooling rate should be less than about $5^\circ\text{C}/\text{min}$. These observations provided valuable information for design of temperature profile for heat treatment of the films.

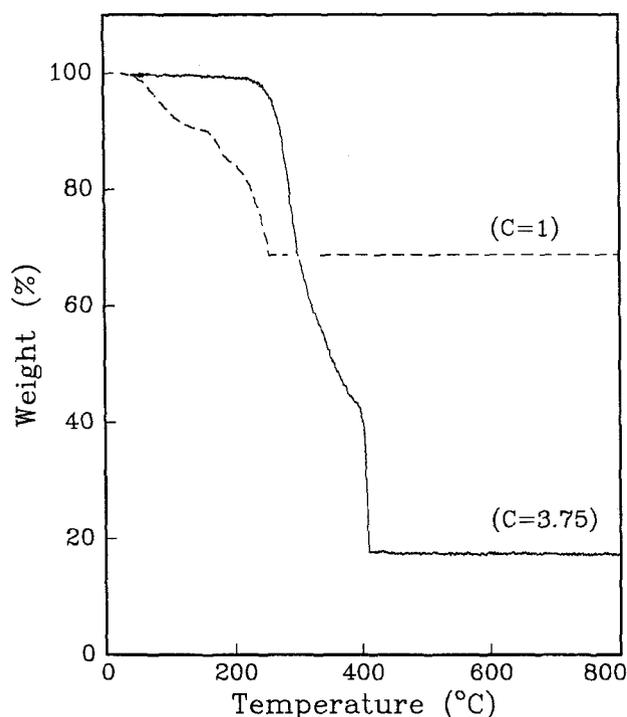


FIG. 3. TGA analyses of two LSCF gels: one with $C = 1$ and the other gel with $C = 3.75$. The temperature scan rate was $1^\circ\text{C}/\text{min}$.

C. Microstructure and morphology of derived films

Representative SEM micrographs of surface and cross-sectional views of an LSCF thin film coating on a SiO_2 substrate are shown in Fig. 4. The film was derived from a single coating of an LSCF solution with the ratio of citric acid to total metal ions equal to 3.75 (or $C = 3.75$). The thickness of the film was about $0.4\ \mu\text{m}$ after firing at 750°C for 1 h. It can be seen from the

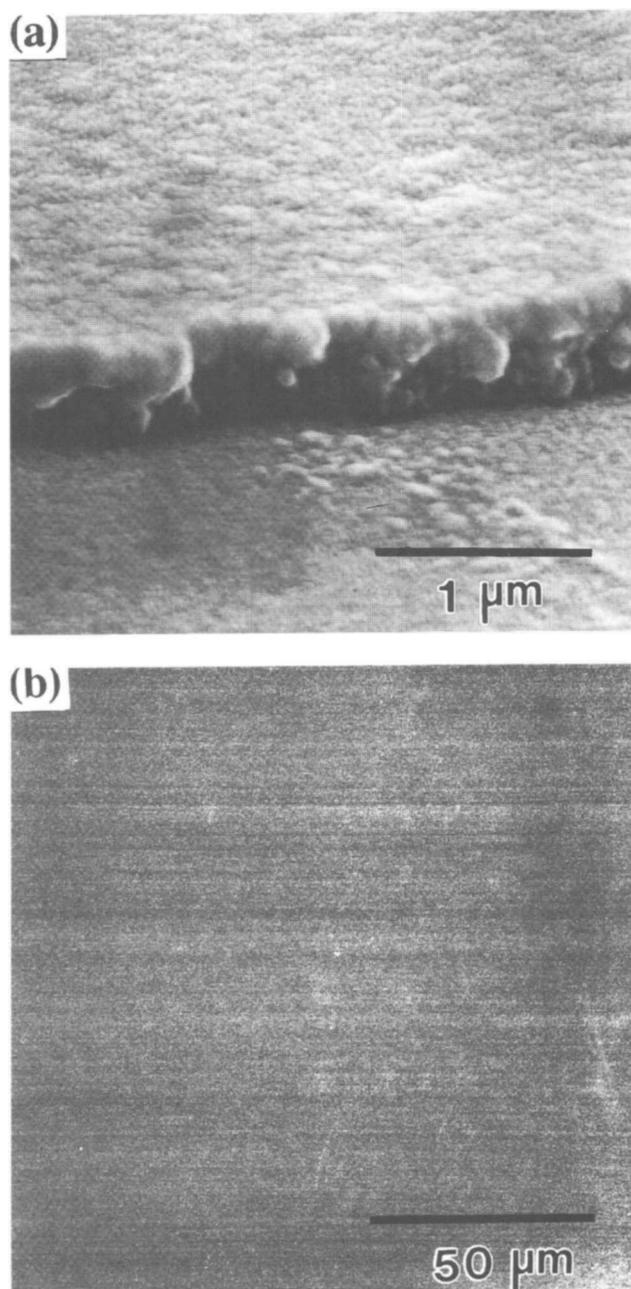


FIG. 4. SEM micrographs of (a) a cross-sectional view and (b) a surface view of an LSCF thin film on a SiO_2 substrate fired at 750°C for an hour. The film was derived from a single coating of an LSCF solution with C ratio of 3.75.

SEM micrographs that the film is smooth, continuous, and nonporous (within the resolution limit of the SEM). More importantly, the grain sizes are uniform and fine (submicron size). Films with an area as large as $2\text{ cm} \times 2\text{ cm}$ free of cracks have been successfully prepared on various dense substrates, including silicon wafer and yttria-stabilized zirconia.

In general, uniform and crack-free thin film coatings were obtained using a relatively high C ratio (e.g., $C = 3$ or above). The optimum molar ratio of precursors used in the preparation of the sol solution is as follows: citric acid: ethylene glycol: total metal ions = 3.75:11.25:1. It was found that the use of ethylenediamine as an additional chelating agent in the preparation of the sol solution enhanced the uniformity and densification of the derived films.

Figure 5 shows the cross-sectional views of films derived from multiple coatings of solutions, indicating that the thickness of a ceramic film can be increased incrementally by approximately the same amount with successive coating applications. Clearly, the thickness of the film derived from two consecutive coatings, Fig. 5(a), is about $0.8\ \mu\text{m}$ and the thickness of the film derived from three consecutive coatings, Fig. 5(b), is about $1.2\ \mu\text{m}$. Thus, each coating of solution consistently adds approximately $0.4\ \mu\text{m}$. It is noted, however, that the film derived from three coatings delaminated partially from the substrate and developed microcracks.

This can be explained as follows. Since each coating was dried and fired sequentially following the same procedures, the ceramic film derived from three coatings went through three thermal cycles between room temperature and $750\ ^\circ\text{C}$. Large mismatch in thermal expansion coefficients (TEC's) of the LSCF film (about $20 \times 10^{-6}/^\circ\text{C}$)¹⁵ and the silica substrate (about $5 \times 10^{-6}/^\circ\text{C}$) is believed to be the major cause of the delamination and microcracks observed. It is also well known that the thinner the film the higher the tolerance to mismatch in TEC's between the film and a substrate. Perhaps this explains why no observable delamination or microcracks were developed in the film derived from two consecutive coatings, Fig. 5(a). The microstructure of this film, in fact, is very similar to that of the film derived from a single coating, Fig. 4. This seems to suggest that there may be a limit to the thickness of an LSCF film, beyond which delamination and cracking may be inevitable due to mismatch in TEC's between LSCF and silica.

In contrast to films derived from an LSCF solution with $C = 3.75$, films derived from a single coating of an LSCF solution with $C = 1$ had extensive cracking and delamination problems. However, each individual fragment of the intact film was quite dense. In fact, delamination and cracking are the main characteristics of films derived from solutions with C ratio less than one, i.e., the solutions in which there are fewer citric

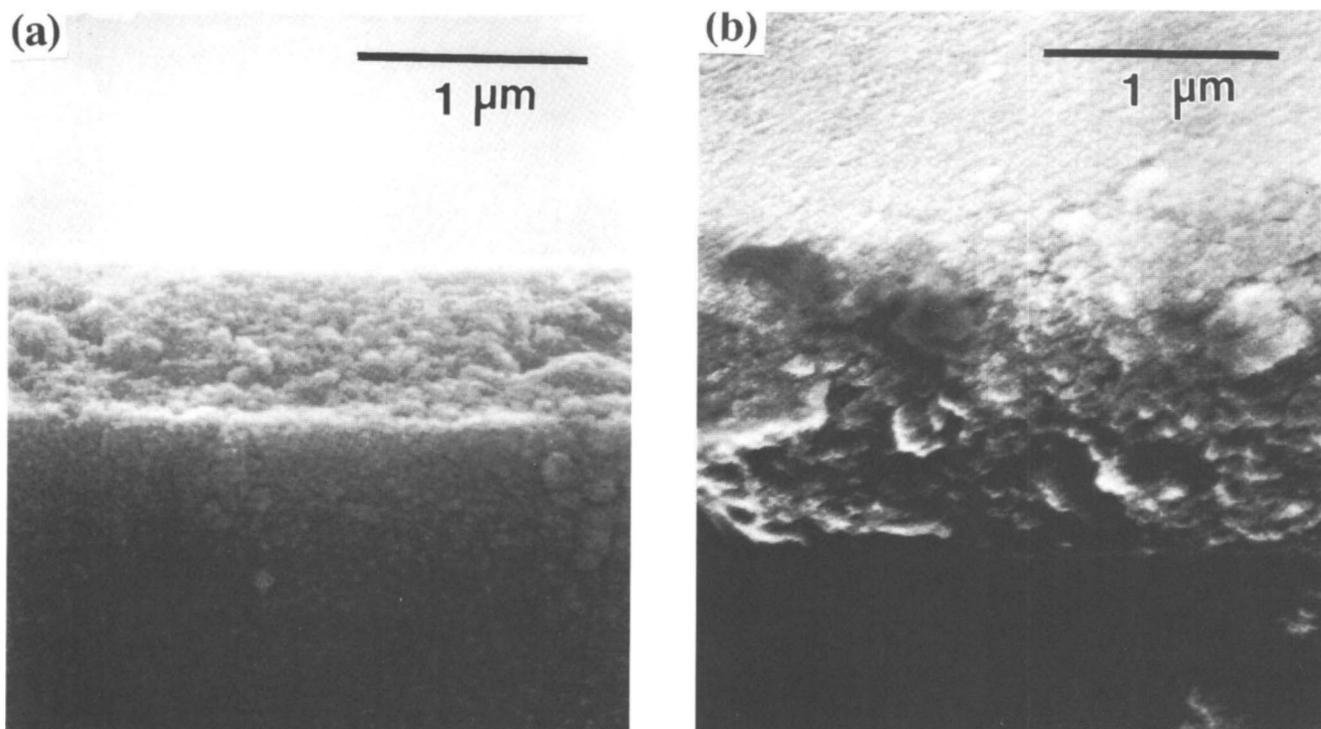


FIG. 5. Cross-sectional views of (a) an LSCF film derived from two sequential coatings and (b) an LSCF film derived from three sequential coatings. Each coating was dried and fired separately following the same procedures. Each coating contributed about $0.4\ \mu\text{m}$ thick film.

acid molecules than the metal ions. Further, it was found that film cracking occurred mainly during pyrolysis of the films rather than drying of the gels. In addition, the gels prepared on a substrate using solutions with a relatively low C ratio also showed serious bloating or a warping problem, whereas the gels prepared using solutions with a relatively higher C ratio did not have the same problem.

Although the quality of the derived ceramic films, particularly the uniformity and morphology, is critically influenced by the ratio of citric acid to total metal ions the ratio of citric acid to ethylene glycol was less important as long as it was kept equal to or smaller than one. This will be elaborated on further in the later sections.

D. Structural evolution

The structural evolution of LSCF thin-film coatings on glass slides was revealed by x-ray diffraction analysis. The films were subjected to heat treatment at different temperatures, and the x-ray diffraction data are summarized in Fig. 6. Clearly, the films remained amorphous up to 400 °C. The expected rhombohedral perovskite phase of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-x}$ was observed when the films were treated at 600 °C for 1 h. As expected, the

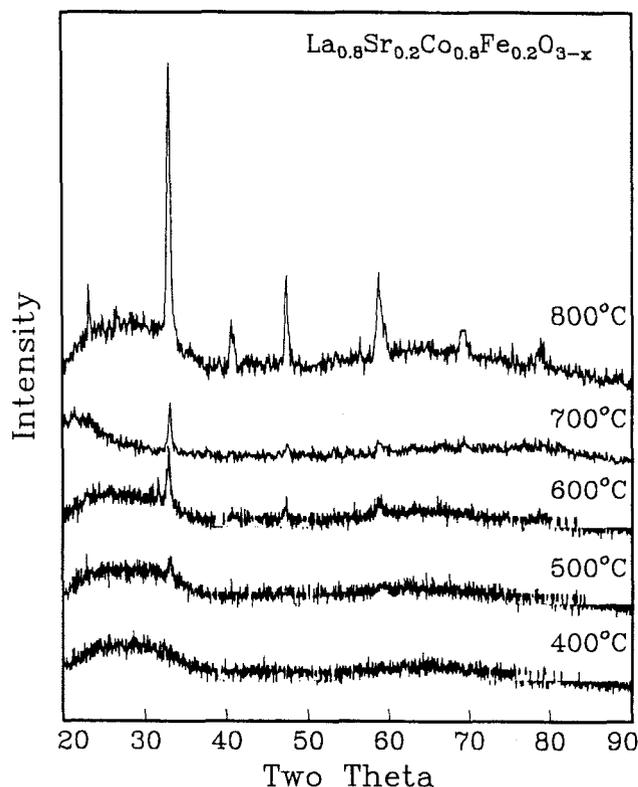


FIG. 6. X-ray diffraction patterns of LSCF thin-film coatings on glass slides fired at different temperatures. The temperature adjacent to each diffraction pattern corresponds to the firing temperature, at which each sample was held for 1 h.

peaks intensities increased with the treatment temperature. In contrast, preparation of LSCF using conventional ceramic processing requires calcination at 800 °C for 8 h to attain the rhombohedral perovskite phase and sintering at about 1300 °C for 6 h to achieve density of greater than 90% of the theoretical value.¹⁵ This suggests that LSCF can be prepared at much lower temperatures using the Pechini process in comparison to conventional ceramic processing.

E. Thin-film membranes on porous substrates

Thin-film membranes of LSCF were also directly deposited on porous substrates. The microstructure and morphology of the surfaces and the cross sections of a porous Al_2O_3 substrate are shown in Figs. 7 and 8. It is noted that the pore structure of the top surface (Fig. 7) is different from that of the bottom one (Fig. 8). The average pore diameter on the top surface is about 0.2 μm , while the average pore diameter on the bottom surface is about 0.12 μm . The porosity of the bottom surface is, however, greater than the porosity of the top surface. Thin film of LSCF sol solutions were deposited on both the top and the bottom surfaces of the substrate in order to study the effect of pore size and porosity of the substrate on film quality.

When LSCF solution was directly deposited on porous Al_2O_3 substrates, reactions between the substrate and LSCF solution were observed. In order to prevent chemical reactions between Al_2O_3 and LSCF solution, porous Al_2O_3 substrates were coated with SiO_2 before application of LSCF sol solutions. The procedure for preparation of this SiO_2 coating is described in Sec. II.

Thin films of LSCF sol solution were then deposited on SiO_2 -coated porous Al_2O_3 substrates by dip coating. Figure 9 shows the microstructure and morphology of an LSCF thin film deposited on the top surface of the porous substrate. It can be seen that even though the sol partially penetrated into the pores of the substrate, a continuous film formed on the top of the porous substrate and the channels inside the porous substrate are still open. The thickness of the film is about 0.1 μm . The surface view indicates that there are some occasional pinholes or voids, which might be due to infiltration of the sol into the pores, leading to nonuniform film formation.

Similarly, Fig. 10 shows the microstructure and morphology of an LSCF thin film deposited on the bottom surface of the porous substrate. The uniformity of the films deposited on the bottom surface seems to be better than the films deposited on the top surface. This indicates that the critical surface pores size probably is more important than the absolute porosity of the porous substrate. In both cases, however, the film quality was not adequate for device applications.

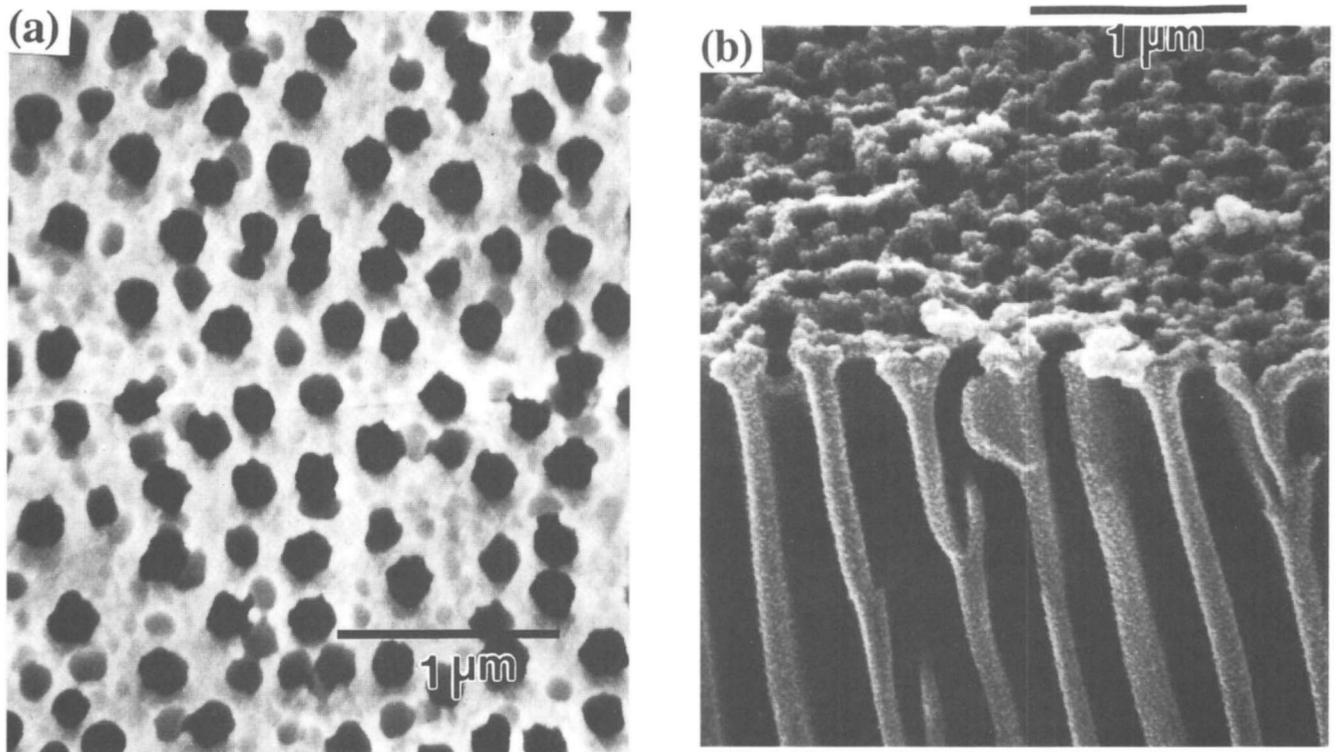


FIG. 7. SEM micrographs of (a) the **top** surface view and (b) the corresponding cross-sectional view of a porous Al_2O_3 substrate with an average surface pore size of about $0.2 \mu\text{m}$.

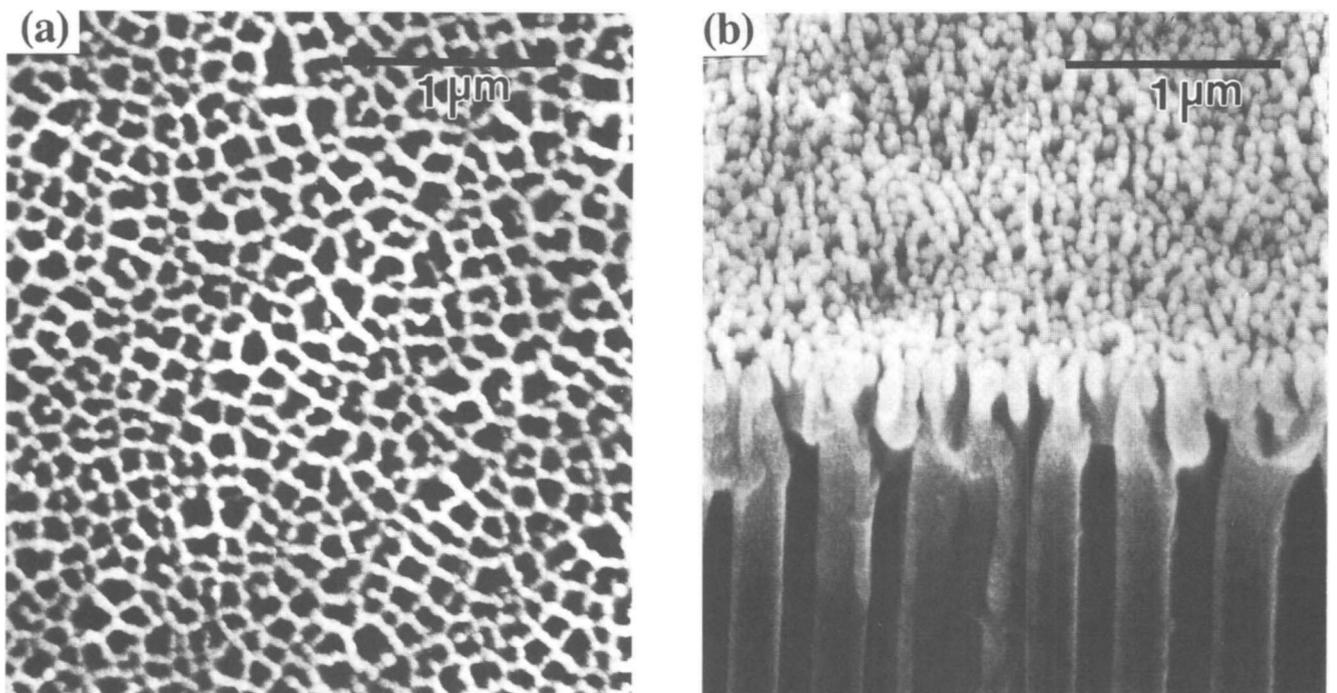


FIG. 8. SEM micrographs of (a) the **bottom** surface view and (b) the corresponding cross-sectional view of the same porous substrate as shown in Fig. 7.

In order to prevent sol from infiltrating into the pores and to eliminate the pinholes in the ceramic films, the surfaces of the porous substrates were further modified with an appropriate polymer film before application of an

LSCF sol solution.¹⁴ The procedure for preparation of an intermediate polymer film on porous Al_2O_3 substrates is described in Sec. II. Figure 11 shows the microstructure and morphology of an LSCF thin-film membrane derived

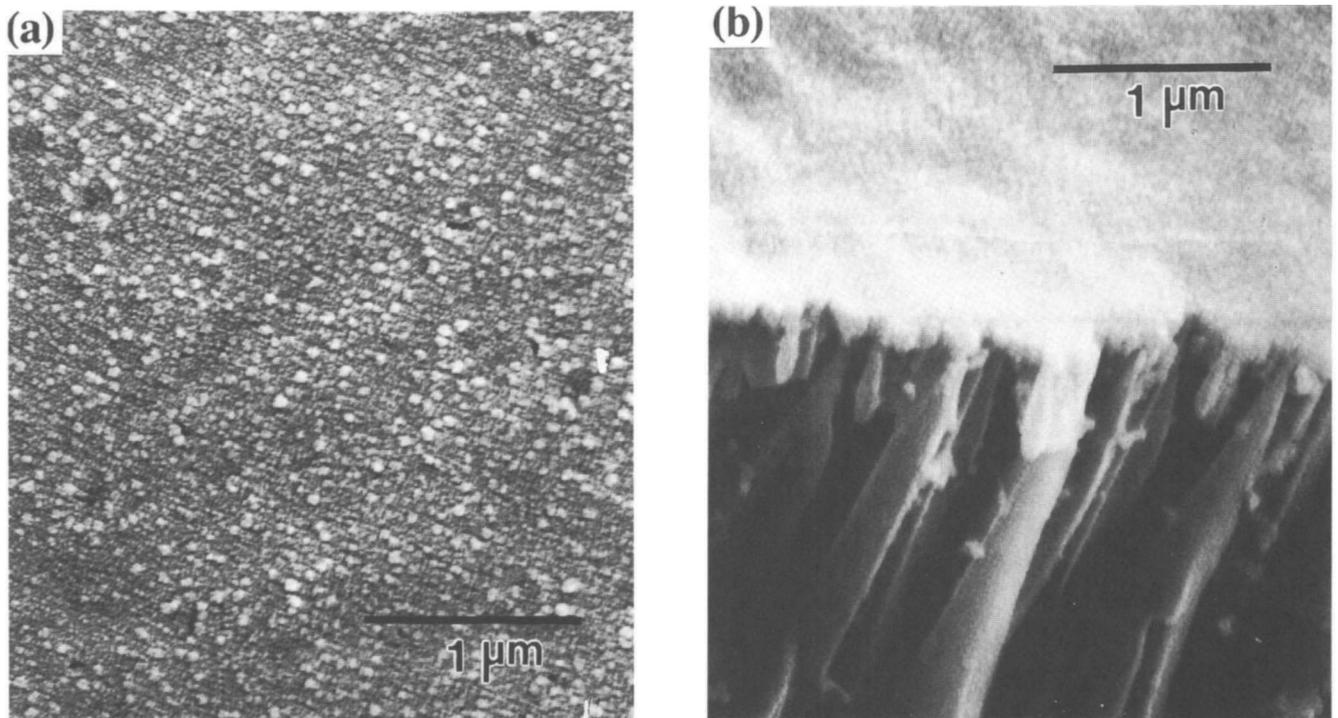


FIG. 9. SEM micrographs of (a) the surface and (b) cross section of an LSCF thin film deposited on the **top** surface of a porous Al_2O_3 substrate.

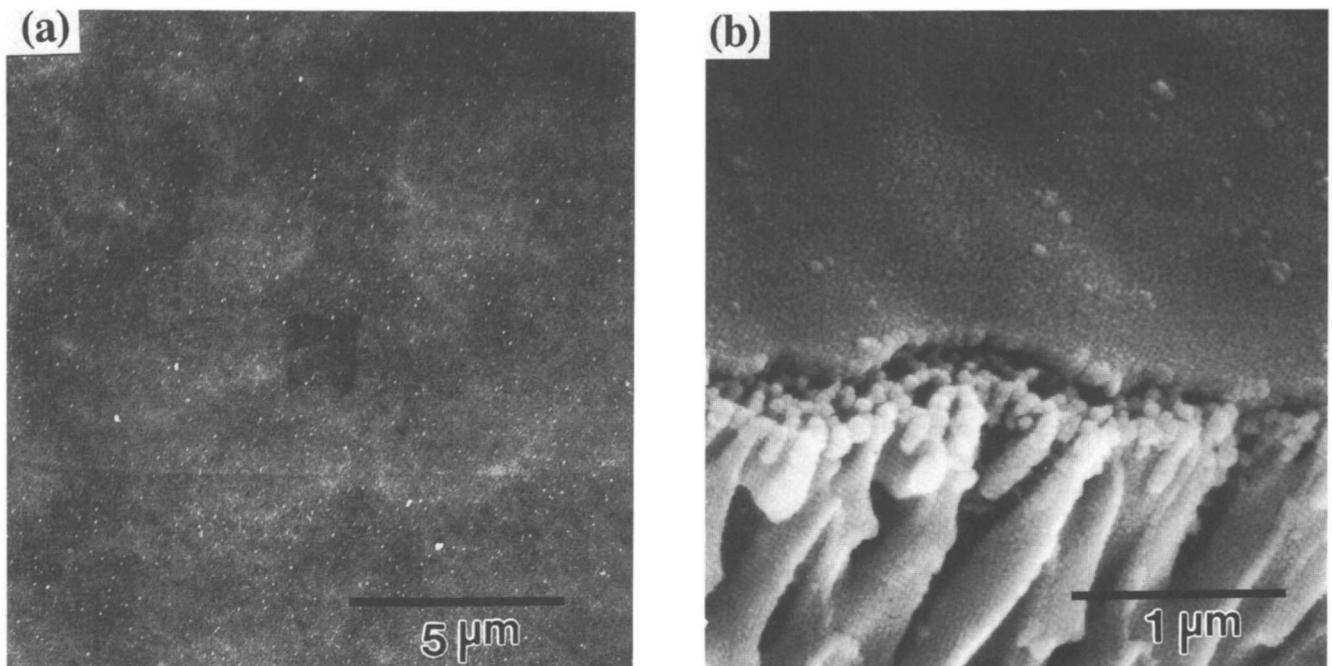


FIG. 10. SEM micrographs of (a) the surface and (b) cross section of an LSCF thin film deposited on the **bottom** surface of a porous Al_2O_3 substrate.

from LSCF sol deposited on a polymer-coated porous substrate. Clearly, infiltration of sol into the pores is considerably reduced, and the uniformity and density of the films are significantly improved. The thickness of the film derived from a single coating is about $0.4 \mu\text{m}$

i.e., the same thickness as the film deposited on a dense substrate, suggesting that the infiltration of sol solution into pores was minimal. Clearly, the quality of this film is much better than that of the films shown in Fig. 9 or Fig. 10.

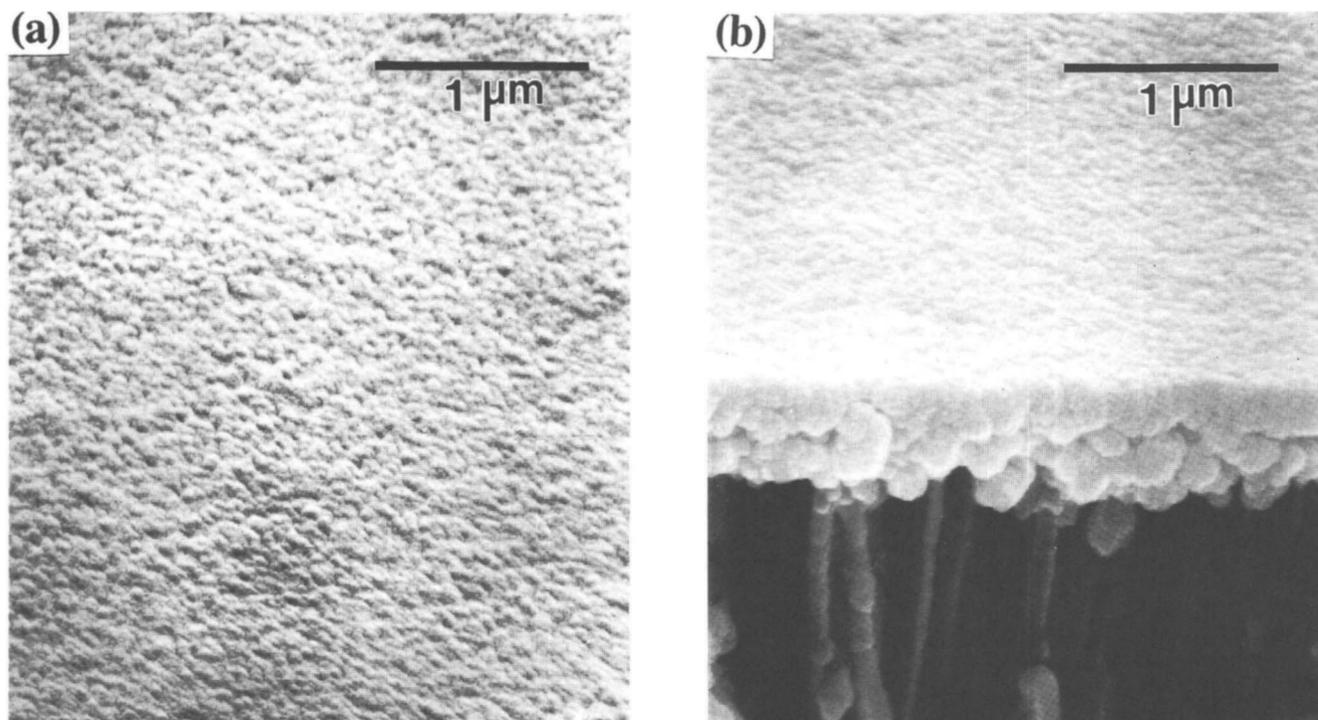


FIG. 11. SEM micrographs of (a) surface and (b) cross section of an LSCF thin film deposited on the top surface of a porous Al_2O_3 substrate. The pores on the surfaces of the porous substrate were sealed off using an intermediate polymer film derived from citric acid and ethylene glycol before a coating of LSCF solution was applied to the substrate.

Successful deposition of thin-film ceramic membranes on porous substrates has significant technological implications. These membranes can be used for various electrochemical processes such as oxygen separation and methane activation and for solid-state ionic devices such as chemical sensors, batteries, and solid oxide fuel cells.

F. Thin-film coatings for catalysis

Mixed conductors are also good electrocatalysts because of their ability to conduct both ionic and electronic species at the same time. Thin-film LSCF coatings were also applied to Pt/YSZ/Pt cells, where YSZ represents yttria-stabilized zirconia with a composition of $\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_2$. The Pt/YSZ/Pt cells were prepared as described elsewhere.¹⁶ The processing procedure for preparation of LSCF coating is the same as outlined in Fig. 2. The electrochemical cells used for impedance measurement are schematically shown in Fig. 12, and can be used as a chemical sensor or as a fuel cell.

Shown in Fig. 13 are the impedance spectra of the Pt/YSZ/Pt cells with and without LSCF coatings, measured in air at different temperatures. Clearly, the interfacial resistances were reduced by the application of LSCF coatings. The reduction in interfacial impedance is more pronounced at lower temperatures, indicating LSCF has higher catalytic activities for oxygen reduction and evolution at lower temperatures. This is very impor-

tant for many solid-state ionic devices involving oxygen to be operated at intermediate or low temperatures.

IV. DISCUSSION

Although the Pechini process has been used in many studies to synthesize high surface area powders,^{8,9} there are only a few studies using the Pechini process to deposit thin films.¹⁰⁻¹³ Among all the parameters concerned, the compositions of the polymerization and chelating agents (i.e., the ratio of citric acid to ethylene glycol) were considered the most important ones. It was reported that the final agglomerate morphology of powder derived from the Pechini process was influenced critically by the ratio of citric acid to ethylene glycol.¹⁷ Logically, this ratio may also play an important role in determination of the film morphology in the thin-film processing.

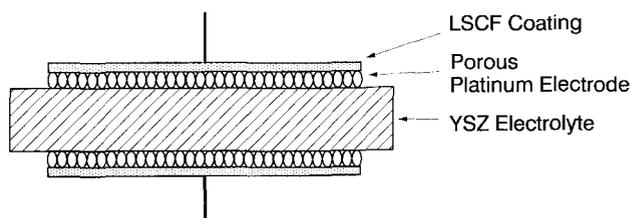


FIG. 12. A schematic illustrating an LSCF thin-film coating on a Pt/YSZ/Pt cell.

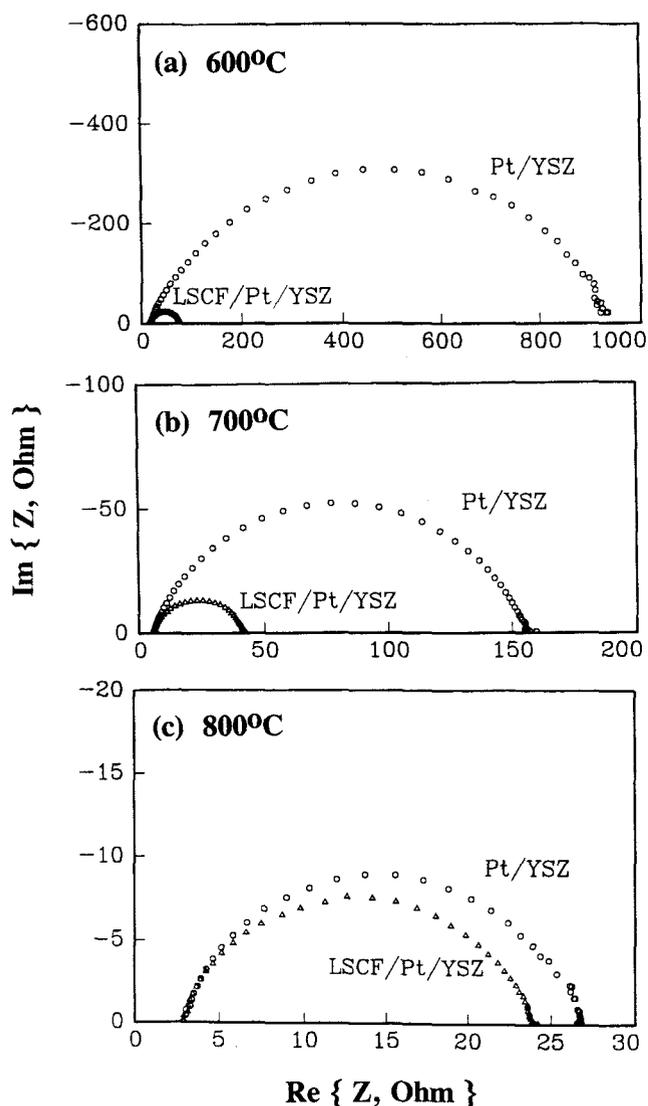


FIG. 13. Impedance spectra of a Pt/YSZ/Pt cell with and without LSCF coatings measured in air at (a) 600 °C, (b) 700 °C, and (c) 800 °C.

Two tactics had been initially laid down for the processing of thin films using the Pechini process. First, it was expected that for thin-film processing, the total amounts of citric acid and ethylene glycol used should be kept minimum in order to reduce the probability of film cracking due to shrinkage during the removal of the organics/polymers. Second, the effect of the composition of the polymer precursors (the ratio of citric acid to ethylene glycol) on the uniformity, density, and cracking had been investigated thoroughly.

This study indicated that the most important processing parameter is the ratio of citric acid to total metal ions (i.e., the C ratio defined earlier). The final film quality and morphology depends critically on this ratio. Typically, films derived from solutions of high C

ratios (e.g., $C \geq 3$) are crack-free (but may not be fully densified), whereas films derived from solutions of low C ratios (e.g., $C \leq 1$) contain cracks and are typically delaminated from the substrates (but each fragment may be quite dense). In contrast, the ratio of citric acid to ethylene glycol is much less critical to the quality of derived films. These observations cannot be fully explained at the present time. However, it is believed that they may be related to the film formation process in this material system.

Clearly, the drying and film formation mechanism in the Pechini process is very different from that in an alkoxide approach. In a sol-gel process using metal alkoxides, partial "ceramic" film (or network) may form even before the gel is dried due to polycondensation among various metal alkoxide precursors, which form mixed-metal-oxide bonds ($\text{M}-\text{O}-\text{M}'$). Cracking usually occurs during drying when the capillary force exceeds the strength of the gels or when there are differential stresses that operate during shrinkage. In contrast, in the Pechini process, the general idea is to obtain a polymer precursor comprising randomly coiled macromolecular chains throughout which the metal cations are uniformly distributed on an atomic level. Low mobility of metal cations in the highly viscous polymeric resin may prevent the metal cations from forming mixed-metal-oxide bonds before the pyrolysis. The solid "ceramic" (or network) will not form until the ignition of the polymeric resin. The ceramic film will form on the substrate only after the organic network is removed. Accordingly, film cracking usually occurs during pyrolysis of the film rather than drying of the film. During the drying stage, the resin film retains its polymeric form, and cracking is avoided. However, there is a large amount of organic residuals to be removed during the pyrolysis stage, depending on the C ratio. Thus, how the ceramic film forms during pyrolysis is the most important factor in determining the quality of the final ceramic film.

Results in this study indicate that the quality of the derived films is influenced dramatically by the C ratios of the starting solutions. It seems, therefore, that the C ratio may have a decisive effect on the structure of the derived polymeric resins and the subsequent ceramic film formation processes during pyrolysis and sintering.

The difference in local structures of the resins with different values of C ratio may be schematically illustrated in Fig. 14. When $C = 1$, each metal cation may be complexed by only one molecule of citric acid, while when $C = 3$ each metal cation may interact concurrently with three molecules of citric acid. Accordingly, it is possible that the resin structure with high C ratio may be more uniform in terms of the spatial distribution of the metal ions and the packing of the macromolecular chains. The chemical interactions among various metal ions thus take place more uniformly. In contrast, the resin structure

is less uniform when the C ratio is relatively low. This is because the lower the C ratio, the fewer the complexation molecules (citric acid) available to each metal ion, and the less uniform the distribution of metal ions in the resin. Further, the fewer the complexation molecules available to each metal ion, the shorter the average distance between metal ions (see Fig. 14), and therefore, the stronger the interactions among metal ions. Accordingly, there is a greater possibility of forming clusters of metal ions, leading to nonhomogeneous resin structure. One observed evidence supporting this speculation is the fact that the bulk gel made with low C ratio suffers extensive warping and buckling. It is this nonhomogeneity that may further lead to the formation of stress concentration centers during the pyrolysis that initiate cracks. This is further supported by the observations that all of the films derived from LSCF solutions with C ratio less than one were extensively cracked.

On one hand, observations suggested that it is necessary to maintain a relatively high C ratio in order to minimize or eliminate nonuniformity in the gels and hence cracking in the final films. On the other hand, the higher the C ratio, the lower the packing density of metal ions, the more the organics to be removed during pyrolysis, the larger the shrinkage, and the more difficult to achieve densification during heat treatment or sintering. High packing density of metal ions (low C ratio) could facilitate densification of ceramic films during sintering. In fact, the films derived from low C ratios were very dense, although they were extensively cracked. Thus, the conditions to eliminate cracking (relatively high C ratio) can be contradictory to the conditions to achieve densification (relatively low C ratio). Of course, excess shrinkage could also cause cracking. Accordingly, selection and optimization of processing parameters are critical to preparation of LSCF ceramic films with desired microstructures and properties.

In order to characterize the differences between the resins derived from solutions with different C ratios,

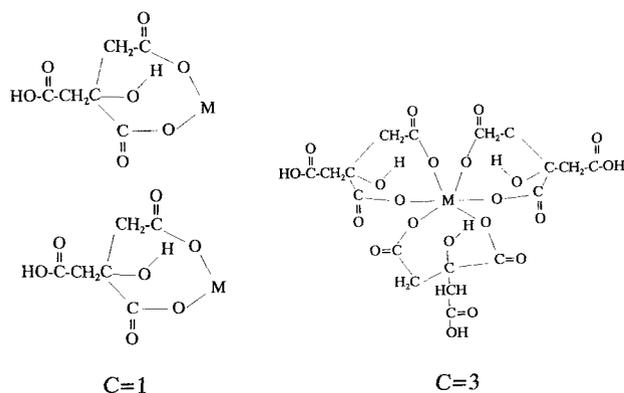


FIG. 14. Schematics illustrating possible local structures of resins derived from solutions with different C ratios: $C = 1$ and $C = 3$.

the difference in thermal evolution of the LSCF gels prepared with different C ratios was studied. Courty *et al.*¹⁸ have proposed two different types of pyrolysis reactions occurring in the Pechini process. The type I pyrolysis is a one-step reaction characterized by a continuous and vigorous reaction. This is commonly observed when precursors contain metal cations having strong catalytic activities for oxidation processes such as Ag, Pt, and Ni. The type II pyrolysis is a two-step process characterized by an intermediate decomposition step, which occurs because of the formation of some intermediate compounds consisting of mixed citrate salts. The thermal analysis of an LSCF gel prepared using a high C ratio ($C = 3.75$), as shown in Fig. 3, indicates that the decomposition of the precursors follows the type II pyrolysis reaction. Rapid weight loss occurs at about 240 °C (step 1). Then the rate of weight loss decreases steadily until about 400 °C where a very rapid weight loss occurs (step 2). Similar thermal analysis was also performed on an LSCF gel with $C = 1$, as shown in Fig. 3. The pyrolysis showed the type II characteristics as well. The only difference in thermal analysis of the two gels is that the pyrolysis of the gel with $C = 1$ started and completed at lower temperatures. Thus, there is no obvious difference in thermal analyses between the two gels with different C ratios. It may be necessary to characterize the microstructural evolution of the films during pyrolysis and subsequent sintering by *in situ* microscopy in order to gain a fundamental understanding of the differences between the gels with different C ratios.

V. CONCLUSIONS

With proper modification, the Pechini process can be readily used to prepare crack-free, uniform, and nonporous (within the resolution limit of the SEM) thin films of LSCF on various dense substrates. A number of processing parameters are important to the quality of the derived thin film. The optimum pH of the solution is about 2. The use of ethylenediamine seems to improve the wetting and adhesion of the sol on substrates. Acetic acid and formic acid seems to be a good dilution medium for the system. The most critical processing parameter, however, is the ratio of the complexation/polymerization agent (citric acid and ethylene glycol) to total metal ions (the C ratio). Films derived from a solution of low C ratio are more amenable to cracking and delamination. This suggests that the polymer structure of the resin significantly influences the ceramic film formation process since the oxide film is formed only during the pyrolysis of the organic residuals. In contrast, the quality of derived films is relatively insensitive to the ratio of citric acid to ethylene glycol. However, the best ratios of citric acid to ethylene glycol range from 1/3 to 1.

In principle, the thickness of the derived films can be increased incrementally with successive coating applications. Each coating of solution may add about $0.4\ \mu\text{m}$ thick film. About $1.2\ \mu\text{m}$ thick LSCF films have been prepared on dense substrates by application of three consecutive coatings. However, the thickness of derived films without cracking is limited by the mismatch in thermal expansion coefficients between LSCF film and substrate.

Further, the Pechini process can be used to deposit nonporous thin-film membranes of LSCF on porous substrates. It is necessary, however, to modify the surfaces of porous substrates before application of LSCF solutions in order to minimize or to eliminate solution infiltration into the substrate. The application of an inert polymer to seal off the pores on the surface of a porous substrate has effectively overcome the problems and has led to high-quality thin film membranes of LSCF on porous substrates.

Finally, LSCF coatings applied to porous platinum electrodes considerably increase the catalytic activity for oxygen reduction and evolution, particularly at low temperatures, suggesting that LSCF coatings are good candidates for catalysts in fuel cells, chemical sensors, oxygen separation, and electrosynthesis.

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