JOURNAL OF MATERIALS SCIENCE **32** (1997) 619–625

Preparation of barium cerate-based thin films using a modified Pechini process

V. AGARWAL, MEILIN LIU
School of Materials Science & Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA

Thin films of $BaCe_{0.8}Gd_{0.2}O_3$ have been successfully prepared on both dense and porous substrates using a modified Pechini process. To increase the extent of chelation, ethylene diamine tetraacetic acid (EDTA) has been used to replace citric acid in the Pechini process. Results indicate that the most important processing parameter is the molar ratio of complexation/polymerization agent (EDTA) to metal ions (C ratio). Films derived from sols with C ratio smaller than 1 are usually cracked, while those derived from sols with C ratio greater than 2.5 are porous. Crack-free and uniform films are obtained from the sols with C ratios between 1.5 and 2.5. Thin-film membranes of barium cerate electrolytes have also been deposited on porous substrates by modifying the surface of the porous substrate with an intermediate polymer film derived from EDTA and ethylene glycol.

1. Introduction

The potential of barium cerate-based electrolytes for intermediate-temperature-solid state ionic devices has been well established in the literature [1–3]. These electrolytes have higher conductivities than yttria-stabilized zirconia (YSZ) electrolyte at similar temperatures. The composition $BaCe_{0.8}Gd_{0.2}O_3$ (BCG) is an attractive choice for electrolyte since it exhibits the highest ionic conductivity among barium cerate electrolytes at intermediate temperatures [1]. When fabricated in a thin-film form, the resistive losses in the electrolyte can be minimized [4] and thus, the processing of these electrolytes in thin-film form assumes significant importance.

The objective of this study is to fabricate thin films of $BaCeO_3$-based electrolytes on dense and porous substrates by modification of the Pechini process [5], which has been successfully used for preparing ceramic powders [6, 7, 8] and thin films [9, 10]. In the Pechini process, desired metal cations are solvated in a solution using a hydroxycarboxylic acid, such as citric acid, as the chelating agent. This solution is then mixed with a polyhydroxy alcohol, such as ethylene glycol, and heated to promote esterification reactions in the solution. Metal ions are chelated by the carboxyl groups and remain homogeneously distributed in the polymeric network [11]. The sol is then deposited on a substrate and subsequently fired at elevated temperatures to form desired oxide. The Pechini process offers several advantages over other techniques [12, 13, 14] for processing of ceramic thin films, including low cost, good compositional homogeneity, high purity, and relatively low processing temperatures [15]. To date, however, attempts to fabricate thin films of $BaCeO_3$-based electrolyte using the Pechini process (in which citric acid is used as the complexing agent) were unsuccessful, although a colloidal processing approach was successful in producing thick films of these electrolytes on dense and porous substrates [16].

In this study, the complexing agent in the Pechini process (citric acid) is replaced by ethylene diamine tetraacetic acid (EDTA) in order to increase the extent of chelation to metal ions in the solutions for $BaCeO_3$-based electrolyte. It is expected that the use of EDTA will improve the uniformity of metal ion distribution in the solution and ultimately influence the structure of the resin, since EDTA has stronger chelating power than citric acid to metal ions. Furthermore, several important processing variables affecting the microstructures of derived films have been systematically investigated and the process parameters are optimized for preparation of crack-free and dense thin films on dense and porous substrates.

2. Experimental procedure

2.1. Preparation of $BaCe_{0.8}Gd_{0.2}O_3$ (BCG) solution

Barium nitrate, cerium nitrate, and gadolinium nitrate were used as precursors for the electrolyte. Ethylene glycol (EG) and EDTA were used as polymerization/complexation agents for the process. Ammonium hydroxide was used to facilitate the dissolution of EDTA in deionized water. The procedure for the preparation of a BCG sol is outlined in the flow chart (Fig. 1). Measured amount of barium nitrate was first dissolved in deionized water at 80 °C, to which measured amounts of EDTA (dissolved in ammonium hydroxide) was added until a clear solution was obtained. The resulting solution had a pH of 9.5 and is labelled as solution A. In a separate beaker,

0022–2461 © *1997 Chapman & Hall*

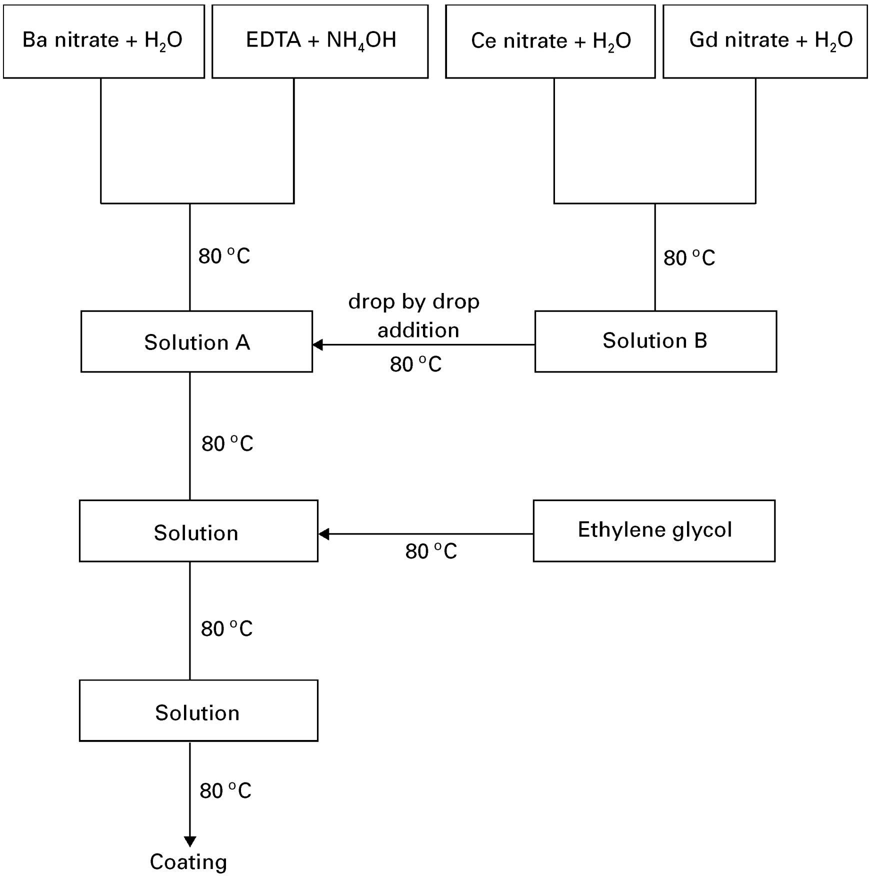

Figure 1 A flow chart illustrating the processing procedure for the preparation of BCG sol solution.

stoichiometric amounts of cerium nitrate and gadolinium nitrate were dissolved in deionized water, resulting in another solution labelled as solution B. The pH of solution B was about 2.5. Solution B was then added drop by drop to solution A to avoid irreversible precipitation. This slow and careful addition was necessary since the addition at a faster rate (even a few drops at a time) caused irreversible precipitation. After the addition of solution B to solution A was completed, a measured amount of ethylene glycol was added to the resulting solution. The amount of EDTA was determined by the molar ratio of EDTA to total metal ions (defined as C ratio) and the amount of ethylene glycol was based on the ratio of EDTA to ethylene glycol (defined as EDTA/EG ratio). The C ratio varied from 0.75 to 3 and the EDTA/EG ratio varied from 1 to 1/6. The solution was stirred at 80 °C to remove the solvents until it reached the desired viscosity to be coated on substrates.

2.2. Preparation of substrates

Slides of Pyrex glass were used as the dense substrates and porous alumina membranes were used as the porous substrates. The porous substrates had precisely-controlled honeycomb-like channels with an average channel diameter of about 0.2 μm. In order to prevent the BCG sol from infiltrating the pores of the porous substrate, an intermediate polymer film without metal cations was prepared on the surface of porous substrate before the deposition of BCG sol. The polymer film used in this study was prepared from a solution containing EDTA and EG, based on an idea developed earlier using citric acid and ethylene glycol [17]. First, EDTA was dissolved in an ammonium hydroxide solution, followed by the addition of ethylene glycol to the solution. The resultant mixture was then heated at 80 °C to promote polyesterification and resin formation. When the mixture had a viscosity of about 0.0035 Pa s (at 80 °C), the porous alumina substrates were dip-coated with the polymer solution and dried at 90 °C in an oven for 5 h. The resultant polymer film was further cured at 200 °C for 5 min. The partially cured polymer film was then kept in an oven at 90 °C for 3–4 h before coating with a BCG sol.

2.3. Coating, drying, and firing

Films of the solution were deposited on dense and porous substrates by dip coating. The films were then dried at 90 °C in an oven for 5–6 h before firing. The heating/cooling rates were carefully controlled to avoid delamination or cracking of films from substrates due to mismatch in thermal expansion between films and substrates. The heating rate used in this study was 0.5 °C min^{-1} from room temperature to 450 °C and 1 °C min^{-1} above 450 °C, and the samples were then held isothermally at the final heat-treatment temperature for 1.5 h. The samples were typically cooled at 5 °C min^{-1}. Unless stated otherwise, all thin-film coatings were heat-treated in air in a tube furnace.

2.4. Characterization

The thermal evolution of gels (after drying at 100 °C) was followed using a Perkin-Elmer thermogravimetric analyser (TGA). The microstructures of prepared thin films were characterized using a Hitachi S-800 field emission scanning electron microscope (SEM). X-ray diffraction (Phillips PW-1800 automated powder X-ray diffractometer) was used to analyse the phase present in derived films.

3. Results and Discussion

3.1. Characteristics of the BCG sols

Three process variables investigated in this study are the C ratio, the EDTA/EG ratio, and the viscosity of BCG sols. For solutions with low C ratios ($C < 1$), it was difficult to keep the metal ions in solution. This may be due to the lack of enough EDTA molecules to solvate metal cations. Adjustment of the pH of the solution by addition of an acid or a base did not help in dissolution of metal salts. For C ratios greater than 1, the solutions formed were clear and it was easy to dissolve the metal ions. A variation in the EDTA/EG ratio from 1 to 1/6 did not have significant effect on the BCG sols.

Fig. 2 shows the variation in viscosity of a sol as a function of time at 80 °C. The C ratio of the sol was 1.5 and the EDTA/EG ratio was 1/3. It was found that viscosity values greater than 0.0025 Pa s were needed for acceptable wettability of BCG sols on glass substrates. Viscosities lower than 0.0025 Pa s resulted in poor wettability. The pH of the solutions decreased from nearly 7 to about 6 as the viscosity increased from 0.0008 to 0.005 Pa s. If the solution was kept at 80 °C for more than 2.5 h, it resulted in viscosities greater than 0.005 Pa s which frequently caused precipitation in the solution. The precipitates in the sol may lead to compositional inhomogeneities during oxide film formation. They may also behave as stress concentration centres, leading to microcracks in the film. Hence, an optimization of the viscosity and the C ratio in the sol is needed to get a stable and transparent sol, i.e. a sol without precipitates.

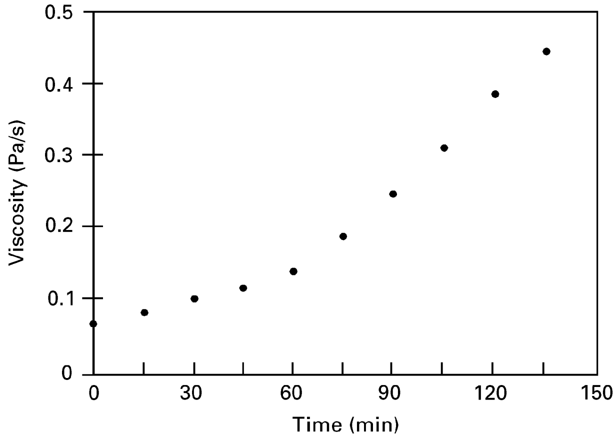

Figure 2 Variation in viscosity of a BCG sol at 80 °C as a function of time (the C ratio of the sol was 1.5 and the EDTA/EG ratio was 1/3).

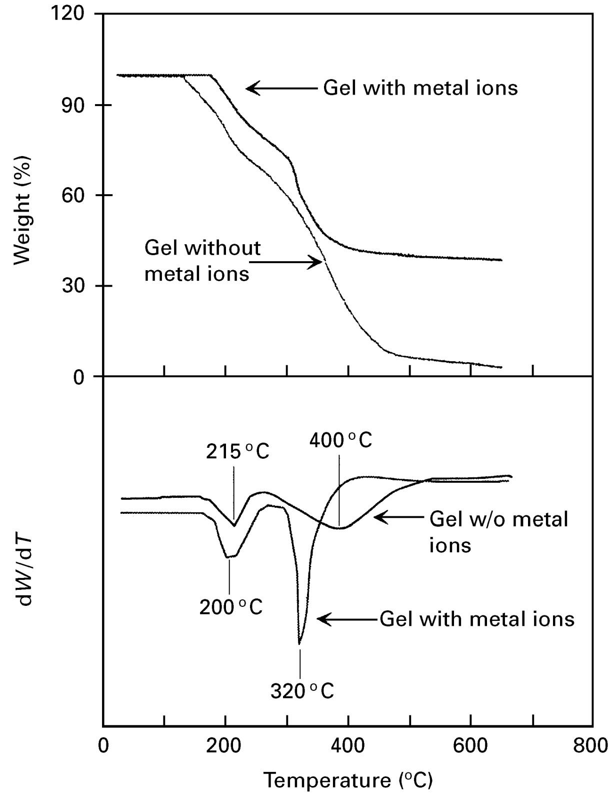

Figure 3 (a) TGA and (b) DTGA analyses of two gels: one gel with metal cations (from a BCG sol with a C-ratio of 1.5) and the other without metal cations (from a sol containing EDTA and EG). The temperature scan rate was 1 °C min^{-1} and EDTA/EG ratio for both sols was 1/3.

3.2. Thermal Evolution

Fig. 3 shows the results of thermogravimetric analysis (TGA) on two dried gels. One gel was from a solution of EDTA and ethylene glycol dissolved in water without metal ions, while the other was from a sol for BCG coatings, i.e. a sol containing 0.008 M $Ba(NO_3)_2$, 0.0064 M $Ce(NO_3)_3$, 0.0016 M $Gd(NO_3)_3$, EDTA, and ethylene glycol. The C ratio of the sol was 1.5. The molar ratio of EDTA to EG for both solutions was 1/3. The gel without metal ions was the one used as the intermediate polymer film to modify the surface of porous substrate. It can be seen that most of the weight loss due to the organic burn-off occurred below 400 °C for the gel with metal cations and below 500 °C for the gel without metal cations. The DTGA curves for both gels exhibited a weight loss peak at about 200 °C which may be due to the evaporation of excess ethylene glycol [18]. An interesting observation from the curves is the occurrence of a sharp weight loss peak at about 320 °C for the gel with metal cations. In contrast, the weight loss peak for the gel without metal cations occurs at about 400 °C and is much more gradual. The much sharper weight loss in the gel with metal ions suggests that the presence of metal ions had a catalytic effect on the pyrolysis of organics in the gel. This is further supported by the observation that pyrolysis of the organics in the gel with metal cations was completed about 100 °C lower (at 400 °C) than that in the gel without metal cations (500 °C). The results also indicate that there was a significant weight loss (nearly 60%) due to the organics burn-off in the gel with metal cations. Hence, the temperature profiles for heat treatment or firing should be carefully designed to allow for a uniform removal of organics in this temperature range.

3.3. Structural Evolution

Shown in Fig. 4 are the X-ray diffraction (XRD) patterns of the films heat-treated at different temperatures. The results indicate that the films remained amorphous up to 400 °C. Some peaks began to appear at 500 °C and the peaks expected for the perovskite phase began to appear at 600 °C. Perovskite phase formation was completed at 750 °C, while the minimum temperature required to form BCG perovskite phase by conventional ceramic processing (solid state reactions) is about 1350 °C [19]. In the Pechini process, the powder particles formed are extremely fine, and thus, highly reactive. These fine particles may have aided the formation of BCG perovskite phase at much lower temperatures. An important implication of this result is that the processing temperatures of the BCG films can be significantly reduced using the modified Pechini process.

3.4. Microstructure of Derived Films on Dense Substrates

Fig. 5 shows the SEM micrographs of the surface and cross-sectional views of a BCG thin film coating on a dense glass substrate. The film was dervied from a single coating of a BCG solution (C = 1.5) of viscosity 0.00325 Pa s (at 80 °C). The ratio of EDTA/EG was 1/3. The thickness of the film was about 0.3 μm after firing at 600 °C for 1.5 h. It can be seen from the micrographs that the film is smooth, crack-free, and non-porous (within the resolution limits of the SEM). The grain sizes are fine (submicron size) and appear to be uniform.

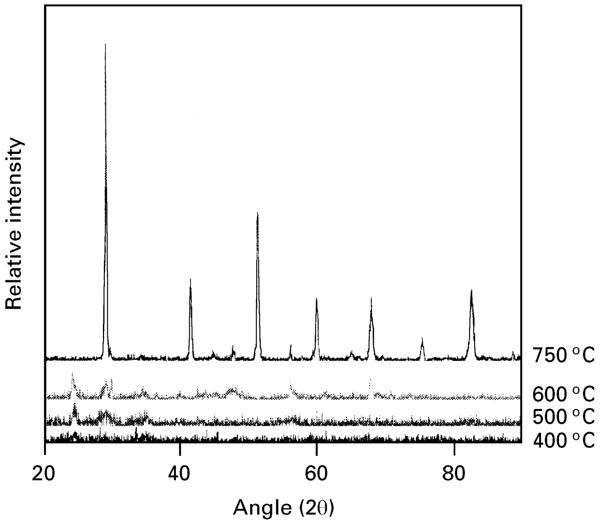

Figure 4 XRD patterns of BCG films fired at different temperatures.

In general, uniform and crack-free thin films were readily obtained using sols with a C ratio between 1.5 and 2.5 and viscosities between 0.003 and 0.0035 Pa s at 80 °C. For C ratios smaller than 1, as discussed earlier, precipitation of metal salts in the solution occurred frequently and, as a result, the films were non-uniform and cracked. For C ratios greater than 2.5, no precipitation was observed, but the derived films were porous.

Clearly, C ratio is a very important factor in determining the microstructure of the derived ceramic films. In addition to determining the amount of organic burn-off during pyrolysis, this ratio may also affect the structure of the polymeric resin. Recently, a possible explanation of the difference in resin

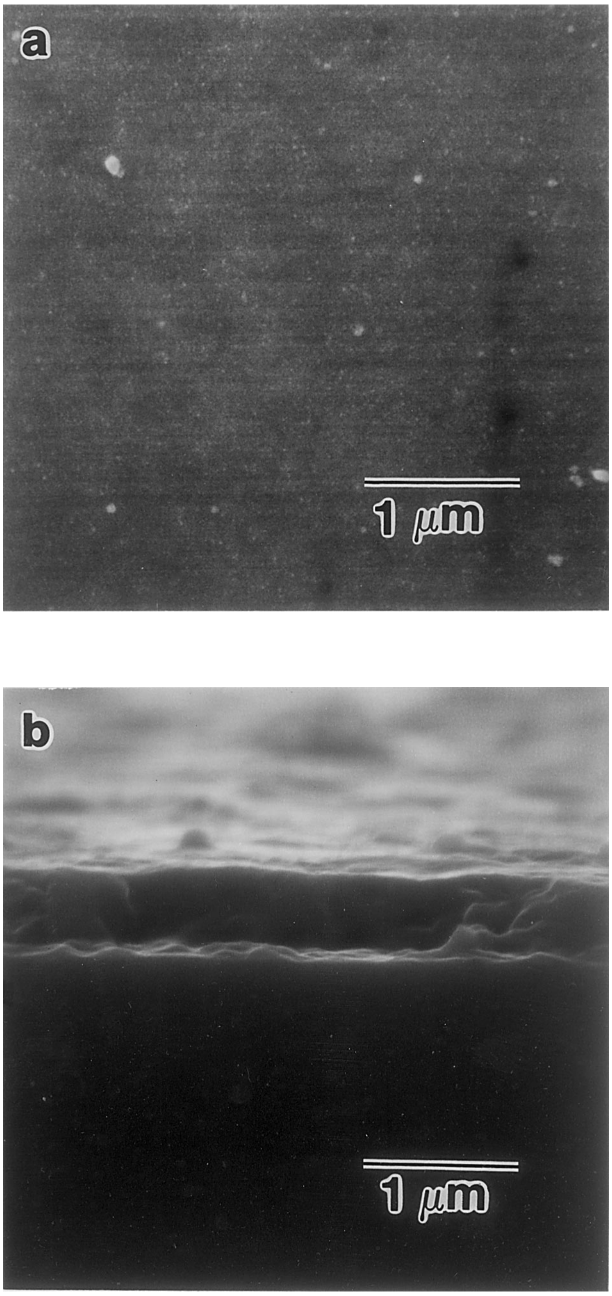

Figure 5 (a) Surface view and (b) cross-sectional view of a BCG thin-film on a dense glass substrate fired at 600 °C for 1.5 h. The film was derived from a single coating of a sol with C = 1.5.

structure and hence in microstructure of the derived films due to different C ratios was given for preparation of $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ films using the citric acid based Pechini process [10]. The explanation of the effect of C ratio on the local structures of the resin for citric acid/EG system may be applicable to the EDTA/EG system as well. The local structure of the resin may be significantly influenced by the C ratios. With C = 1, each metal ion may be complexed by only one molecule of EDTA, while when C = 2 each metal cation may complex with 2 molecules of EDTA. It is thus possible that the resin structure with C = 2 may have more uniform spatial distribution of metal ions, preventing clustering or non-homogeneity in the structure. With C = 1 or smaller, the resin structure may be less uniform and there may not be enough complexation molecules to hold the metal ions in solution. For higher C ratios (C = 2.5 or greater), the resin structure will be uniform but the amount of organics to be removed and hence shrinkage will be excessive. Accordingly, it will be difficult to form a continuous film. This is further supported by the observations that all of the films derived from the BCG solutions with C ratios greater than 2.5 were quite porous.

Thus, two opposing factors are simultaneously affecting the microstructure of derived films. On one hand, a relatively high C ratio is needed to maintain the uniformity of metal ions in the solution and to prevent cracking. On the other hand, the C ratio should be sufficiently low (i.e. the organics to be removed and shrinkage should be sufficiently small) so that a continuous film can be formed during firing. Thus, the selection and optimization of processing parameters is critical to preparation of crack-free and dense BCG ceramic films.

EDTA was chosen in this study (instead of citric acid) as complexing agent due to its stronger chelating power to metal cations. As seen in Fig. 6, with one molecule of citric acid, the metal ion may be chelated by three bonds while this number is six with EDTA [20]. Thus, EDTA may provide stronger interactions with metal ions in the BCG system, resulting in a favourable resin structure for film formation. The stronger (almost double) chelating power of EDTA is further supported by the observation that the optimum C ratio for dense-film formation in EDTA/EG system (C = 1.5) is nearly half of that observed for the CA/EG system (C = 3.5) [10]. It may be argued that a larger amount of citric acid may help the attainment of stronger chelating power; but the prohibiting factor in that case would be the increase in the amount of organics to be removed. The advantage of using EDTA in place of citric acid is that it provides about twice the chelating power but does not introduce twice the amount of organics to be removed during firing. This is because the molar weight of citric acid is 210.14 g while that of EDTA is 292.24 g. Thus, the molar weight ratio of EDTA to citric acid is 1.39, while the chelating power ratio of EDTA to citric acid is about 2. This has a significant implication in this process. The detailed molecular interactions and their influence on the film formation mechanisms in the EDTA/BCG system is still under investigation.

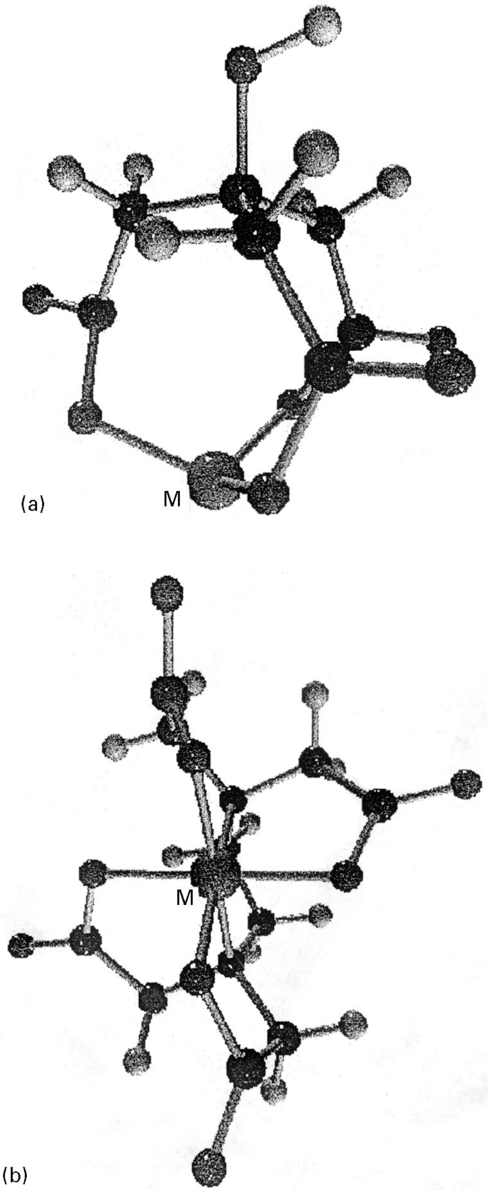

Figure 6 Schematics showing the chelation interactions of a metal ion M with (a) a citric acid (CA) and (b) an ethylenediamine tetraacetic acid (EDTA) molecule.

The ratio of EDTA to ethylene glycol had no significant effect on the film microstructure within the range investigated in this study. Viscosity of the sol also affected the film morphology. The films derived from the sols of viscosities greater than 0.0045 Pa s were usually cracked. This is because high viscosity sols result in thicker films which would be less tolerable to mismatch in thermal expansion between the film and the substrate. Thermal stresses generated during heat-treatment led to cracking in thick films.

3.5. Thin-film Membranes on Porous Substrates

The thin-film membranes obtained by direct deposition of sol on porous Al_2O_3 substrates were discontinuous and porous due to infiltration of large amounts of sol into the porous substrates. In order to prevent sol from infiltrating into the porous substrates, the surfaces of the porous substrates were modified with a polymer film as described in the experimental section.

Fig. 7 shows the microstructures and morphologies of two BCG thin-film membranes derived from a BCG sol deposited on a polymer-coated porous substrate. The surfaces of the films appear to be uniform and dense with a fine particle size as shown in Fig. 7a. A cross-sectional view of a film derived from a single coating is shown in Fig. 7b. The thickness of the film is about 0.3 μm. Application of successive coatings resulted in thicker films. Fig. 7c shows the cross-sectional view of a film derived from three successive coatings. The thickness of the film is about 0.9 μm and the film is dense and uniform. Thus, each coating increased the thickness of the membrane by approximately 0.3 μm. Films derived from more than three coatings developed microcracks. One possible factor resulting in microcracking is mismatch in thermal expansion coefficients (TECs) between the film and the substrate because thicker films are less tolerable to mismatch in TECs between a film and a substrate. Further, the repeated thermal cycles during processing for successive coatings may also generate thermal stresses responsible for cracking in the film.

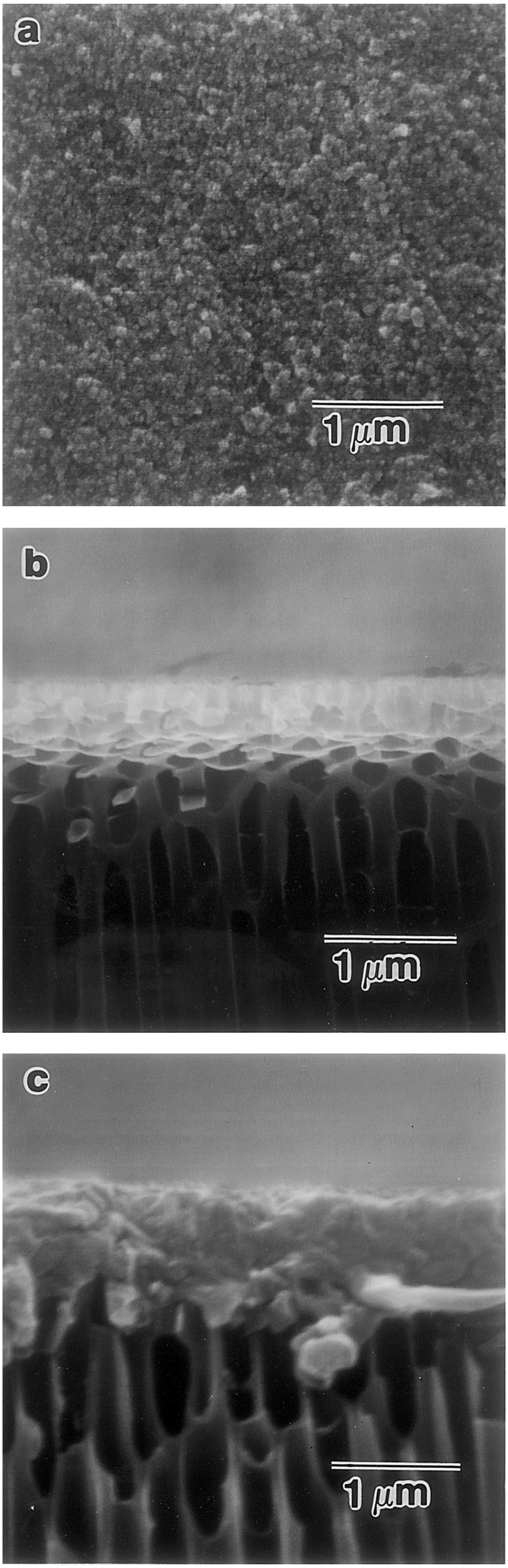

Figure 7 SEM micrographs of BCG films on porous alumina substrates fired at 750 °C for 1.5 h: (a) surface view of a film derived from a single coating and cross-sectional views of films derived from (b) a single coating and (c) three coatings.

4. Conclusions

Crack-free, uniform, and non-porous thin films of $BaCe_{0.8}Gd_{0.2}O_3$ electrolyte have been successfully prepared using a modified Pechini process in which ethylene diamene tetraacetic acid (EDTA) is used to replace citric acid in order to improve the solvation of metal cations in the sol solution. The most critical processing parameter is the ratio of complexation agent (EDTA) to total metal ions (C ratio). Crack-free and uniform electrolyte films are obtained only at intermediate C ratios ($1.5 < C < 2.5$). It is believed that the C ratio affects the resin structure and the amount of organics to be removed during firing, which, in turn, affects the final film microstructure. Viscosities of the sols also affect the quality of derived films. Sols with high viscosity result in thick films which are more prone to delamination or cracking due to thermal stresses during heat-treatment. Thin films were also deposited on porous substrates by modifying the surface of the porous substrate with an intermediate polymer film.

Acknowledgements

This work was supported by Electric Power Research Institute (EPRI) under Contract No. RP 1676-19 and by National Science Foundation (NSF) under Award No. DMR-9357520. The authors gratefully acknowledge EPRI and NSF for their financial support of this research. Also, one of the authors (V. Agarwal) would like to acknowledge Dr Angus Wilkinson (Dept. of Chemistry, Georgia Tech.) and Dr Vinod Nair (Dept. of Textile Engineering, Georgia Tech.) for many valuable discussions.

References

1. N. TANIGUCHI, K. HATOH, J. NIKURA, T. GAMO and H. IWAHARA, *Solid State Ionics* **53–56** (1992) 998.
2. N. BONANOS, B. ELLIS, K. S. KNIGHT and M. N. MAHNOOD, ibid. **35** (1989) 179.
3. H. IWAHARA, ibid. **52** (1992) 111.
4. T. W. KUEPER, S. J. VISCO and L. C. D. JONGHE, ibid. **52** (1992) 251.
5. M. P. PECHINI, "Method of preparing lead and alkaline earth titanates and niobates and coating method using the same to form a capacitor", U.S. Patent 3,330,697 (1967).
6. H. U. ANDERSON, M. J. PENNELL and J. P. GUHA, *Advances in Ceramics* **21** (1987) 91.
7. D. J. ANTERTON and F. R. SALE, *Powd. Metall.* **1** (1979) 14.
8. S. KUMAR and G. L. MESSING, in Proceedings of the Materials Research Society Symposium San Francisco, April 1992, edited by M. J. Hampden-Smith, W. G. Klemperer, and C. J. Brinker (Materials Research Society, Pittsburgh, PA, 1992) p. 95.
9. C. C. CHEN, M. M. NASRALLAH and H. U. ANDERSON, *J. Electrochem. Soc.* **140** (1993) 355.
10. M. LIU and D. S. WANG, *J. Mater. Res.* **10** (1995) 3210.
11. S. L. PESCHLE, M. CIFTICIOGLU, D. H. DOUGHTY and J. A. VOIGHT, in Proceedings of the Materials Research Society Symposium, San Francisco, April 1992, edited by M. J. Hampden-Smith, W. G. Klemperer, and C. J. Brinker (Materials Research Society, Pittsburg, PA, 1992) p. 101.
12. N. Q. MINH, *J. Am. Ceram. Soc.* **76** (1993) 563.
13. A. A. HUSSAIN and M. SAYER, *Vacuum* **44** (1993) 41.
14. M. A. AERGERTER, *J. Non-Cryst. Solids* **151** (1992) 195.
15. C. J. BRINKER and S. P. MUKHERJEE, *Thin Solid Films* **77** (1981) 141.
16. VISHAL AGARWAL and MEILIN LIU, *J. Electrochem. Soc.* accepted.
17. M. LIU and D. S. WANG, U.S. Patent disclosure (1994).
18. L. V. INTERRANTA, Z. JIANG, and D. J. LARKIN, *ACS Symposium Series* **377** (1988) 168.
19. W. RAUCH and M. LIU, "Role of ceramics in advanced electrochemical systems", edited by P. N. Kumta, G. S. Rohrer and U. Balachandran. Ceramics Transactions, 65 (American Ceramic Society, Westerville, OH, 1996) p. 73.
20. JOHN KOTZ and KEITH PURCELL "Chemistry and chemical reactivity" (Saunders College Publishing, New York, 1987).

Received 6 February
and accepted 21 May 1996