DEPOSITION OF SAMARIA-DOPED CERIA ELECTROLYTE USING SPRAY PYROLYSIS

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ABSTRACT

A spray pyrolysis technique was applied to deposit thin, dense samaria-doped ceria (SDC) electrolyte films. The SDC films were deposited on porous NiO-YSZ substrates at deposition temperatures between 400°C and 450°C. The influence of process parameters such as deposition temperature and salt concentration on film morphology was studied. A smooth dense film was successfully deposited using the precursor cerium nitrate and samarium nitrate dissolved in butyl carbitol (33.3 vol%), 2-methoxy-1-propanol (33.3 vol%), and ethanol (33.3 vol%) solvent mixture.

INTRODUCTION

Doped ceria is a promising candidate material for the electrolyte in intermediate temperature solid oxide fuel cells (SOFCs) operating in the range 500-700°C. Accordingly, extensive efforts are focused on fabrication of SOFCs based on samaria-doped ceria (SDC), yttria-doped ceria (YDC), or cerium gadolinium oxide (CGO) electrolytes. So far, various ceramic manufacturing processes have been used for preparation of ceria electrolytes. In general, the manufacturing processes can be classified into two broad categories: ceramic powder processing methods, such as tape casting (1), screen printing (2), and dry pressing (3); and various deposition methods, such as spray pyrolysis (4), electrostatic spray deposition (ESD) (5), flame assisted vapor deposition (FAVD) (6), and metal-organic chemical vapor deposition (MOCVD) (7).

It has been demonstrated that SOFCs with a ceria electrolyte can operate at intermediate and low temperatures using hydrogen as fuel; the SOFCs designed were either self supported electrolyte or anode supported. Due to ohmic losses the electrolyte supported SOFC can operate efficiently in the temperature range of 700 to 800°C. The maximum power density of 290 mW/cm² was achieved for the 600 μm thick self supported SDC electrolyte at 800°C (3). In the case of a thinner electrolyte support, reasonable power density was generated at 700°C as well. The maximum power density for the SOFCs based on 500 μm (8) and 380 μm (9) thick ceria electrolytes reached 100 mW/cm² and 250 mW/cm², respectively, when the fuel cells were operated on hydrogen at 700°C. Encouraging performance of a six cell 500 μm electrolyte stack was demonstrated with a peak power density of 100 mW/cm² at 700°C (10). Further performance improvements were obtained in the case of anode supported SOFC design. Zheng et al. (2) compared
two fuel cell arrangements incorporating either tape cast thick film (5-10 \( \mu \text{m} \)) or a self supported (300 \( \mu \text{m} \)) CGO electrolyte. Due to the greater resistance of the self supported electrolyte, at 650°C cell power reached 45 mW/cm\(^2\) whereas over 120 mW/cm\(^2\) was obtained from the anode supported fuel cell. Xia et al. (11) prepared higher quality SDC films (with thickness of 30 \( \mu \text{m} \)) onto porous NiO-SDC substrates by a screen-printing technique. At 600°C the fuel cell was showing excellent performance with a peak power density of 400 mW/cm\(^2\). Even at lower temperatures, an anode supported SOFC can generate reasonable power density as reported by Doshi et al. (12). At 500°C a fuel cell based on a tape cast 30 \( \mu \text{m} \) thick film CGO electrolyte attained a maximum power density of 140 mW/cm\(^2\). In the case of a 25 \( \mu \text{m} \) thick SDC electrolyte the maximum power density reached was 235 mW/cm\(^2\) at 535°C (13).

Further performance improvements can be obtained by using an electrolyte of less than 25 \( \mu \text{m} \). The spray pyrolysis technique provides the potential to produce thin (0.1 to 10 \( \mu \text{m} \)) gas tight ceramic films, which can be used as electrolytes for SOFCs with an operating temperature of 500°C. Due to the growth of electrolyte layer directly onto the electrode surface, large electrochemically active surface area and low interface polarization losses can also be expected. This thin film deposition method is rather simple and cost-effective. The composition of the film can be easily controlled by the precursor solution. Porous electrodes (6, 14, 15) and dense electrolytes (4, 16, 17) were already deposited using the spray pyrolysis technique. However, little work has been previously reported on the doped ceria deposition. Rupp et al. (18) investigated grain growth of dense 0.5 \( \mu \text{m} \) thick CGO electrolytes deposited onto sapphire substrates. The spray pyrolysis technique has been also used to deposit highly porous films of CGO onto stainless steel substrates and dense buffer layers of YDC onto YSZ electrolytes (4, 5).

Here we present the results of thin film SDC deposition onto a porous SOFC anode substrate. The influence of the spray pyrolysis parameters such as deposition temperature, salt concentration and precursor solution flow rate are investigated.

**EXPERIMENTAL**

The SDC electrolytes were prepared using a spray pyrolysis setup shown in Fig. 1. The spray pyrolysis technique involves atomization of the precursor solution to an aerosol, which is then transported by air flow to a heated substrate, where a film is formed.

![Figure 1. Schematic drawing of the spray pyrolysis apparatus.](image-url)
Porous NiO-YSZ anode substrates (about 600 μm thick) were fabricated using the tape casting route. Thin SDC films were deposited onto the substrates using spray pyrolysis. We have used the spray pyrolysis technique with a custom-made air blast atomizer. The atomizer to substrate distance was 20 cm. Dense films of an SDC electrolyte were deposited onto the substrate by spraying samarium nitrate hexahydrate (Sm(NO₃)₃·6H₂O; Alfa Aesar) and cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O; Alfa Aesar) dissolved in a solvent mixture consisting of 33.3 vol% diethylene glycol monobutyl ether commonly known as butyl carbitol (C₆H₁₄O₃; Alfa Aesar), 33.3 vol% 2-methoxy-1-propanol (C₄H₁₀O₂; Alfa Aesar), and 33.3 vol% ethanol. The precursor solution was prepared according to the stoichiometry of the required (Ce₀.₈(Sm₀.₂)₀.₂ film. The overall concentration of salts in the solution was either 0.1 or 0.5 mol/L. The precursor solution was atomized to an aerosol by exposing it to a stream of air. The deposition temperature was varied from 400 to 450°C. The flow rate of the precursor solution was either 15 or 30 mL/h. The surface morphology and the cross-section of the deposited films were characterized using scanning electron microscopy (SEM) (Hitachi S-3500N).

RESULTS

The substrate temperature is the most important spray parameter. Fig. 2 shows different film morphologies of films deposited using the spray pyrolysis technique at different temperatures. The deposited droplets are still rich in solvent at temperatures of 400°C and below. Consequently, the film cracks due to stresses which develop during the process.

Figure 2. The effect of deposition temperature, a) 400°C; b) 425°C; c) 440°C; d) 450°C. Deposition time: 1h.
of drying a large quantity of solvent on the substrate (see Fig. 2a). Above 425°C, the impacting droplets contain less solvent due to the higher solvent evaporation rate. Therefore, the drying step is more homogeneous and consequently does not cause any stresses, this leads to a crack-free film (see Fig 2b, c, d). At too high temperatures (>450°C) the impacting droplets are almost dry. The droplets are too viscous leading to a slow spreading rate and consequently causing poor coverage of pores. Therefore, many pores remained open after the deposition at 450°C (see Fig. 2d). The SDC film of the highest quality was deposited at 440°C (see Fig. 2c).

The cross-section of the SDC film deposited at the optimal experimental conditions is shown in Fig. 3. The thin electrolyte film of approximately 2.6 μm was deposited in two hours. It follows that a deposition rate of 1.3 μm/h was achieved. The longer deposition time of two hours was chosen to make sure that the pinholes remaining after a one-hour deposition will be closed.

![Figure 3. SEM micrograph of the cross section of SDC film deposited on a porous NiO-YSZ substrate at 440°C. Deposition time: 2h.](image_url)

In order to increase the film deposition rate the precursor solution concentration was increased from 0.1 mol/L to 0.5 mol/L. A smooth and crack-free film was deposited in the case of the 0.1 mol/L precursor solution (see Fig 4a). In contrast, a cracked film was formed when the precursor solution of 0.5 mol/L concentration was sprayed (see Fig. 4b). A consequence of an increased concentration is that more material arrives on the substrate. This causes large volume changes during the precursor decomposition. Therefore stresses leading to the cracks occur. Micrometer sized pores on a NiO-8YSZ anode substrate were completely covered by the SDC film in the both cases (Fig. 4).

In this study the precursor solution was sprayed at either a 15 or 30 mL/h flow rate. We have not observed any significant change in the morphology of the film when the flow rate was varied. In both cases the deposited films were smooth and homogeneous.

Electrochemical fuel cell tests are in progress.
CONCLUSIONS

Dense and smooth SDC films have been successfully deposited onto porous NiO-YSZ anode substrates at 440°C. An increase of the precursor concentration from 0.1 mol/L to 0.5 mol/L caused cracking of the SDC film. The precursor solution flow rate within the investigated range did not influence the film morphology. A deposition rate of 1.3 μm/h was achieved.

ACKNOWLEDGEMENTS

The authors thank the National Research Council (NRC) Fuel Cell / Hydrogen Program for financial support of the reduced temperature SOFCs project.

REFERENCES

1. M. Gödicke-meier, K. Sasaki, L. J. Gauckler, I. Riess, Solid State Ionics, 86-88, 691 (1996).
2. K. Zheng, B. C. H. Steele, M. Sahibzada, I. S. Metcalfe, Solid State Ionics, 86-88, 1241 (1996).
3. S. Seike, H. Suwahara, T. Noguchi, C. Imazawa, M. Haba, in SOFC-V, U. Stimming, S. C. Singhal, H. Tagawa, W. Lehnert, Editors, PV97-40, p. 1096, The Electrochemical Society Proceedings Series, Pennington, NJ, (1997).
4. D. Perednis, L. J. Gauckler, Solid State Ionics, 166, 229 (2004).
5. I. Taniguchi, R. C. van Landschoot, J. Schoonman, Solid State Ionics, 160, 271 (2003).
6. K. L. Choy, W. Bai, S. Charojrochkul, B. C. H. Steele, J. Power Sources, 71, 361 (1998).
7. G. Y. Meng, H. Z. Song, H. B. Wang, C. R. Xia, D. K. Peng, Thin Solid Films, 409, 105 (2002).
8. T. Mori, J. Drennan, J.-H. Lee, J.-G. Li, T. Ikegami, Solid State Ionics, 154-155, 461 (2002).
9. C. Lu, W. L. Worrell, R. J. Gorte, J. M. Vohs, J. Electrochem. Soc., 150, A354 (2003).
10. C. Milliken, S. Guruswamy, A. Khandkar, J. Electrochem. Soc., 146, 872 (1999).
11. C. Xia, F. Chen, M. Liu, Electrochem. Solid-State Lett., 4, A52 (2001).
12. R. Doshi, V. L. Richards, J. D. Carter, X. Wang, M. Krumpelt, J. Electrochem. Soc., 146, 1273 (1999).
13. X. Zhang, M. Robertson, C. Decès-Pétit, Y. Xie, R. Hui, S. Yick, M. Staite, E. Styles, J. Roller, S. Tang, J. Jankovic, R. Maric, D. Ghosh, in these Proceedings.
14. I. Taniguchi, R. C. van Landschoot, J. Schoonman, Solid State Ionics, 156, 1 (2003).
15. A. Princivalle, D. Perednis, R. Neagu, E. Djurado, Chem. Mater., 16, 3733 (2004).
16. N. H. J. Stelzer, J. Schoonman, J. Mater. Synthesis and Processing, 4, 429 (1996).
17. T. Nguyen, E. Djurado, Solid State Ionics, 138, 191 (2001).
18. J. L. M. Rupp, E. Jud and L. J. Gauckler, in Sixth European Solid Oxide Fuel Cell Forum Proceedings, M. Mogensen, Editor, p. 1202, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).