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Short communication

Electrical properties of thin bilayered YSZ/GDC SOFC electrolyte elaborated by sputtering

C. Brahim [a], A. Ringuedé [a,*], E. Gourba [a], M. Cassir [a], A. Billard [b], P. Briois [b]

[a] *Laboratoire d'Electrochimie et de Chimie Analytique, ENSCP, UMR 7575 CNRS, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France*
[b] *Laboratoire de Science et Génie des Surfaces, UMR7570 CNRS, Institut National Polytechnique de Lorraine, Parc de Saurupt, 54042 Nancy Cedex, France*

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Abstract

One of the present challenges for the commercialisation of planar solid oxide fuel cell is the reduction of its operating temperature, which requires the optimisation of the electrolyte nature and ionic conductivity. Thin layer technology seems suitable to decrease the electrolyte resistance at lower operating temperatures. Bilayered electrolytes are proposed and studied in terms of electrical performance. They are constituted of a gadolinia-doped ceria (GDC) layer (the most suitable candidates for IT solid oxide fuel cells (SOFC) in terms of ionic conductivity) protected by an ultra-thin YSZ layer (as electronic barrier). This work analyses the feasibility of bilayered GDC/YSZ electrolyte elaborated by DC magnetron spectroscopy. The bilayer was deposited on the state-of-the-art SOFC porous cathode, strontium-doped lanthanum manganite (LSM). The analysis of the electrical properties of such layers was performed by impedance spectroscopy. Experimental difficulties in order to obtain reliable results and interpretations are discussed.

Keywords: Electrolyte; Impedance spectroscopy; Intermediate temperature SOFC; Sputtering; Thin layers

1. Introduction

The decrease in the solid oxide fuel cells (SOFC) working temperature in order to reduce the costs and increase the fuel cell lifetime is a major technological challenge for their development. Nevertheless, the reduction of the SOFC operating temperature causes several problems such as ohmic drop through the electrolyte and electrode overpotentials. To overcome these cell performance losses, the reduction of the electrolyte resistivity is necessary. This can be achieved by lowering the thickness of the electrolyte [1]. Considering the most usual electrolyte material, the state-of-the-art YSZ, the reduction in the working temperature leads to an insufficient ionic conductivity. Ceria-based electrolytes are more attractive in terms of conductivity at low temperature, but these materials are well-known to be reducible at very low oxygen partial pressure [2–4]. This is the reason to protect them by an electron blocking layer avoiding cell efficiency losses. Therefore, we have selected the bilayer gadolinia-doped ceria (GDC) electrolyte, which is one of the most studied ceria-based electrolyte due to its high ionic conductivity, protected by an ultra-thin layer of YSZ on the anode side [5]. The purpose of this work is to determine by impedance spectroscopy the influence of the YSZ layer, deposited onto the GDC electrolyte, in terms of electrical behaviour. Only the global behaviour will be discussed in this paper, without considering each layer, separately.

2. Experimental procedure

2.1. Elaboration conditions

Bilayers constituted by GDC and YSZ coatings were sputter-deposited by direct sputtering of metallic Zr–16 at.% Y and Ce–10 at.% Gd targets, 50 mm in diameter, in argon–oxygen reactive mixtures. The experimental device is a 40 l sputtering chamber pumped down via a turbo molecular pump, allowing a base vacuum of 10^{-4} Pa. Argon and oxygen flow rates are controlled by MKS flowmeters and the pressure is measured thanks to an absolute Baratron gauge. The substrates are positioned on

* Corresponding author.
E-mail address: Armelle-Ringuede@enscp.fr (A. Ringuedé).

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a substrate holder at the draw distance of about 50 mm. The targets, mounted on an unbalanced magnetron, are powered by pulsed DC supplies, an Advanced Energy Pinnacle.

GDC thin layers have been first sputter-deposited onto the strontium-doped lanthanum manganite (LSM) substrate (commercialised by Indec BV), under an oxygen:argon mixed atmosphere (2.5:40 sccm). The total pressure in the chamber was slightly varying from 0.77 to 0.74 Pa during the total deposition time, close to 10 h to produce 2 μm. The current discharge is maintained at constant value of 0.7 A (pulse frequency of 20 kHz). These GDC layers were next covered by a thinner YSZ layer. The YSZ coating was sputtered under 2.6 sccm O_2 flow rate and 40 sccm Ar flow rate at 0.75 Pa. The current discharge is maintained at constant value of 0.5 A (pulse frequency of 20 kHz).

2.2. Characterisations

Coating thickness was measured using the step method with a Talysurf profilometer allowing an accuracy of 20–30 nm. The structure of the films is determined using a $\theta/2\theta$ Siemens D500 diffractometer in the range $2\theta = 20$–140° ($K\alpha_1$ Co). Scanning electron microscopy (SEM) observations were performed using a Phillips FEG XL30S.

2.3. Electrical measurements

Impedance spectroscopy measurements were carried out under ambient air, as a function of the temperature, using a PGSTAT20 Autolab Ecochemie BV. A specific two-electrode configuration was performed as depicted in Fig. 1. Due to the low thickness of the bilayer electrolyte (see Table 1 for details), no Pt ink was used for the electrode or current collector, to avoid potential metal diffusion through the layers, leading to short-circuits. Thus, it is not possible to establish a symmetrical configuration in such a case, with a well-controlled interface without painting. A Pt point electrode constitutes the working electrode and the current collector, on the external YSZ side since the substrate, associated to a Pt spiral, can be considered as the counter-electrode. With respect to the system linearity, a 200 mV ac signal amplitude (ΔV) was applied, without DC polarisation. Each impedance measurement was carried out in the 1 MHz–10 mHz frequency range, with 11 points per decade. The temperature varied from 300 °C to 600 °C.

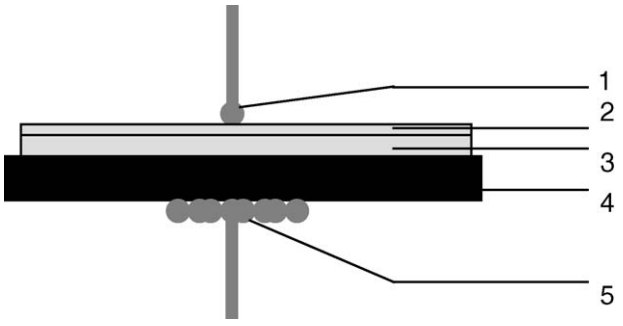

Fig. 1. Schematic view of the two-electrodes configuration: (1) Pt point electrode as working electrode; (2) YSZ thin layer; (3) GDC electrolyte; (4) LSM substrate as counter-electrode; (5) Pt spiral as current collector.

Table 1
Analysed samples with their respective thicknesses t_{GDC} and t_{YSZ}

Sample	t_{GDC} (μm)	t_{YSZ} (μm)	t_{GDC}/t_{YSZ}	$t_{GDC} + t_{YSZ}$
1	4.0	0.86	4.65	4.86
2	1.9	0.86	2.21	2.76
3	5.9	0.86	6.86	6.76
4	5.9	0.40	14.75	6.3
5	4.0	0.40	10.00	4.4

Five samples were elaborated and studied, depending on the total bilayer thickness ($t_{YSZ} + t_{GDC}$) from 2.76 μm to 6.76 μm and the thickness ratio from 2 to 15. The corresponding characteristics are presented in Table 1. The YSZ layer is, in all cases, significantly thinner than GDC.

3. Results and discussion

XRD measurements, registered on the bilayered samples, confirm the same features for YSZ deposited on GDC than for the two simple layers considered separately. Both present pure cubic phases. A SEM micrograph of a bilayer (1.9 μm of GDC and 1.26 μm of YSZ) is presented in Fig. 2 and permits to distinguish both dense layers, even on the porous LSM substrate. The GDC layer seems more compact with finer microstructure than YSZ, presenting a columnar structure.

Two main parts can be distinguished on the impedance diagrams registered on the bilayered electrolyte. As illustrated in Fig. 3, a very large impedance response is observed at frequencies lower than 10,000 Hz, and was ascribed to the electrode behaviour. For frequencies higher than 10 kHz, due to the non-influence of signal amplitude variation (from 100 to 300 mV), the response corresponds to the electrolyte contribution, i.e. both layers. This decomposition in two main parts is possible for samples 1, 2, 4 and 5 (Fig. 4). Considering sample 3, the impedance is largely higher (10 MΩ) reaching the resolution of the frequency response analyser. Thus, only the first high frequency semi-circle was clearly registered.

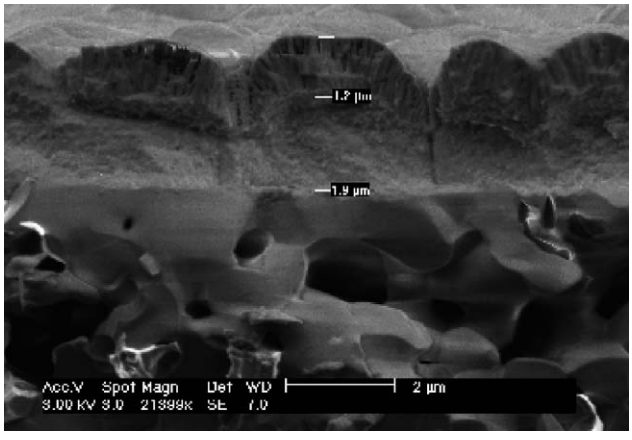

Fig. 2. SEM cross-sectional micrograph of YSZ–GDC bilayer deposited by DC magnetron sputtering on LSM substrate.

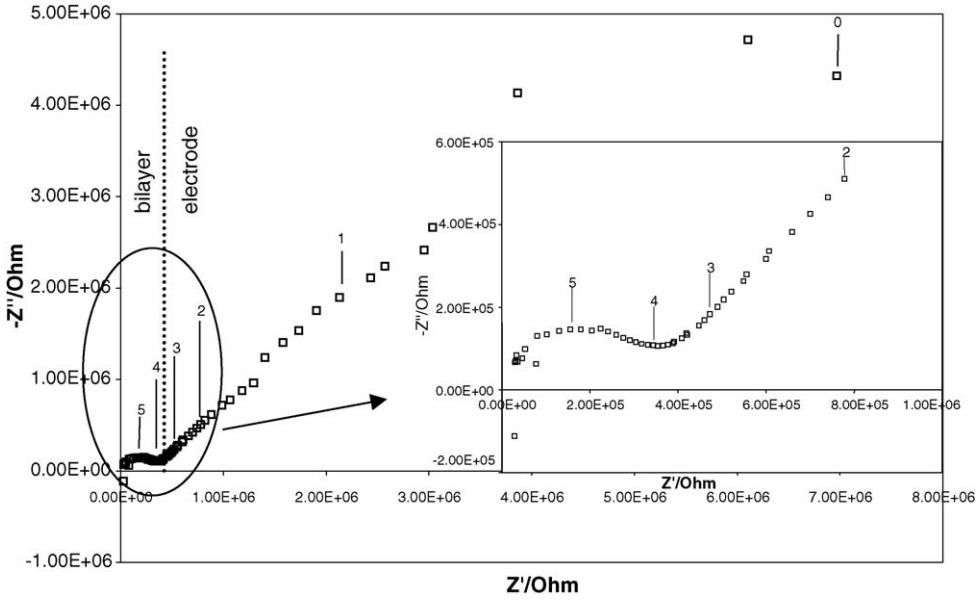

Fig. 3. Impedance diagram registered on sample 1 (YSZ: 0.86 μm and GDC: 4 μm), at $T = 510\,^{\circ}C$, under air, $\Delta V = 200$ mV. Frequency logarithms are represented.

It was already shown that the electrical behaviour of a thin single layer was quite different than for a sintered ceramic. Only one main semi-circle is attributed to the layer, while a minimum of two semi-circles were observed for a ceramic, corresponding to the bulk and to blocking elements (grain boundaries, porosity, etc.) [6–8]. In the case of a bilayer, composed of GDC and YSZ, even with different thickness ratios, it is difficult to separate two contributions. In this work, the total electrolyte resistance is considered, and the corresponding Arrhenius plots are reported in Fig. 5.

As shown in Fig. 5, four samples have a similar behaviour: the bilayer electrolyte resistance decreased when heated, with an activation energy of nearly 1.3 eV. This is the case of "high" thickness ratio samples (1, 3, 4, 5), when the GDC layer is more than five times thicker than YSZ layer. For the lowest ratio, i.e. 2.21, a singular behaviour is observed, with a lower activation energy, close to 1 eV.

Considering more precisely the evolution of the resistance when increasing the thickness of one of the layers, it looks quite difficult to prospect the behaviour of the whole sample. By increasing the GDC thickness, the total resistance increases. The same behaviour can be deduced when GDC layer is fixed and YSZ varies from 400 nm to 860 nm. These observations are not verified by comparing the resistance evolution for samples 1 and 4. Sample 1 resistance is higher, while the total thickness and the GDC thickness are lower. Thus, it seems that YSZ has more influence than the GDC layer. This is confirmed by the variation of the bilayer "conductivity" as reported in Fig. 6. Nevertheless, comparing samples 1 and 3, a relatively low influence of the GDC layer can be observed: the "conductivity" values are lower

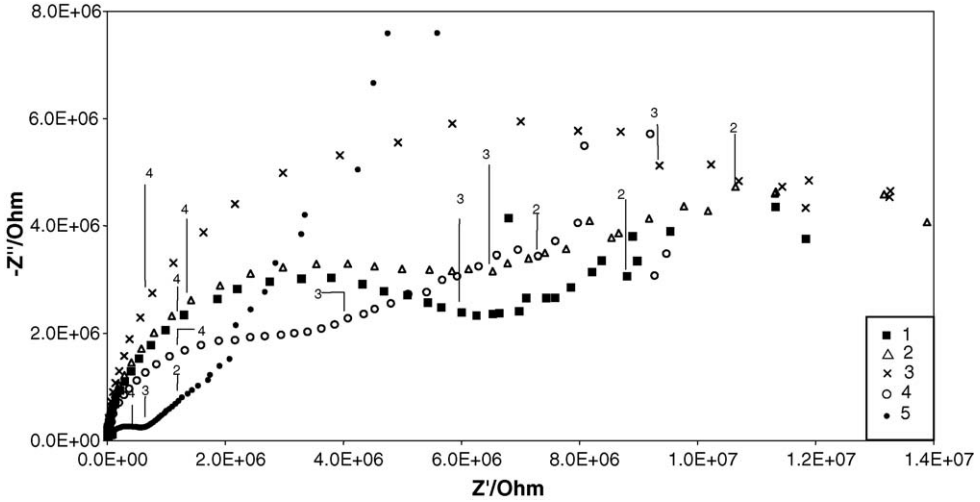

Fig. 4. Impedance diagrams registered on samples 1, 2, 3, 4, 5, at $T = 420\,^{\circ}C$, under air, $\Delta V = 200$ mV. Frequency logarithms are represented. Samples references are detailed in Table 1.

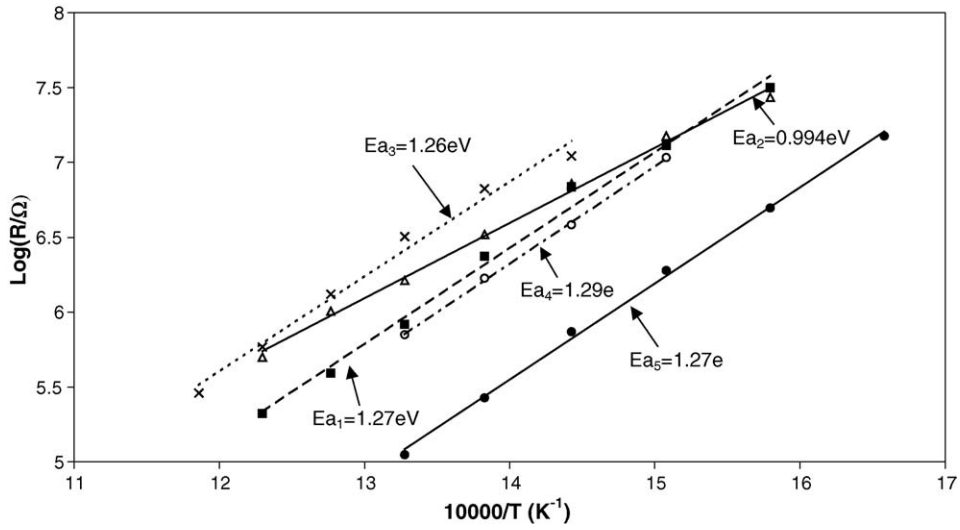

Fig. 5. Arrhenius plots of the bilayer resistance, for different thicknesses. Samples references are detailed in Table 1.

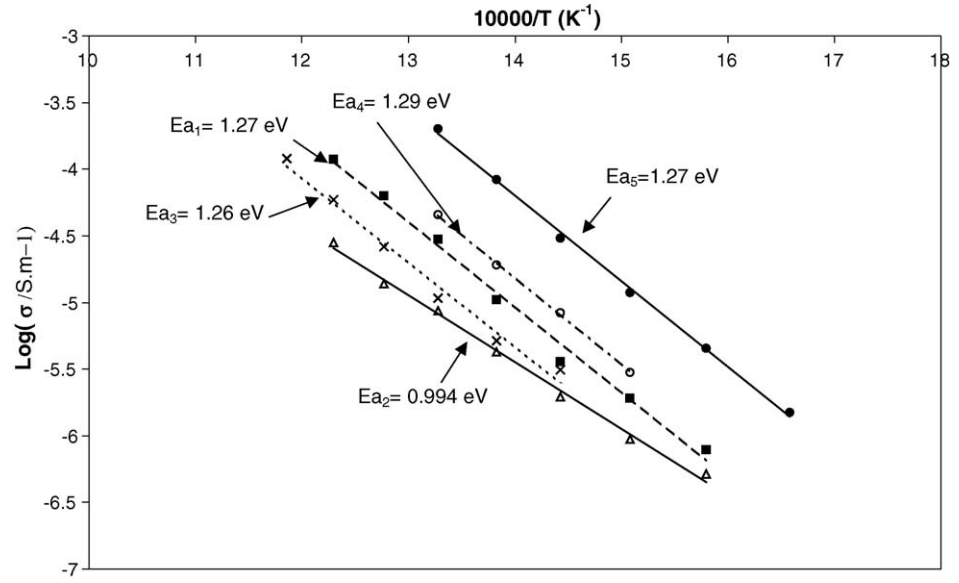

Fig. 6. Arrhenius plots of the bilayer "conductivity", for the different thicknesses. Samples references are detailed in Table 1.

for sample 1 ($t_{GDC} = 4\,\mu m$) than for sample 3 ($t_{GDC} = 5.9\,\mu m$), with the same value of t_{YSZ} (0.86 μm).

In order to understand what is the consequence of adding a YSZ thin layer on the GDC electrolyte, a pseudo bilayer conductivity was defined and calculated from the usual formula:

$$\sigma = \frac{1}{R_{meas}} \frac{t}{S}$$

where R_{meas} is deduced from the high frequency semi-circle associated to the bilayer resistance of the impedance diagram, t is the total thickness of the bilayer ($t_{YSZ} + t_{GDC}$), and S is the estimated contact surface between the Pt point electrode and the YSZ layer (optical microscopy measurement).

These calculations and the pseudo conductivity variations clearly revealed the important contribution of the YSZ layer to the global electrical performance.

All the samples containing more YSZ (860 nm) are less conductive whatever be the GDC layer thickness.

4. Conclusion

The electrical behaviour of ultra-thin layers has already been analysed in the case of GDC and YSZ monolayers [8,9], with a certain range of thicknesses (0.3 μm–5 μm) and two different sputtering techniques, DC reactive and RF magnetron spectroscopy. In this study, the electrical behaviour of a bilayered electrolyte, constituted of a thin YSZ layer deposited onto a GDC thicker layer, was investigated. At this stage of the work, it is difficult to isolate the corresponding monolayer behaviour. A thorough analysis of each individual YSZ and GDC monolayers with strictly the same electrochemical device, synthesis conditions (DC reactive sputtering) and the same thicknesses

than in the bilayered sample, is necessary. It should be added that very few data on the electrical behaviour of ultra-thin layers can be found in the literature, which means that reference values are still required. Nevertheless, we were able to correlate the thickness ratio t_{GDC}/t_{YSZ} with the total electrolyte "conductivity".

It was shown that YSZ plays a very important role in the electrical properties. Not only the thickness must be reduced in order to increase the total conductivity, but a specific attention is required to optimise the thickness ratio between GDC and YSZ.

It was clearly revealed that, in the case of a low ratio (close to 2.2) corresponding also to the lowest total thickness, the conductivity is lower compared to all the other samples presenting a ratio higher than 5.

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