

Thin Film Solid Oxide Fuel Cell (SOFC) for Intermediate Temperature Operation (700°C)

K.Honegger, E.Batawi, Ch.Sprecher and R.Dietelhelm*

Sulzer Innotech Ltd, P.O.Box

*Sulzer HEXIS Ltd

CH-8404 Oberwinterthur, SWITZERLAND

ABSTRACT

Yttria stabilised Zirconia (YSZ) 4 µm thick films have been deposited by closed loop unbalanced reactive magnetron sputtering from a ZrY-alloy target in O₂-Ar plasmas onto microporous NiO/YSZ substrates. At 700°C an open circuit voltage of 0.97 Volts was obtained for air/humidified H₂. Cells with 4.2 cm² active area using stainless steel current collectors showed maximum power densities of 1.0 W/cm² at 725°C but considerable degradation within 500 hours operation. The degradation was reduced by the addition of a 1 µm thick CeO₂ 10 mol % Y₂O₃ solid solution (CYO) layer on top of the YSZ thin film electrolyte. Cells with the bilayer electrolyte were operated for over 1800 h with tolerable degradation. The YSZ-CYO bilayer electrolyte cells survived thermal cycling without electrochemical performance degradation or structural ageing.

INTRODUCTION

Due to its high ionic conductivity as well as chemical and thermal stability over a wide range of conditions YSZ is the commonly used electrolyte for oxygen sensors and solid oxide fuel cell (SOFC) applications. The use of thin films of YSZ is advantageous for reducing resistance and to operate devices at lower temperatures (1). For SOFC applications temperatures of around 700°C are envisaged. Low cost stainless steels could then be used for interconnectors and for auxiliary components in SOFC systems. YSZ thin films of thickness 4 to 10 µm would generate a tolerable ohmic loss in the cell assuming an area specific resistance (ASR) of 0.05 Ωcm² for the electrolyte. However a dense and crack free microstructure of the electrolyte films is required to avoid electronic short-circuiting of the electrodes and voltage losses due to mixing of the working gases.

A number of ceramic processing techniques exist to deposit thin films onto porous substrates as for example screen printing (2), calendering (3), sol-gel multilayers (4), electrophoretic multilayers (5). The deposited films have to be densified by subsequent

sintering at temperatures higher than 1000°C. NiO/YSZ cermet anode compositions are mostly used as substrates to avoid unwanted reaction products in the bilayer structure during sintering.

With chemical vapour deposition (CVD) and physical vapour deposition (PVD) thin YSZ films have been deposited on planar substrates (6,7). The CVD, OMCVD and ECVD techniques require substrate temperatures above the envisaged operating temperature of 700°C. During PVD substrate temperatures stay well below 400°C. Compared to radio frequency (rf) sputtering of YSZ targets, DC reactive magnetron sputtering of Zr-Y alloy targets yields higher deposition rates (8,9).

In this paper we report on the development of a planar, substrate supported SOFC. Special attention is given to the following fabrication and cost aspects:

- chemically clean interfaces between functional layers of the cell
- reliable, high yield, automated fabrication process for 200 cm² diameter components
- minimum quantities of costly raw materials
- low-cost current collectors

We present results of the electrochemical behaviour of anode supported SOFC using thin film electrolytes prepared by unbalanced magnetron sputtering. The cells are operated with stainless steel current collectors at 650°C to 750°C.

PREPARATION OF ANODE SUBSTRATE

The NiO/YSZ anode substrate was prepared as a double layer structure composed of a microporous support on top of a macroporous ceramic foam (Figure 1). The support acted as anode and as surface for thin film deposition. The ceramic foam functioned as carrier of the anode and as fuel flow distributor and current collector. The support was produced using conventional tape casting. The ceramic foam was produced by impregnation of a fully reticulated polyurethane foam.

Identical slurry compositions were used for tape casting and impregnation. Commercial NiO/YSZ powder mixtures (Praxair Specialty Ceramics) were deflocculated in organic solvent by ball milling. By adding suitable binder and plasticiser an uniform and consistent slip for casting and impregnation was obtained. The slurry was tape casted and dried into green sheets of around 250 µm and 500 µm thickness respectively. Discs of 38 mm diameter were punched out of the sheets. Polyurethane foams of 38 mm diameter and 4 mm thickness with 45 pores per inch (ppi) were impregnated with the slurry and dried. The green foams and the green discs were pressed together and cosintered at 1400°C for 1 hour in air. The sintered compounds were 30 mm in diameter, the support showed a thickness of 100 µm and 200 µm respectively.

The porosity of the foam straths and the support was about 5 to 10 % in the sintered state. After reduction of NiO to Ni a microporous, permeable structure was obtained with 1 to 2 µm wide pores. The planar compound structure with 25 % of the bulk density of NiO/YSZ showed sufficient strength under a load of 0.2 kg/cm² at 700°C.

DEPOSITION OF ELECTROLYTE THIN FILMS

A UDP Plasmatron (TEER Ltd, GB) with four symmetrical vertical magnetrons was used for DC reactive sputtering (10). For the reactive deposition of 8 mol% yttria stabilised zirconia (YSZ) a Zr82Y18-Alloy (wt.%) target of 100 x 300 mm size was used. Ceria 10 mol% Yttria solid solutions (CYO) were reactively deposited from a Ce86Y14-Alloy (wt.%) target. The substrates were mounted on a cylindrical sample holder and rotated in front of the target. The vacuum chamber was evacuated using a turbo-molecular pump to a base pressure of typically 10⁻⁶ mbar. The residual gases were analysed by mass spectroscopy before backfilling the chamber with sputtering gas. Argon (99.99) was used for the plasma atmosphere. The reactive deposition process for the formation of the oxide was controlled by a technique based on optical emission spectroscopy. An optical emission monitor (OEM) was combined with a photomultiplier to monitor the intensity of the metal species, either Zr or Ce, near the target surface in the plasma. A rapid response piezoelectric valve controlled the flow of reactive oxygen (99.99%) into the system chamber. It maintained the plasma intensity precisely at the pre-set level by closed-loop feedback control with the OEM allowing the deposition of films with defined stoichiometry. The NiO-YSZ substrates were sputter cleaned for 60 minutes prior to film deposition by applying a RF bias to the substrate holder with a power of 500 Watt. The cleaning process raised the substrate temperature up to 170°C. Reactive sputtering was carried out at chamber pressure of 1.5 to 3.5 mbar, operating the alloy target with a current of 5 Amps. The substrate temperatures monitored by IR-spectrometers reached maximum values of 200°C during sputtering. Typical deposition rates of 5 µm per hour for YSZ and 4 µm for CYO were obtained under these conditions.

After deposition the films appeared black to grey depending on the OEM value setting during the reactive sputter process. The colouring reflected the oxygen substoichiometry of the YSZ, black representing films with the highest oxygen substoichiometry of around ZrO_{1.8}. The films were fully crystalline showing a cubic lattice. After annealing in air for 1 hour at 500°C the well adherent films appeared totally transparent. A decrease in the cubic lattice constant of about 1 % was observed between the as deposited and the annealed samples. The surface and the fracture cross section of a typical bilayer YSZ-CYO film are shown in Figure 2 and 3. The morphology of the film is dense at the substrate surface and ends up in dense columns of size between 0.5 to 1 µm. The YSZ films were very well adherent to the support surface. The CYO film growth continued epitaxially on the YSZ surface.

PVD-CELL PREPARATION

For fuel cell performance testing a cathode with the composition La_{0.6}Sm_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF-6428) was prepared by mixing the powder (Praxair Specialty Ceramics) with solvent and binder into a slurry. Polyurethane tissues were impregnated with the cathode slurry and placed onto the electrolyte. The PEN structure was sandwiched between two stainless steel current collectors (AISI 446). Two probes for voltage and current leads were welded on each of the plates. The sandwich was mounted into an alumina housing containing the fuel and air supply tubes and placed in a furnace. Without sintering of the cathode the cell was heated up to the working temperatures of 650°C to 800°C and operated with humidified hydrogen on the anode and air on the cathode side. Due to the open test set-up higher fuel massflows than

necessary were needed flushing the anode chamber to obtain reasonable OCV values.

RESULTS AND DISCUSSION

Open Circuit Voltage

A scatter of Open Circuit Voltages (OCV) values between 0.92 and 0.98 Volts were obtained at 700°C for humidified H₂ and air, considerably lower than the theoretical value of 1.1 V. However no correlation between electrolyte thickness and OCV was observed. The low OCV values were attributed to leakage of oxygen from the cathode side to the anode chamber. Variable amount of structural defects in the support surface induced growth defects in the thin film morphology. Especially pore sizes larger than 3µm and microcracks in the support as well as high surface roughness caused cracks and pin holes in the electrolyte.

Performance

Figure 5 shows the performance of a PVD-cell at different temperatures after 24 hours of operation. In the operating point at 0.7 V a current density of 1 A/cm² was observed for 720°C and 0.8 A/cm² for 680°C. Lowering the temperature increased the area-specific resistance (ASR) from 0.24 Ωcm² to 0.36 Ωcm². Cell resistivity values in the same range were obtained at 700°C operating temperature with YSZ electrolytes fabricated with ceramic thin film methods (3, 4). The high power outputs with the PVD-cell were obtained at low fuel utilisation corresponding to the entrance conditions of a 4120 mm HEXIS cell configuration e.g. H₂ massflow 1.0 to 1.5 g/h (R.Dietheim et al., this volume). Within 260 hours of operation the performance of the cell degraded to a current density of 0.65 A/cm² at 0.7 V increasing the ASR to 0.44 Ωcm². The reduction of the fuel flow rate to 0.5 g/h reduced the OCV but had only little effect on the ASR as shown in Figure 6.

Longterm Performance

Single electrolyte PVD-cells showed a continuous degradation. Within the first 500 hours the ASR typically increased from 0.25 Ωcm² to about 0.58 Ωcm². The continuous degradation of performance observed in the YSZ-thin film cells was attributed to formation of reaction products between the LSCF-6428 cathode and the electrolyte as already mentioned by Cheng et al. (11). By adding a diffusion barrier layer of CYO between the YSZ electrolyte and LSCF-6428 cathode an attempt was made to suppress the chemical reactions. The long-term performance of PVD-cells using YSZ-CYO bilayer electrolytes is shown in Figure 7. Over 1800 hours of operation the ASR increased from 0.15 Ωcm² to 0.61 Ωcm². In contrast to single electrolyte PVD-cells no effects of electrical load changes on degradation rate was observed in bilayer electrolyte PVD-cells. Contact resistivity measurements on stainless steel AS1446 - LSCF-6428 combinations showed that the oxidation of the current collectors increased up to 0.1 Ωcm² ASR over 2000 hours. Subtracting the resistivity contribution of both current collectors from the overall ASR of the PVD-cell is not sufficient to explain the degradation. Suspected reasons for the voltage loss are the deactivation of the LSCF-6428 cathode due to grain growth and destructions of the cell materials in hot spot areas due to leakage through the electrolyte membrane.

Thermal cycling

In a series of four thermal cycles the application of small scale cogeneration SO₂/C for daily use was simulated with a cell standby to cell operating ratio of 6 to 18 hours in

a 24 hours cycle. The PVD-cell withstood the thermal cycling without ageing or degradation of the performance as shown in Figure 8. The thermal cycling resistivity of planar PVD-cells can be explained by the foam structure of the anode support and the compliant behaviour of thin films towards thermal stresses.

CONCLUSIONS

The process controlled reactive magnetron sputtering is a promising, reliable method for the deposition of YSZ and CYO electrolytes on composite anode supports. The anode surface quality has a strong influence on the OCV of cells with membrane thickness below 10µm. Diameter 35 mm cells using YSZ (4 µm)/CYO (1 µm) bilayer electrolytes showed maximum power densities of up to 1W/cm² at an operating temperature of 720°C at low fuel utilisation however. At this temperatures stainless steel current collectors can be used as demonstrated successfully over 1800 hours operation of a PVD-cell. PVD-cells stay structurally stable. However the degradation rate of the electrochemical performance is still too high for commercial applications. The PVD-cells exhibit high resistivity to thermal cycling as well as to electric load changes. Work is in progress to demonstrate the PVD-cell concept in a 120 mm diameter 5-cell HEXIS stack.

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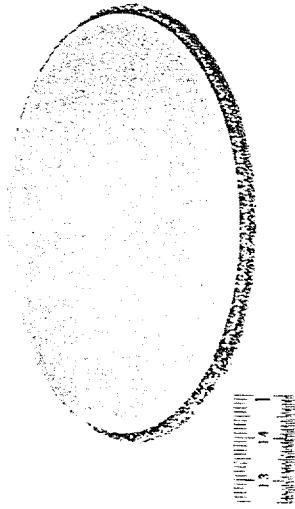


Figure 1: Sintered anode substrate samples diameter 120 mm composed of foam and coverplate (scale in cm)

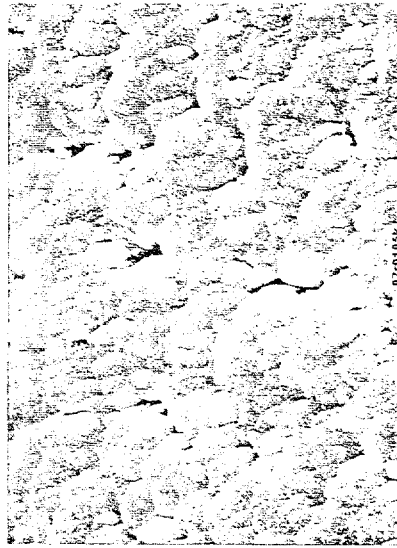


Figure 2: Sputtered YSZ-CYO bilayer thin film on NiO/YSZ anode substrate showing the surface morphology of CYO.

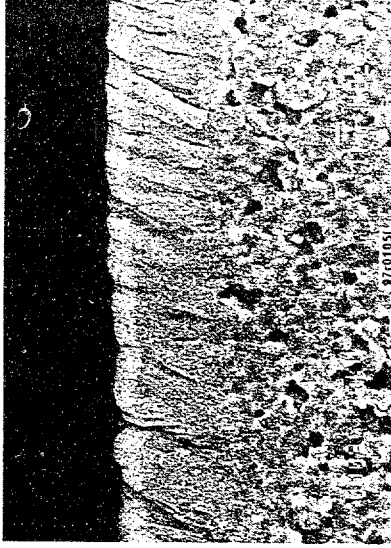


Figure 3: Morphology of sputtered bilayer thin film on NiO/YSZ anode substrate. Backscattered image showing CYO layer on top of YSZ.

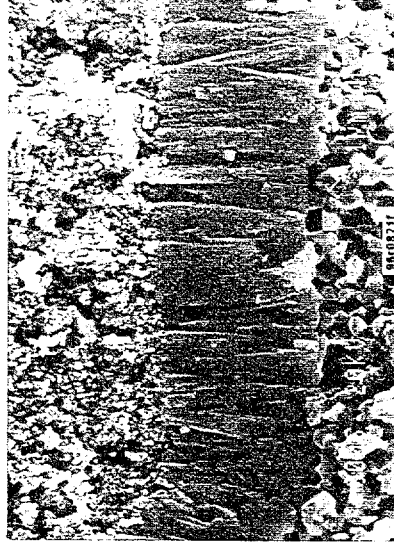


Figure 4: Fracture cross section of PVD-cell after 500 hours of operation at 715°C. From top to bottom: LSCF-6428 cathode, YSZ thin film electrolyte, Ni/YSZ anode

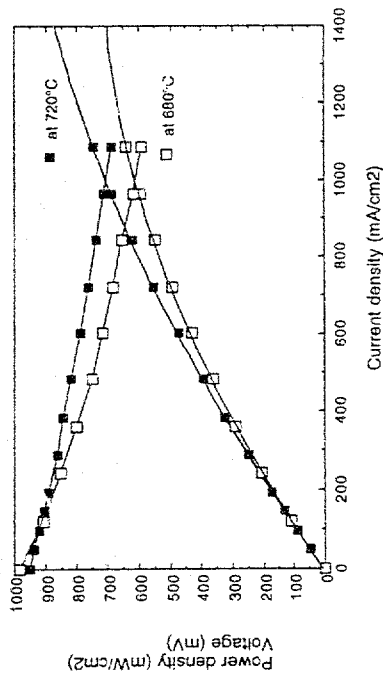


Figure 5: Temperature dependence of PVD-cell discharge characteristic after 24 hours of service. Fuel: humidified H₂, Oxidant: air.

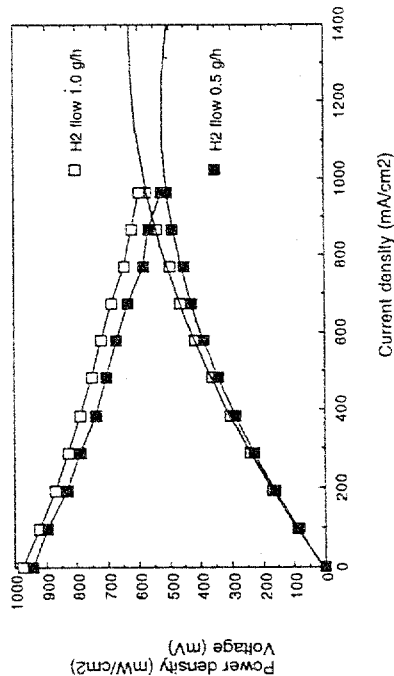


Figure 6: Influence of fuel massflow on PVD-cell performance after 260 hours of service at 720°C. Fuel: humidified H₂, Oxidant: air.

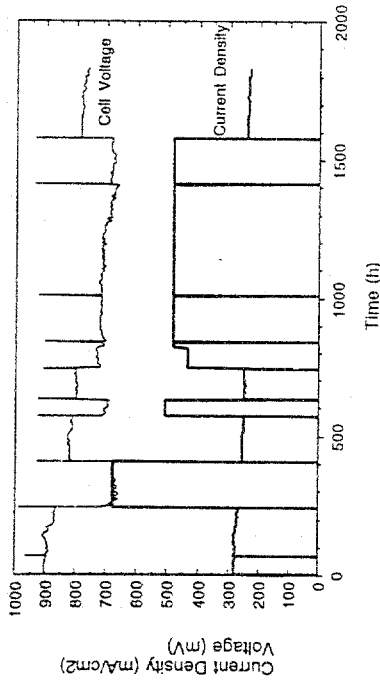


Figure 7: Longterm operation of PVD-cell at 716°C with varying current load conditions, interruptions show OCV values. Fuel: humidified H₂, Oxidant: air.

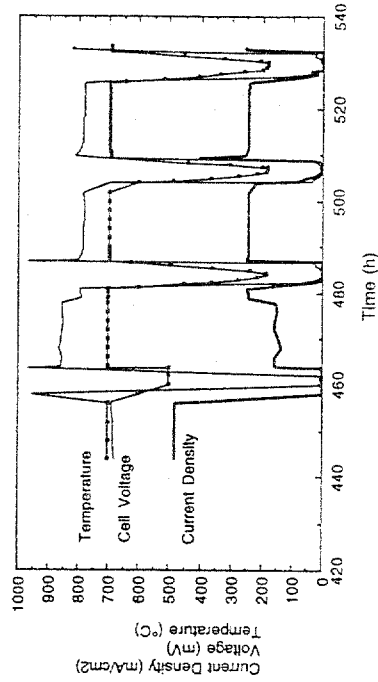


Figure 8: Thermal cycling behavior of PVD-cell between 720°C and 200°C with 4%/min gradients. Fuel: humidified H₂, Oxidant: air.