

# Colloidal Spray Deposition Technique for the Processing of Thin Film Solid Oxide Fuel Cells

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# COLLOIDAL SPRAY DEPOSITION TECHNIQUE FOR THE PROCESSING OF THIN FILM SOLID OXIDE FUEL CELLS

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## ABSTRACT

An improved version of the colloidal deposition technique is described. Using an ultrasonic atomizer to gently lay down the colloidal solution on a heated substrate, high quality thin films of various materials were prepared. Dense yttria-stabilized-zirconia (YSZ) films of thickness ranging from 1 to 100  $\mu\text{m}$  were successfully deposited on NiO/YSZ substrates as well as on porous  $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$  substrates. The technique was also used to deposit a bi-layer thin film of YSZ and  $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$  with a graded interface.

## INTRODUCTION

A Solid Oxide Fuel Cell (SOFC) is a solid state electrochemical device that converts the chemical energy in fuels directly into electricity. SOFCs are highly efficient and have very low emissions; they are thus an attractive option for clean and efficient power generation for the 21<sup>st</sup> century. However, despite many successful demonstrations by Siemens Westinghouse, the SOFC commercialization is still not viable in a short-term future because of the high fabrication cost. In order to reduce this cost, it is thus highly desirable to develop novel low cost fabrication techniques and processes.

A number of thin films processing techniques that are directly applicable to SOFC fabrication have been explored recently (1-3). The techniques are based essentially on colloidal deposition, which can be dip coating, spin coating, slurry painting, electrophoretic deposition, etc. Dense, crack-free, high quality films are generally produced. However, most of these coating techniques are limited to films having thickness generally less than 10  $\mu\text{m}$ . Thicker films require repeating the process several times, leading to long processing time, and consequently high cost. For certain applications, such as the case of the Siemens Westinghouse tubular fuel cell, electrolyte films thicker than 10  $\mu\text{m}$  are desirable to insure stable long term operation. Indeed, the Siemens Westinghouse fuel cell operates at 1000°C, a temperature high enough that diffusion of the different components of the cathode, the anode and the interconnect can result in short-circuiting, if the electrolyte film is not thick enough. Attempts to use colloidal deposition techniques to deposit films thicker than 10  $\mu\text{m}$  in a single step coating have generally resulted in crackings of the green film after drying.

In this paper, we report the development of an improved version of the colloidal deposition technique. Our objective is to develop a highly versatile and low cost thin film processing technique that can be used for the deposition of thin and thick films for both tubular and planar fuel cells. The films can be dense for use as electrolytes as well as porous for use as electrodes.

## PRINCIPLE OF THE CSD TECHNIQUE

During conventional colloidal dip coating of thick films, cracking occurs because of the large volume change during the drying step. Therefore, an approach to circumvent this problem is to minimize the solvent amount present on the film by removing it in-situ, i.e. during film deposition. This can be accomplished by spraying the colloidal solution on a substrate that is heated above or close to the boiling point of the solvent. The solvent will evaporate rapidly when it comes in contact with the hot substrate. The remaining powder forms a compact layer that will build up with time if the spraying continues. Since the solvent is continuously removed, there is no film shrinkage as in dip coating process. However, if the substrate is flooded in case of over spraying, cracking may occur because of the same volume change problem. Therefore, the technique used to spray the colloidal solution is critical to the deposition of crack-free films. Usually, air-pressure spray guns are not appropriate because of high risks of over-spray and because the spray jet is too strong. The most appropriate spraying technique requires the use of ultrasonic atomizers that generate fine mist with low velocity. The solvent is also critical to the success of the deposition process. Low volatility solvents will require higher heating temperatures, which may adversely decompose the additives in the colloidal solution (dispersant, binder, plasticizer). Highly volatile solvents may dry up too fast and too early. Porous films will result as a consequence of the deposition of the dry powder. Therefore, the technique requires the adjustment of the solvent, mostly by mixing many solvents together in order to have the desired range of volatility.

## EXPERIMENTAL

Substrates: A number of substrates were prepared. Yttria-stabilized-zirconia (YSZ) powder (Tosoh) was mixed with nickel oxide (J.T. Baker) in the ratio of 50% by weight, then ball milled for 10 hours. The mixture was then pressed into pellets using a uniaxial press. The disks were subsequently partially sintered at 900°C for 2 hours. These pellets served as substrates for anode-supported thin film cells. For cathode-supported thin film cells,  $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$  (LSM) powder from Praxair Specialty Ceramics was mixed with 15 wt% of starch and then pressed into pellets. The pellets were heated to low temperatures to decompose starch and then partially sintered at 900°C for 2 hours.

Colloidal solutions: YSZ colloidal solution was prepared by dispersing YSZ powder in a solution containing water and isopropanol (50 vol%). An ultrasonic probe was used to break down the agglomerates. For thin film electrode coatings, a solution containing both NiO and YSZ (50wt%) was prepared. A dispersant was introduced to stabilize the suspension. Colloidal solutions of  $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$  (CYO) and  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$  (CSO) powders obtained from Praxair Specialty Ceramics, were also prepared.

Thin film deposition: the partially sintered pellet substrates were put on a hot plate. The temperature on the plate was approximately 160°C. An ultrasonic atomizer (Sonotek) operating at the frequency 120 kHz was used to spray the colloidal solutions. Programmable syringe pumps were used to deliver the liquid to the atomizer at control rates. After deposition, the substrates with the coatings were sintered at 1400°C and 1500°C for 2 hours for YSZ and CYO films respectively. For the LSM substrate, the sintering temperature was limited to 1300°C, in order to avoid excessive reaction with the YSZ film.

Film characterization: the prepared films were characterized using scanning electron microscopy (SEM) and/or electron microprobe whenever necessary. One disk with a YSZ thin film was tested in fuel cell conditions to check for film porosity (by measuring the open-circuit voltage). Pt was used as the cathode. An EG&G potentiostat model 273 was used to determine the current-voltage characteristic of the fuel cell.

## RESULTS AND DISCUSSIONS

### Coatings

As an example of coating on anode substrate, fig. 1 shows a SEM micrograph of the cross section of a 13  $\mu\text{m}$  YSZ thin film on a porous Ni/YSZ disk. The film is dense, without cracking and has very few non-connecting pores.

As an example of coating on cathode substrates, fig. 2 shows a SEM micrograph of the cross section of a 40  $\mu\text{m}$  YSZ thin film on a porous LSM substrate. Although the film was sintered at lower temperature, it appears to be dense and of high quality too. No cracking was observed. Films as thick as 100  $\mu\text{m}$  have actually been deposited with a similar quality.

Beside the use for thin film electrolyte coating, the CSD technique was also used to deposit porous electrode on fully dense substrate. For example, fig. 3 shows a SEM micrograph of a 70  $\mu\text{m}$  Ni/YSZ thin film deposited on a fully dense YSZ disk. The film has been reduced in hydrogen before SEM characterization. A very homogeneous microstructure can be observed through out the film. Thus, the CSD technique can be used for the processing of both the fuel cell electrolyte and either one of the two electrodes, the other one serving as substrate. Such a possibility could represent a simplification in the fuel cell processing equipments.

The CSD technique also offers the possibility to process multilayer thin films as well as compositionally graded films for improved fuel cell performance. For instance, bi-layer of YSZ and doped-ceria has been proposed in the literature in order to take advantage of the high ionic conduction and high surface oxygen exchange of doped-ceria (4-6). While doped-ceria has significantly higher ionic conduction than YSZ, it also has non-negligible electronic conduction in fuel conditions. Thus, doped-ceria cannot be used as an electrolyte by itself. A YSZ layer is needed to effectively block the electrons. However, since doped-ceria usually has higher thermal expansion coefficient than YSZ,

cracking and/or delamination have been observed sometimes (6). Fig. 4 shows the bi-layer YSZ and  $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$  on a porous Ni/YSZ substrate. A clear delamination is observed at the interface of the two layers. The tortuous microstructure of the ceria film seems to indicate the presence of high stress. Replacing samarium by yttrium with smaller ionic radii in doped-ceria can reduce the mismatch effect at the interface. However, cracking still occurs easily. One possible solution to relax the mechanical stress at the interface is to have a graded interface where the composition changes progressively from YSZ to CYO. Such a continuously graded interface is difficult to be processed using existing thin film deposition techniques. Using the CSD technique with two separate liquid pumps, one for YSZ solution and one for CYO solution, we have been able to deposit such a film with the graded zone extended over several microns (fig. 5). No visible interface was observed. Fig. 6 shows the concentration profile of the graded film as determined by electron microprobe analysis. The film starts with a pure YSZ layer of about 22  $\mu\text{m}$  on top of the Ni/YSZ substrate. Then, there is a graded composition zone extended over 10  $\mu\text{m}$ , followed by a pure CYO layer. The film microstructure as seen in fig. 5 correlates well with the microprobe analysis. Indeed, there is a clear contrast in microstructure between the YSZ layer and the rest of the film. The graded layer and the CYO layer have smaller grain size than the YSZ layer due to the higher refractory character of ceria materials. Since YSZ and CYO form a complete solid solution at temperatures higher than 1300°C (7), the graded film is not a composite but a single phase material with composition changing progressively from pure YSZ to pure CYO. A more detailed study will be reported in the future.

### **Fuel cell testing**

Fuel cells with YSZ thin film on NiO/YSZ substrate and Pt electrode were tested in air/hydrogen. The cell was brought slowly to the test temperature and the NiO electrode was reduced to Ni. The open-circuit voltage was 1.1 V at 900°C, close to the theoretical voltage, indicating there is no leakage in the film. The current voltage characteristic at 900°C is shown in fig. 7. The short-circuit current density is 1.2  $\text{A}\cdot\text{cm}^{-2}$  and the power density reaches 0.55  $\text{W}\cdot\text{cm}^{-2}$ . The I-V curve clearly indicates a concentration polarization at high currents, presumably due to the Pt cathode. Higher fuel cell performance using improved electrodes will be reported in the future.

## **CONCLUSION**

We have developed the colloidal spray deposition process as an improved version of conventional colloidal deposition techniques. Although colloidal techniques and spraying techniques are well documented in the literature, we are not aware of any similar work that can yield dense thin films of thickness greater than 10  $\mu\text{m}$  in a single step coating. The CSD technique has been shown to be actually much more versatile than conventional approaches. The technique can be used to deposit dense electrolyte layers of thickness up to 100  $\mu\text{m}$  as well as porous electrodes. It can also be used to process complex film structures such as composite and graded films. Although we have done coatings on planar samples only, coating on tubular substrates is also possible if the substrate can be rotated.

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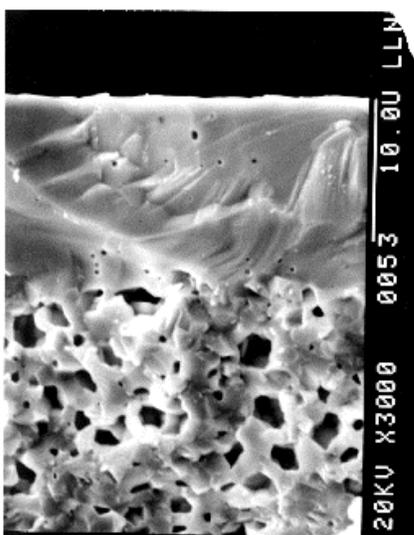


Fig. 1: 13  $\mu\text{m}$  YSZ film on Ni/YSZ substrate.

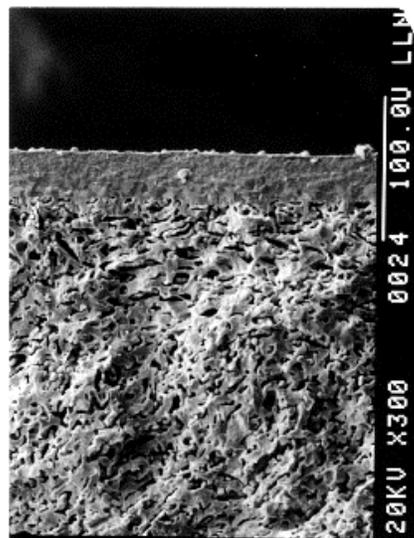


Fig. 2: 40  $\mu\text{m}$  YSZ film on porous  $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$  substrate.

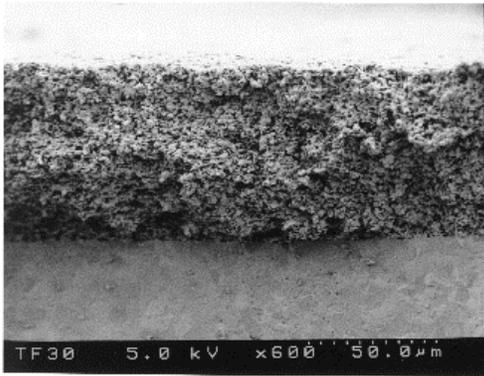


Fig. 3: 70  $\mu\text{m}$  porous Ni/YSZ film on YSZ disk

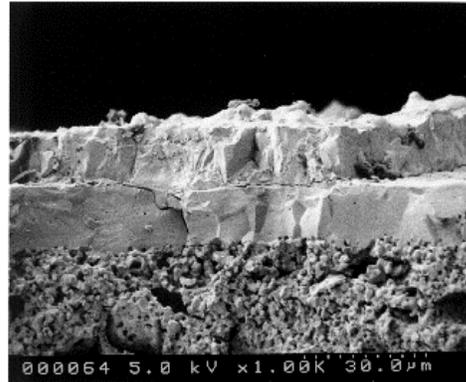


Fig. 4: Bi-layer of YSZ and CSO film on Ni/YSZ substrate. Delamination is clearly visible at the interface between the two layers.

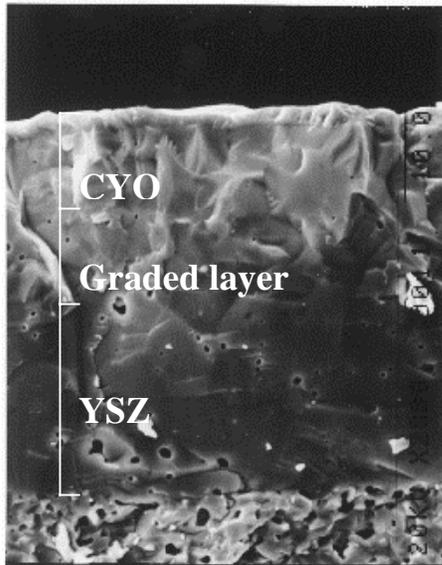


Fig. 5: 40  $\mu\text{m}$  YSZ and CYO film with a graded interface

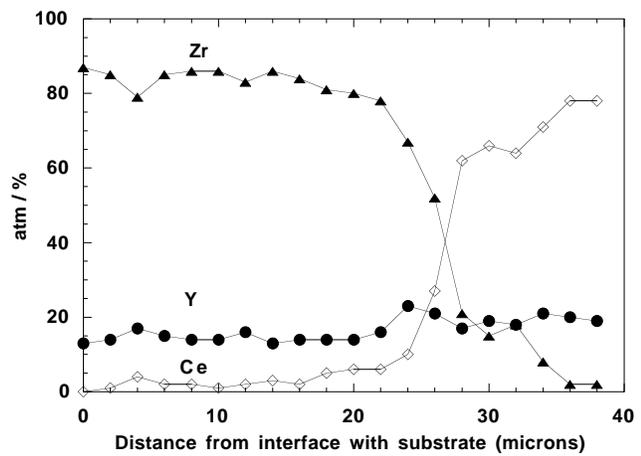


Fig. 6: Composition profile of the YSZ/CYO graded film.

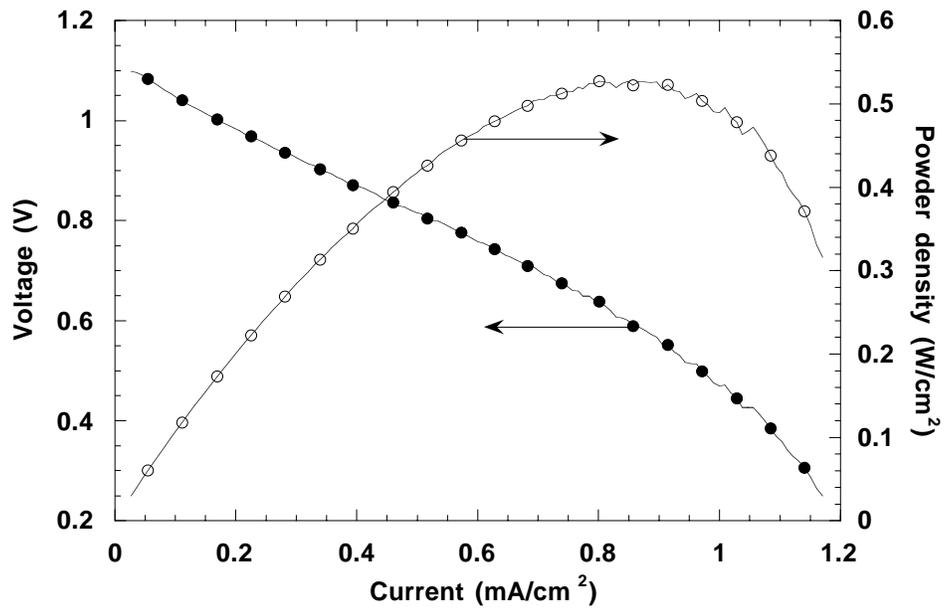


Fig. 7: I-V curve of anode-supported thin film fuel cell with Pt electrode at 900°C in air/ H<sub>2</sub> + 3% H<sub>2</sub>O.