FABRICATION OF CATHODE SUPPORTED SOFC
BY COLLOIDAL PROCESSING

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ABSTRACT

Electrophoretic deposition (EPD) has been used to grow thin films of solid oxide fuel cell components on a porous cathode support. EPD exploits a surface charge on particles in a stable suspension migrating in the presence of an appropriate electric field to effect the consolidation of particles onto any shaped substrate. In this investigation, both flat and tubular supports have been used. Both types of supports were fabricated using tape casting followed by lamination. Suspension chemistries containing LSM-YSZ, YSZ and NiO-YSZ have been standardized. The thickness of the films as developed for the cathode functional layer, electrolyte, and anode were 15, 5 and 50 μm respectively. The electrophoretically deposited coatings resulted in high quality, crack-free green (unfired) films and even after firing the surface remained smooth, continuous and homogeneous.

INTRODUCTION

Electrophoretic deposition (EPD), a simple and inexpensive colloidal technique, has been used in the past for fabrication of SOFC components (1-10). EPD is a process where charged particles in a stable suspension are drawn towards an oppositely charged electrode when an electric field is applied. The direction and the rate at which the particle travels depend on: i) charge on the particle surface, ii) conditions of the medium in which the particle is suspended, iii) conditions at the electrodes, iv) the applied electrical potential, and v) the characteristics of the particle itself (11,12). Often, the surface charge on a particle can be varied by changes in the pH, the concentration of electrolyte in the medium or addition of some polymers. EPD can produce particulate coatings that are uniform and have a controlled thickness. EPD has also been successfully used for fabrication of micro-tubular SOFCs (13,14). Unlike other colloidal approaches, in the case of EPD, a post-firing step is required to obtain a rigid body with the appropriate microstructure. In certain cases, repeated post-deposition + firing has been reported, for instance, to form an impervious zirconia electrolyte layer (10). However, such an approach may not be suitable for mass production. In more recent work, this problem was eliminated by use of a single-step deposition + firing (3-9) instead of multiple deposition and firing steps.

The aim of the present investigation was to fabricate thin films of SOFC cell components, viz., cathode functional layer (CFL), electrolyte and anode sequentially on the porous LSM support (in the form of discs or tubes).
EXPERIMENTAL

Conventional materials were used for cell components: 20 mol% Sr-substituted LaMnO$_3$ (LSM) as cathode, 8 mol% yttria stabilized ZrO$_2$ (YSZ) as electrolyte, Ni-YSZ as anode and LSM-YSZ as the cathode functional layer (CFL). The LSM support was prepared by conventional tape casting and lamination technique. Tape casting grade LSM powder was procured from two sources: NexTech Materials, USA and Praxair, USA. The LSM powder was mixed with polyvinyl butyral (PVB), butyl benzyl phthalate (BBP) and fish oil and dissolved in mixtures of ethanol and toluene (15). Fugitive phase carbon powder was added to create 30-35% porosity. The tape casting slurry was prepared by ball milling for two days. The slurry was then cast to make flexible LSM tapes, using the doctor blade and tape casting machine. The tapes were first laminated in the green condition to form the support (discs and tubes) of sufficient thickness. The LSM support discs or tubes were pre-fired at 1100°C for 2 h in air to obtain sufficient mechanical strength. After pre-firing, the dimensions of the LSM supports were: a) for discs: 30 mm diameter and 2 mm thick and b) for tubes: 25 mm diameter and 150 mm long. Onto these supports, the cell components were deposited utilizing EPD. A schematic of cell laminate is shown in Figure 1.

![Figure 1. Schematic for EPD of three layers (thin films) on porous LSM support.](image)

To perform EPD, stable suspensions of LSM-YSZ, YSZ and NiO-YSZ were prepared following the same technique as described earlier (3-5). As with tape casting, 5-20 wt% carbon powder was added to the suspension containing LSM-YSZ (CFL) and NiO-YSZ (anode) to give a final 30-35% porosity after firing. No pore former was added in the case of the YSZ (electrolyte) suspension. In each case, the particulates acquire positive charges and migrate towards the negative electrode (LSM support) when an electric field is applied. The applied electric field used was 100-200 V/cm. Depending on the requirement for the film thickness, the deposition time was varied from 10 sec to 2 min. To facilitate deposition experiments on discs and tubes, two homemade apparatuses were designed and constructed (Figure 2). Three separate Teflon containers were used for the three suspensions.

RESULTS AND DISCUSSION

The cathode functional layer, LSM-YSZ, was deposited first on the pre-fired (1100°C) porous LSM support (disc) and fired at 1300°C for 2 h. The cross-section of a fired CFL is shown in Figure 3 to be about 18 µm. Different contents of carbon (5-20 wt%) were added. Figure 4 shows the surface morphology of such films. The average porosity in the film depends on the amount of fugitive phase present. Very dense microstructures were obtained below 10 wt% carbon (Figures 4a and b). It is possible that during deposition
Figure 2. Schematic of EPD apparatus for depositing on porous LSM support; (Top) flat plate and (Bottom) tube.

Figure 3. Cross-section of LSM-YSZ functional layer on porous LSM support (carbon addition: 20 wt%).

(application of electric field), the particulates of carbon and CFL material (LSM-YSZ) migrate with different mobilities. As a result, there may be a difference between the
suspension concentration of carbon and deposited carbon content. However, a 30% average porosity was achieved when 20 wt% of carbon was added (Figure 4c).

![Figure 4. Surface morphology of LSM-YSZ fired at 1300°C/2h having various amounts of carbon addition: (a) 5, (b) 10 and (c) 20 wt%.](image)

The next step was to lay down the electrolyte (YSZ) layer on the top of green CFL layer supported by the pre-fired LSM. After deposition of YSZ, the composite was fired at 1300°C for 4 h. The cross-sectional image and the surface morphology are shown in Figure 5. Fully dense, crack-free YSZ electrolyte was obtained. By controlling the deposition parameters, such as electric field, deposition time etc., it was possible to vary the thickness of the electrolyte. An applied electric field of around 100 V/cm was applied for about 45 sec to obtain an 8 μm film (Figure 5a).

Next, the anode (NiO-YSZ) layer was deposited on the top of green YSZ layer, once again by EPD. The final co-firing of the three layers viz., LSM-YSZ, YSZ and NiO-YSZ along with the LSM support was done at 1300°C for 4 h in air. The final microstructure of the electrophoretically deposited cell components is shown in Figure 6. The thickness of the CFL, electrolyte and anode films was 15, 5 and 50 μm, respectively. The surface morphology of the NiO-YSZ cermet layer (top surface of Figure 6) had sufficient porosity (around 25%). However, after reduction of NiO to Ni, the porosity is expected to increase further.

![Figure 5. Cross-sectional image (a) and surface morphology (b) of porous LSM supported cathode functional layer (LSM-YSZ) and electrolyte (YSZ) coating.](image)
The same methodology was applied to tubular geometry. By using pre-fired (1100°C) homemade LSM cathode tubes as the substrate and the experimental apparatus as shown in Figure 1b, all the three layers, viz., LSM-YSZ (CFL), YSZ (electrolyte) and NiO-YSZ (anode) was sequentially deposited as described above in case of flat discs samples. Photos of as-deposited thin films (green-stage/unfired) on pre-fired LSM tubes (right) and after co-firing at 1300°C for 4 h (left) are shown in Figure 7. Microstructural studies have been carried out and similar morphology as that of flat plate (discs) was observed. It is worth mentioning here that in all the cases, whether the deposition was carried out on flat discs or on tube supports, the electrophoretically deposited coatings offered excellent quality, crack-free green (unfired) compaction and even after firing the surface remains smooth, continuous and crack-free. Relatively large samples can be made by deposition as shown in Figure 7. For performance evaluation of these tubes, a single cell measurement apparatus has been designed but tests have not yet been completed.
CONCLUSIONS

Tape casting and electrophoretic deposition techniques have been used to develop cathode supported thin film SOFC structures. Both fabrication methods have the potential for scaling up. EPD was used to obtain both fully dense and porous films. For example, porosity between 30-35% was achieved for cathode functional layer (LSM-YSZ) and anode (NiO-YSZ). The thickness of the films was controlled by varying the electric field and the deposition time during the EPD process. Deposition times of 30 sec under an electric field of 100 V/cm could produce a 5 μm thick electrolyte (YSZ) film. The thickness of the films for the cathode functional layer (CFL), electrolyte, and anode were 15, 5 and 50 μm respectively. It is worth mentioning here that, in all the cases, whether deposition was carried out on the flat discs or on tube supports, the electrophoretically deposited coatings offered high quality crack-free green (unfired) compaction and even after firing, the surface remains smooth, continuous and crack-free. Although the optimization of the process parameters for tape casting and thin film depositions were primarily carried out with flat plate (discs) geometry, the same procedure was used to develop cathode-supported SOFC tubes. Performance evaluation of such tubular cells has not been completed.

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REFERENCES

1. G. Savo, A. D’Epifanio, R. Polini, E. Traversa, in SOFC-VIII, S. C. Singhal and M. Dokiya, Editors, PV2003-07, p. 246, The Electrochemical Society Proceedings Series, Pennington, NJ, (2003).
2. F. Chen and M. Liu, J. Euro. Ceram. Soc., 21, 127 (2001).
3. I. Zhitomirsky and A. Petric, Materials Lett., 50, 189 (2001).
4. I. Zhitomirsky and A. Petric, J. Euro. Ceram. Soc., 20, 2055 (2000).
5. I. Zhitomirsky and A. Petric, J. Metals, 53, 48 (2001).
6. R. N. Basu, C. A. Randall, M. J. Mayo, J. Am. Ceram. Soc., 84, 33 (2001).
7. R. N. Basu, O. Altin, M. J. Mayo, C. A. Randall and S. Eser, J. Electrochem. Soc., 148, A506 (2001).
8. R. N. Basu, C. A. Randall, M. J. Mayo, in SOFC-VI, S. C. Singhal and M. Dokiya, Editors, PV99-19, p. 153, The Electrochemical Society Proceedings Series, Pennington, NJ, (1999).
9. R. N. Basu, C. A. Randall and M. J. Mayo, in New Materials for Batteries and Fuel Cells, D. H. Doughty, H-P. Brack K. Noi and L. F. Nazar, Editors, 575, p. 303, The Materials Research Society Proceedings Series, Warrendale, PA, (2000).
10. T. Ishihara, K. Shimose, T. Kudo, H. Nishiguchi, T. Akbay and Y. Takita, *J. Am. Ceram. Soc.*, 83, 1921 (2000).

11. P. Sarkar and P. S. Nicholson, *J. Am. Ceram. Soc.*, 79, 1987 (1996).

12. O. O. Van der Biest, L. J. Vandeperre, *Annual Rev. Mater. Sci.*, 29, 327 (1999).

13. H. Negishi, N. Sakai, K. Yamaji, T. Horita, H. Yokokawa, in *SOFC-VI*, S. C. Singhal and M. Dokiya, Editors, PV99-19, p.885, The Electrochemical Society Proceedings Series, Pennington, NJ, (1999).

14. P. Sarkar and H. Rho, in *SOFC-VIII*, S. C. Singhal and M. Dokiya, Editors, PV2003-07, p. 135, The Electrochemical Society Proceedings Series, Pennington, NJ, (2003).

15. R. E. Mistler and E. R. Twiname, *Tape Casting: Theory and Practice*, p. 239, The American Ceramic Society, Ohio, (2000).