THIN FILMS SOFCs DEPOSITED ONTO POROUS NICKEL SUBSTRATES

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ABSTRACT

Thin films of Yttria Stabilized Zirconia (YSZ) have been deposited onto porous nickel substrates. The porous nickel substrate serves as the anode as well as the substrate in the thin film device. The physical vapor techniques of RF and DC sputtering technique have been compared relative to deposition rate and film quality. The DC sputtering technique that we have used requires a post oxidation treatment to obtain the desired oxide; whereas the RF technique directly prepares the desired oxide. The effects of deposition temperature, deposition power, substrate porosity, and post oxidation treatments have been analyzed and compared to film morphology.

INTRODUCTION

Solid oxide fuel cells (SOFC) have potential advantages over other fuel cell types based on their all-solid-state design and their high operating temperature, 1000°C, which allows for better efficiency and higher power densities. But, at this high operating temperature, costly heat-resistive materials are needed in particular for seals and interconnects. It would be desirable to reduce the operating temperature from 1000°C to about 800°C. However, as the operating temperature is lowered, the ionic conductivity across the 'standart' YSZ electrolyte decreases (1,2), thus limiting cell power density. There are two alternatives for overcoming this problem. One is to develop new solid electrolytes having the same conductivity at 800°C that YSZ has at 1000°C. The other one is to reduce the YSZ electrolyte thickness from that used in conventional planar cells (100 to 200 μm) to approximately 10 μm. We feel that preparing thin film YSZ will be a promising way to obtain performance at reduced temperature (< 800°C) similar to or better than those obtained with conventionnal SOFCs.
For fabricating thin electrolyte films onto porous substrates, potentially low-cost SOFC fabrication methods such as sputtering are of interest since production cost is a primary barrier to SOFC commercialization. Previous studies have shown that it is possible to deposit YSZ thin films by sputtering processes (3,4,5,6,7,8,9). The present discussion will focus on the sputter deposition of several micron thick (4 μm) YSZ thin films onto porous nickel substrates, which can be used as an anode in a SOFC, using either DC magnetron sputtering or RF sputtering. We have studied the DC and RF sputtering techniques to determine which is optimum to obtain a defect-free YSZ film continuous (ie adherent) with the surface of a porous substrate. Before the sputtering deposition of the electrolyte, the surface of the as delivered porous nickel substrates was modified, resulting in an homogeneous porosity of 1-2 μm.

EXPERIMENTAL

The target used for our RF sputtering system was a 20 cm diameter 91 % ZrO₂ - 9 % Y₂O₃ ceramic prepared by Alcatel. The RF sputtering unit itself is a SCM 400 (13.5 MHz) Alcatel with a 1000 W power source. The target used for the DC magnetron sputtering system was a 10 cm diameter 82 % Zr - 18 %Y alloy metallic target. The DC magnetron (Seavom) was powered by a 1000 W DC power supply. Scanning electron microscopy was performed using a Leica Stereoscan 440 and films were analyzed for crystallinity and phase purity by powder X-ray diffraction (Philips XRD PW 1710, using Cu Kα radiation). Film thickness was determined either with a profilometer (Dektak 3ST) on a dense substrate or by electron microscopy.

SPUTTER DEPOSITION OF YSZ USING RF AND DC SPUTTERING

We have used porous nickel pellets which show good mechanical strength and high permeability to the gas flow and consequently allow us to use it as the anode as well as the substrate in the thin film device. The as delivered substrates have a pore size of 10 to 20 μm. In order to prepare dense and crack-free electrolyte thin films with a thickness of 4 μm, we have reduced the pore size on the surface of the porous nickel pellets to 1-2 μm.

RF sputtering

The advantage of RF sputtering is that the target material used can be insulating. The ceramic target we used had a original composition of 91% ZrO₂ - 9% Y₂O₃. The system was evacuated to a base pressure of 10⁻⁶ mbar with a turbo molecular pump prior to introducing pure dried argon into the system via a mass flow controller. We deposited...
films onto substrates using $5.10^{-2}$ mbar as the working pressure of argon. Samples deposited on either dense nickel or silica substrates were previously prepared and examined by X-ray powder diffraction (10). The patterns clearly showed the cubic YSZ phase expected for this level of doping (~9% mol.). We have also previously demonstrated a correlation between deposition rate and RF power (10) (0.25 µm/h for 400 W and 0.5 µm/h for 800 W). In figures 1 and 2 are shown respectively the surface of YSZ thin films deposited at a power of 500 W (i.e., a growth rate of 0.3 µm/h) on our prepared porous nickel substrate heated at 500°C and non heated. We observe that heating the substrate results in a surface without apparent cracks compare with the non heated one.

We have to investigate if higher growth rates can be obtained by increasing the power densities, and if these higher growth rates will yield very dense films using elevated substrate temperatures.

**DC magnetron sputtering.**

A DC sputter deposition process has been developed to synthesize Yttria Stabilized Zirconia (YSZ) films from a Zr-Y alloy target. For DC magnetron sputtering, we must use a conducting target of Zr-Y alloy. The principle of DC sputtering is described elsewhere (10). So as to obtain the desired stabilized zirconia phase from the metallic Zr-Y alloy, one must perform an oxidation of the metallic film after its growth on the substrate, or an oxidation of the metallic film during the sputtering process using reactive sputter deposition.

Several groups have recently reported results on reactive sputter deposition of stabilized zirconia (6, 7, 8, 9). However, by reactive sputter deposition, we find it difficult to control the reactive sputtering conditions and to obtain reproducible results. Details of these results are given in (10). By metallic deposition and subsequent oxidation, we have obtained more promising results. We observed by thermogravimetric analysis that the complete transformation of a Y-Zr film to zirconia is achieved at 500°C (10). First, we have deposited a YSZ film (4 µm) by metallic deposition and subsequent oxidation on the as delivered porous nickel substrate (average pore size: 10 to 20 µm). We obtained the desired phase of zirconia. But, as can be seen on figures 3 and 4, the film morphology shows cracks and there is poor adhesion onto the substrate, due to the stresses generated at the interface substrate/film during the oxidation step. So as to obtain a dense crack free film, we felt that these stresses could be substantially lowered by reducing the porosity of the substrate (to 1 to 2 µm average pore size), by limiting the thickness of the oxidized film and by controlling the oxidation step.

We performed the metallic deposition of 4 µm on a modified porous nickel substrate (average pore size: 1 to 2 µm), that we subsequent oxidized at 500°C in air over 1 hour time period. The oxidation step includes controlled heating and cooling. We obtain a defect-free YSZ film, no cracks have been formed during the oxidation as shown in figure 5. We then deposited a YSZ film of 6 µm on a similar porous substrate by metallic deposition and subsequent controlled oxidation. The film morphology shows cracks as can be seen on the electron micrograph shown in figure 6. We also performed metallic
deposition and subsequent oxidation (directly heated to 500°C) so as to obtain a thin film of 4 µm onto a similar porous nickel substrate.

We find that to obtain a dense and crack-free film, by metallic sputtering and subsequent oxidation, on a porous nickel substrate, the pore size of the substrate must be limited to 2 µm. We also find that the maximum deposition thickness that we can prepare in one step is 4 µm, and that we must control the increase and decrease in temperature during the oxidation.

By metallic deposition (1 hour) at a deposition rate of 4 µm/h with a subsequent oxidation of 1 hour up to 500°C, we obtain dense stabilized zirconia films of 4 µm onto porous nickel substrates (1 to 2 µm average pore size), leading to a growth rate of 2 µm/h. By metallic deposition and subsequent oxidation, we have obtained more promising results than with reactive sputter deposition, which has a deposition rate of 0.4 µm/h.

CONCLUSION

The deposition of YSZ thin films by sputtering on a porous nickel anode with 1 to 2 µm average pores size offers a promising path towards reduction in SOFC operating temperature and the required conservation of power density. We have demonstrated that completely dense stabilized zirconia electrolyte (<5 µm thick) films can be prepared on porous nickel substrates (1 to 2 µm pore size) both by DC sputtering and subsequent oxidation and RF sputtering on porous nickel substrates (1 to 2 µm pore size).

In standard RF sputtering, dense columnar YSZ thin films may be easily prepared from a target of ceramic electrolyte. However, the growth rate of 0.3 µm/h is too low if this technique is to become technologically viable. We are investigating if 1 µm/h is obtainable with our RF system and which temperature will be sufficient at this growth rate to obtain highly dense film. With DC magnetron sputtering a 4 µm YSZ thin film can be prepared by metallic deposition of the metal alloy Zr-Y and subsequent oxidation at 500°C for one hour. With this technique, the deposition rate (2 µm/h) is higher than with RF sputtering or reactive sputtering.

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Fig 1 - Scanning electron micrograph (secondary electron detector) of the surface of a YSZ thin film deposited by RF sputtering at 500 W on a non heated nickel substrate anode.

Fig 2 - Scanning electron micrograph (secondary electron detector) of the surface of a YSZ thin film deposited by RF sputtering at 500 W on a heated nickel substrate anode at 500°C.
Fig 3 - Scanning electron micrograph (secondary electron detector) of the surface of a YSZ thin film deposited by DC sputtering and subsequent oxidation at 500°C on a as deliverated porous nickel substrate

Fig 4 - Scanning electron micrograph (secondary electron detector) of the edge of a YSZ thin film deposited by DC sputtering and subsequent oxidation at 500°C on a as deliverated porous nickel substrate
Fig 5 - Scanning electron micrograph (secondary electron detector) of the surface of a YSZ thin film (~4 μm) deposited by DC sputtering and subsequent oxidation at 500°C on a modified porous nickel substrate.

Fig 6 - Scanning electron micrograph (secondary electron detector) of the surface of a YSZ thin film (~6 μm) deposited by DC sputtering and subsequent oxidation at 500°C on a modified porous nickel substrate.