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Electrical and microstructural investigations of cermet anode/YSZ thin film systems

Darja Kek [a,*], Peter Panjan [a], Elke Wanzenberg [b], Janez Jamnik [c]

[a] *Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia*
[b] *Institut für Werkstoffe und Verfahren der Energietechnik, Forschungszentrum Jülich, D-52425, Germany*
[c] *National Institute of Chemistry, Hajdrihova 19, SI-1000 Ljubljana, Slovenia*

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Abstract

We describe the preparation, electrochemical and structural properties of the thin film Y-stabilized ZrO_2 (YSZ), of interest for solid oxide fuel cell (SOFC) at an operating temperature of 800°C. Thin films of YSZ were prepared by reactive sputtering deposition of Zr–Y targets in Ar–O_2 mixture atmospheres. The thickness of the YSZ film, deposited onto the porous NiO–YSZ substrates, is approximately 8 μm. The microstructure of the YSZ film was investigated using scanning electron microscope. The electrochemical properties of a thin film cell Ag/NiO–YSZ/YSZ/Ag were studied using impedance spectroscopy. The electrolyte and electrode (substrate) resistances were measured under different atmospheres as a function of temperature. Above 600°C the ohmic resistance of the cermet electrode (substrate) is comparable to the ionic resistance of the solid electrolyte. This is probably influenced by the cermet electrode microstructure.

Keywords: Films; Fuel cells; Impedance; Y_2O_3; ZrO_2

1. Introduction

Oxide ion conductors, such as yttria stabilized zirconia (YSZ) are used as an electrolyte in solid oxide fuel cells (SOFC), oxygen sensors in automotive and steel making applications and water electrolyser. As an anode materials in SOFC, a Ni–YSZ cermet is mainly used which has been subject of a number of research and development programs. The reduction of the existing operating SOFC temperature of 1000°C to less than 800°C is of prime research interest in the field. Operation of SOFC at lower temperature have several advantages: lower corrosion rate of cell components, relatively inexpensive metal components may be used for fabrication of interconnecting and structural material. The problems associated with the lowering of the operating temperature are: (1) the increase of interfacial resistance at the anode/electrolyte and cathode/electrolyte interfaces and (2) the increase of the YSZ electrolyte resistance. The increase of the interfacial resistances can be overcome by finding a new electrode material with a high electrochemical reaction rate. The difficulties due to higher electrolyte resistance can also be solved by decreasing the electrolyte thickness. For the operation temperature of SOFC of 800°C, the thickness of YSZ electrolyte of around 10 μm is reported. At even lower operating temperature, e.g. 650°C, the electrolyte YSZ thickness should be between 1 and 2 μm.[1] The thin electrolyte films are formed on a porous electrode substrate by a suitable deposition technique,[2] i.e. DC sputtering.[3,4]

In this work thin films of YSZ were prepared by reactive DC-sputtering. By controlling partial pressure of oxygen in the atmosphere, thin films with different microstructures (from columnar growth to polycrystalline structure) were fabricated as is presented in details in the first contribution.[5] Using a metallic target a more dense and compact YSZ film can be achieved by post-oxidation of sputtered YSZ film in air. Impedance spectroscopy was used to determine the electrochemical properties of thin sputtered film and porous anode substrate. No significant contribution of grain boundaries on the electrical conductivity was found. The microstructure of the thin film, anode substrate and of anode/thin film interface was characterised by scanning electron microscope (SEM).

* Corresponding author. Tel.: +386-1-4773276; fax: +386-1-1425 9244.

E-mail address: darja.kek@ijs.si (D. Kek).

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2. Experimental

2.1. Film preparation

Thin films of YSZ were deposited on porous anode substrates (YSZ–NiO) by reactive sputter deposition in a plasma-beam sputtering apparatus Sputron (Balzers). This is an independent discharge system in which the plasma is supported by the termoionic emission from a heated filament. A metallic Zr–Y target (80:20 at.%) was sputtered in Ar–O_2 mixture atmospheres (the argon pressure 0.2 Pa, the oxygen pressure 2×10^{-2} Pa). With the sputter power 60 W/cm^2 a deposition rate of 1.5 μm/h was achieved. The substrate temperature was 700°C. By using metal target the under-stehiometric oxide is formed on substrate. After deposition, the films were heated-sintered in oxygen (air) at 1100°C. In this way a more compact and gas tied layer was fabricated.

2.2. Microstructural characterisation

The microstructure and thickness of both the thin film and the anode substrate/thin film interface were characterised by scanning electron microscopy, (Jeol JSM-T220). After reduction of the substrate/thin film system at 500°C in 5% H_2 in Ar atmosphere, the microstructure of anode substrate itself, were checked by SEM. The thickness of the YSZ film, deposited onto the porous NiO–YSZ substrates, has been determined by profilometer and compared to the thickness estimated under the SEM.

2.3. Electrical characterisation

The measuring cell with three electrodes was prepared (Fig. 1). For impedance studies of thin films the whole "sandwich", Ag/NiO–YSZ/YSZ/Ag was connected while for the characterisation of the substrate itself, the cell terminals displayed on the left hand side of Fig. 1, was used (Ag/NiO–YSZ/Ag). The cell was assembled by alumina discs and contacted through Ag paste, DEMETRON Leitsilber 200 and Pt wires.

The ionic conductivity of thin films and electrical conductivity of the anode substrate in Ar atmosphere (predominantly ionic conductivity), and electronic conductivity in the mixture of 95% Ar/5%) were measured using impedance spectroscopy. Impedance spectra were obtained in the frequency range 1 MHz–20 Hz with the amplitude of the excitation signal of 100 mV (HP 4284 A). This was done at temperatures between 250 and 600°C in two different atmospheres; in Ar (99.999%) and the mixture of 5% H_2 in Ar, to reduce the NiO grains in porous substrate, such that the electronic conductivity of the anode could be detected.

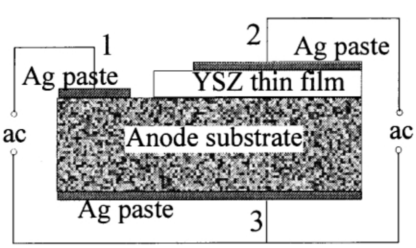

Fig. 1. The scheme of the measuring cell with three electrodes. For the characterisation of thin films the whole "sandwich", Ag/NiO–YSZ/YSZ/Ag was connected while of the substrate itself the cell terminals displayed on the left side (Ag/NiO–YSZ/Ag).

3. Results and discussion

3.1. Microstructure of the polycrystalline thin films

Fig. 2a shows an unpolished cross-section fracture of the deposited YSZ film on porous substrate. A rather porous structure of the anode substrate, on the left hand side, and a dense sputtered film of thickness around 7.5 μm can be estimated. Fig. 2b shows the same interface at higher magnification. It can be seen, that the sputtered YSZ film grows epitaxially. On the substrate

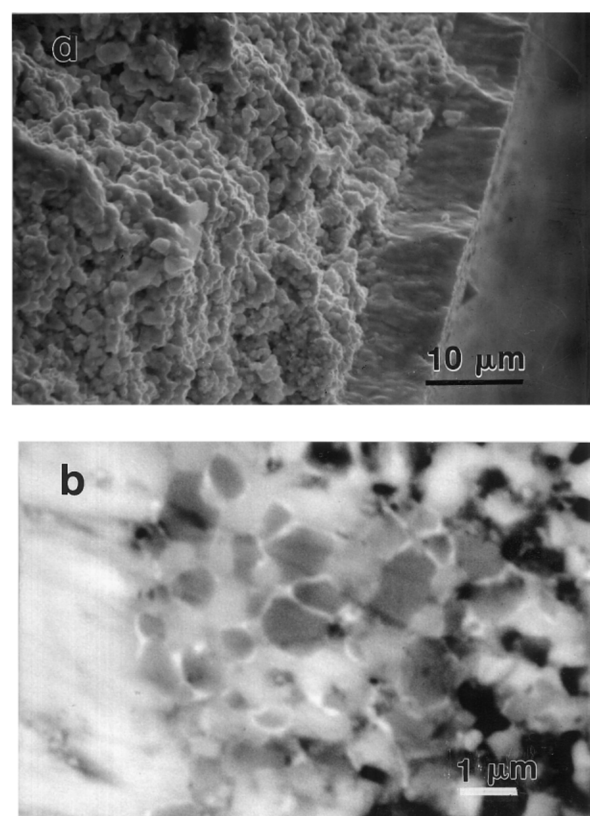

Fig. 2. (a) Cross-section image of the thin sputtered film, as deposited. The thickness of the YSZ thin film can be estimated. (b) The anode substrate/YSZ thin film interface in the higher magnification. The sputtered YSZ film grows epitaxially. On the substrate anode side, the dark NiO grains were partially reduced (a brighter coating layer of metal Ni on NiO grains).

anode side, the dark NiO grains, by the film, were partially reduced. In Fig. 2b, this is shown as a brighter coating layer of metal Ni on NiO grains. This is probably due to the use of metallic target. The conversion to an oxide thus causes a reducing condition. This statement was confirmed by EDX element analyses.

In Fig. 3 the microstructure of predominantly reduced anode substrate itself is shown. The mapping of this figure shows that the Ni phase in the porous substrate percolates. As will be shown later in the electrical measurements, this structure exhibits a pure electronic conductivity.

3.2. Electrical properties

3.2.1. Impedance measurements of anode substrate

The porous NiO–YSZ anodes were measured in the inert and reduce atmosphere (between electrodes 1 and 3 in Fig. 1). In the inert Ar atmosphere impedance spectra exhibit hysteresis between heating and cooling (250–600–250°C). The impedance spectra, showing this effect, at 337°C are presented in Fig. 4. In early stage of the temperature ramp the impedance spectra consist of the two overlapping semicircles, while in the cooling cycle, measured at the same temperature, both semicircles become distinguishable and the overall resistance decreases. The equivalent circuit used for fitting the measured data is shown in the onset of Fig. 4. The magnitude of the capacitance values, of both detected processes (semicircles), are in the range of 0.01–1 nF/cm^2. This suggesting that both relaxation processes refer to bulk rather than interfaces. The equivalent circuit consists of two *RQ* elements in series. Symbol *R* denotes the resistance and symbol *Q* the constant phase element whose impedance, Z_{CPE}, is defined as:

$$Z_{CPE} = Y^{-1}(j\omega)^{-n} \quad (1)$$

For $n=1$, the *Q* element reduces to an ideal capacitor with the capacitance *Y*, and for $n=0$ to a simple resistor with the admittance *Y*.

The typical values of model parameters are shown in Table 1, for the temperature 337°C. The R_1 resistance parameters decrease for factor two, while R_2 resistance stays the same. The temperature dependence, in the range of 250–450°C, of the fitted parameter R_1 and R_2, are shown in Fig. 5. Open symbols refer to the high frequency semicircle and filled symbols to the low frequency

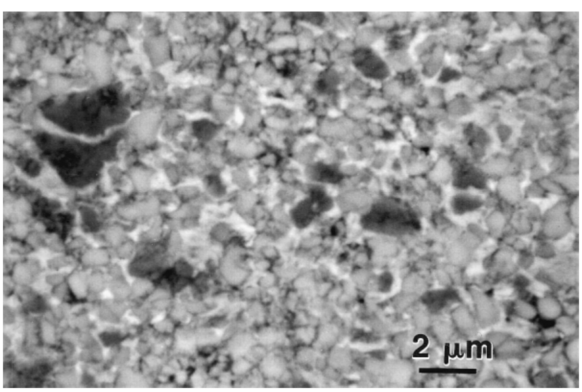

Fig. 3. Microstructure of anode after exposing in reduction atmosphere.

Table 1
Typical values of model parameters for cermet anode in Ar atmosphere at temperature 337°C

	R_1	Q_1	n_1	R_2	Q_2	n_2
Heating	1.06×10^{6}	1.02×10^{-11}	0.87	1.31×10^{6}	2.40×10^{-10}	0.78
Cooling	5.10×10^{5}	3.55×10^{-11}	0.93	1.30×10^{6}	1.68×10^{-9}	0.70

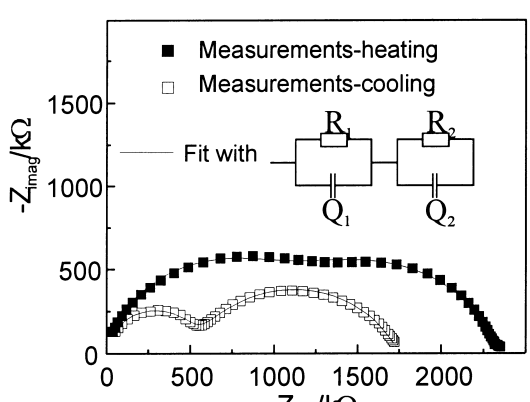

Fig. 4. Impedance response of anode substrate (YSZ–NiO) in the inert atmosphere at 337°C. Filled symbols show impedance spectra in the early stage of the temperature ramp, open symbols exhibit response while cooling.

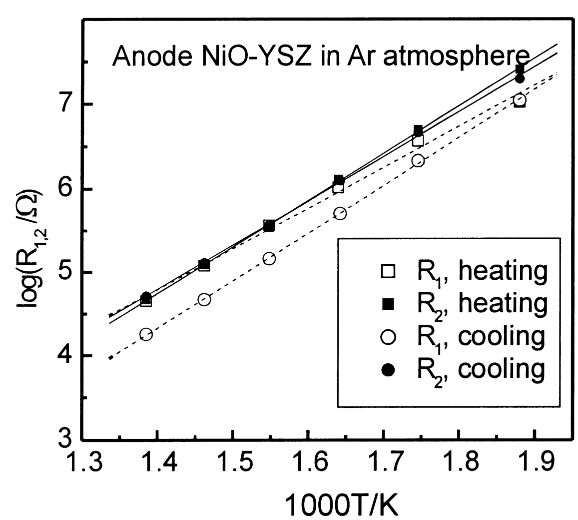

Fig. 5. The temperature dependence of the fitted parameters (R_1 and R_2) in equivalent circuit on Fig. 4. Open symbols refer to the high frequency semicircle and filled symbols to the low frequency one.

one. The values of R_2 do not change during heating and cooling cycle, while R_1 decreases during the cooling cycle. However, the value of R_1 remains the same if the next heating/cooling cycle was applied. Despite of the fact, that the samples were kept in the inert atmosphere, partially reduced NiO can re-oxidise. Another reason could be the changes of the microstructure.

If the NiO–YSZ anodes were exposed to the reduce atmosphere, the pure electronic conductivity was detected as shown in Fig. 6. Obviously NiO was reduced, continuous Ni pathways were formed. This hypothesis is supported by the SEM image (Fig. 3). From this image the changes in the microstructure before (Fig. 2a) and after reduction (Fig. 3) can be seen.

3.2.2. Impedance measurements of sputtered thin films

Detection of sputtered YSZ thin film was possible only after reduction of anode substrate. A typical impedance spectrum is shown in Fig. 7. Impedance spectra consist of high frequency semicircle, caused by bulk YSZ film and low frequency inclined line ascribed to the interfaces between YSZ thin film and adjacent electrodes (Ag-paste and substrate, respectively, see Fig. 1). The spectra were analysed by equivalent circuit shown in the onset of Fig. 7. The conductivity was determined in the temperature range between 250 and 600°C. From Arrhenius plot the activation energy for ion conductivity was estimated to be 1.05±0.05 eV. Table 2 shows the conductivity for the set of the YSZ films sputtered on the anode substrate, with different temperature pre-treatment. The conductivity of 0.5–1.8 mS/cm was found at 600°C. The lowest conductivity was found for the pre-treatment anode at 1300°C, the highest for the temperature pre-treatment at 1400°C.

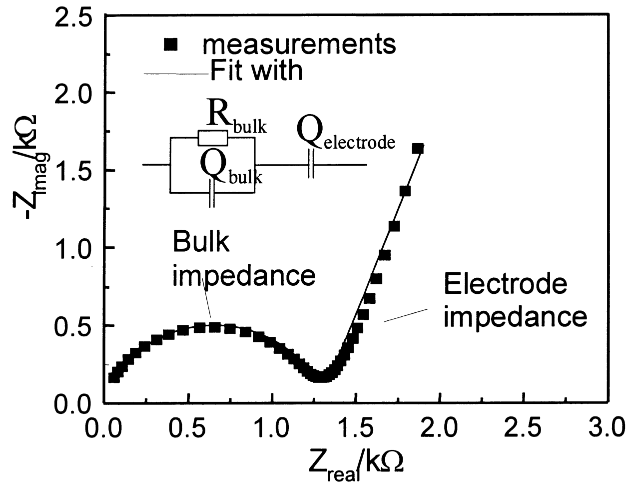

Fig. 7. Impedance spectrum of the thin film YSZ at 337°C, after the substrate reduction.

The influence of grain boundaries on the electrical conductivity was not observed. One of the reasons could be columnar growth of YSZ where detection of grain boundaries is negligible. Above 600°C the ohmic resistance of the cermet electrode (substrate) is comparable to the ionic resistance of the solid electrolyte. This is probably influenced by the cermet electrode microstructure.

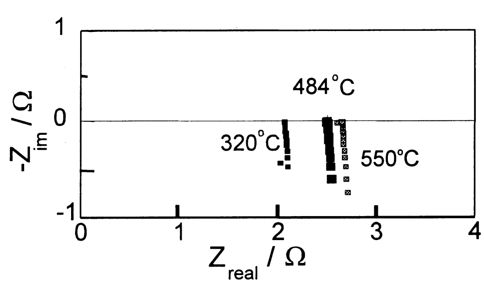

Fig. 6. Impedance spectra of anode substrate, exposed to the reduce atmosphere. Pure electronic conductivity was determined in the temperature range of 250–600°C.

Table 2
Conductivity and film thickness on different substrates

Sintering T of anode (°C)	Thickness of YSZ film (μm)	σ at 600°C (S cm^{-1})	σ at 800°C (S cm^{-1})	σ at 1000°C (S cm^{-1})
1300	8	0.45×10^{-3}	0.663×10^{-2}	0.039
1320	8.5	1.57×10^{-3}	2.14×10^{-2}	0.17
1340	4	1.45×10^{-3}	1.82×10^{-2}	0.11
1380	7	1.1×10^{-3}	1.40×10^{-2}	0.09
1400	7.5	1.76×10^{-3}	1.92×10^{-2}	0.13

4. Conclusions

YSZ films with a thickness of 4–8.5 μm were prepared by sputtering on porous NiO–YSZ substrates. Ionic conductivity was determined for a set of YSZ film sputtered on porous anode substrate, pre-sintered at different temperature. At 600°C, the ionic conductivity of YSZ films has been found to be 0.5–1.7 mS/cm. Above 600°C the ohmic resistance of the cermet electrode (substrate) is comparable to the ionic resistance of the solid electrolyte. The influence of grain boundaries on the electrical conductivity was not observed.

The electrical properties of the porous substrate change upon heating and cooling in the inert atmosphere. Most significant is the decrease of the resistance of the high frequency process. This probably reflects the (i) changes of the composite microstructure or (ii) the oxidation of Ni within the cermet.

Acknowledgements

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References

1. Steele, B. C. H., State-of-the-art SOFC ceramic materials. In *Proceedings of First European Solid Oxide Fuel Cell Forum*, ed. U. Bossel. Vol. 1, 1994, pp. 375–397.
2. Will, J., Mitterdorfer, A., Kleinlogel, C., Perednis, D. and Gackler, L. J., Fabrication of thin electrolyte for second-generation solid oxide fuel cells. *Solid State Ionics*, 2000, **131**, 790–796.
3. Skrivasatva, P. K., Quach, T., Duan, Y. Y., Donelson, R., Jiang, S. P., Ciacchi, F. T. and Badwal, S. P. S., Thin film oxide fuel cells prepared by DC magnetron sputtering for intermediate temperature operation. In *Second European SOFC Forum*, ed. B. Thorstensen. European SOFC Forum, Oslo, 1996, pp. 761–772.
4. Charpentier, P., Fragnaud, P., Schleich, D. M. and Lunot, C., Thin films deposited onto porous nickel substrates. In *Proceedings of the Fifth International Symposium on, S.O.F.C., PV97-*, ed. U. Stimming, S. C. Sighal, H. Tagawa and W Lehnert. The Electrochemical Society Proceedings Series, Pennington, NJ, 1997, pp. 1169–1176.
5. Hobein, B., Tietz, F., Stöver, D. and Panjan, P., DC sputtering of yttria-stabilized zirconia thin films for solid oxide fuel cell applications. *J. Eur. Ceram. Soc.*, in press.