



Short communication

Properties of bias-assisted sputtered gadolinia-doped ceria interlayers for solid oxide fuel cells

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ARTICLE INFO

Article history:

Received 2 March 2009

Received in revised form

21 September 2009

Accepted 26 September 2009

Available online 7 October 2009

Keywords:

Solid oxide fuel cells

Bias-assisted sputtering

Ceria interlayer

Mixed ionic–electronic cathode

Anode supported

ABSTRACT

The growth and electrochemical properties of gadolinia-doped ceria (GDC) interlayers deposited by bias-assisted magnetron sputtering in solid oxide fuel cells have been investigated. Such interlayers act as diffusion barriers to protect the yttria-stabilized zirconia electrolyte, preventing possible degradation when mixed ionic–electronic conductor (La,Sr)(Co,Fe)O_{3-δ} is used as the cathode. The dependence of the applied bias during the sputtering deposition on both the interlayer microstructure and fuel cell performance has been studied in anode-supported single cells. The main experimental results showed that bias-assisted sputtering of GDC interlayers produced microstructures denser than those of unbiased depositions, which resulted in increased electrochemical properties of fuel cells.

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1. Introduction

The anode-supported solid oxide fuel cell (SOFC) has as main advantage the substantially lower ohmic resistance of the yttria-stabilized zirconia (YSZ) electrolyte, which allows for the operation at intermediate temperatures (600–800 °C) [1–4]. Those devices have proven their capacity to generate electrical power in several demonstration units, while still preserving the ability to use different fuels [5]. Nevertheless, the development of SOFC component materials with improved performance and durability is still an important matter [4,6,7]. Decreasing the operation temperature of the SOFC to 600–800 °C range is considered as an important advance, which allows for a wider choice of materials and processes that contribute to both lower the cost and improve the thermal stability of the system. Degradation processes are slowed down due to lower diffusion rates of chemical species at reduced temperatures. On the other hand, thermally activated electrochemical reactions are retarded, and high-performance electrolyte and electrodes are necessary in order to sustain high-power density at intermediate operating temperatures.

In this scenario, the development of electrode materials with enhanced electrical properties at intermediate temperatures is of relevance [4,6,7]. The conventional SOFC cathode, La_{1-x}Sr_xMnO_{3-δ} (LSM), has shown good performance at high operating temperatures (800–1000 °C) with suitable activity for oxygen reduction and adequate electrical properties [4,6,7]. However, at temperatures ≤800 °C LSM exhibits sluggish performance, and the largest contribution to the total overpotential losses in anode-supported SOFC is from the cathode [1,4]. Therefore, different materials have been proposed as alternative cathodes, and among them the ferrite–cobaltite perovskite (La,Sr)(Co,Fe)O_{3-δ} (LSCF) is being considered as a promising substitute for the LSM [4,6,7]. Both the mixed ionic–electronic transport properties and catalytic activity of LSCF enhance the three-phase boundary for the electrochemical reactions, and superior performance of SOFC operating at intermediate temperatures (600–800 °C) has been reported [6,7]. Although the LSCF exhibits good activity towards oxygen reduction, the main drawback of such an oxide is its reactivity with the YSZ electrolyte. The cation interdiffusion across the electrolyte/cathode interface, in which the main mechanism is the Sr²⁺ ions migration from the cathode, results in the formation of resistive phases that rapidly degrades the SOFC performance [6,8,9].

Diffusion barrier interlayers, deposited onto the electrolyte, have demonstrated to be an effective way to avoid the Sr²⁺ diffusion from LSCF cathode and, consequently, to prevent the degradation of the SOFC [8,9]. Ceria-based oxides have been reported as convenient materials for such barriers due to good transport

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properties and reasonable compatibility with both YSZ electrolyte and LSCF cathode [8,9]. One of the main challenges is the fabrication of cost effective and reproducible protective interlayers, at sufficiently low temperatures in order to avoid undesired reactions between YSZ and ceria. The effectiveness of the diffusion barrier is closely related to its microstructural properties, and high density and homogeneous interlayers are desirable for such an application. Different processing technologies have been used for the fabrication of doped ceria protective interlayers, such as the deposition of ceramic suspensions, like screen printing, and physical vapor deposition methods [9,10]. Detailed studies, comparing deposition techniques, provided compelling evidence that single cells with ceria interlayers fabricated by reactive magnetron sputtering exhibited enhanced performance, a feature possibly associated with the higher density of such layers attained at relatively lower temperature than by wet ceramic deposition techniques [9,10]. Although sputtering is a scalable industrial process, further optimization is necessary for the production of SOFC protective interlayers. Several experimental parameters of reactive sputtering deposition, like temperature, oxygen flow, and pressure, have been investigated, resulting in interlayers that do not require an extra sintering step, as it is necessary for depositions by wet ceramic methods [9,10]. However, additional features of the sputtering technique can be used to further enhance the properties of the deposited layers.

Bias voltage-assisted sputtering was found to produce films with better quality when compared to those of unbiased depositions [11]. The bias voltage alters the distribution of the potential in the plasma and converts the substrate in a secondary sputtering target. The overall effect of the applied bias voltage is the change of both the energy and flux of particles bombarding the substrate, accelerating positively charged ions onto the substrate. Because the nucleation and growth processes are closely related to this bombardment, essentially, every property of sputtered films can be controlled by the applied bias voltage. One of the reported effects is the increased electrical conductivity of biased sputtered films, reaching the bulk conductivity value for optimized applied bias [11].

In this context, the effects of applied bias voltage during sputtering of gadolinia-doped ceria (GDC; $(\text{Ce,Gd})\text{O}_{2-\delta}$) diffusion barriers over yttria-stabilized zirconia electrolytes were studied. Microstructural analyses of GDC barriers revealed that the applied bias voltage inhibits the columnar structure of sputtered interlayers, resulting in dense microstructures. Such a feature was reflected

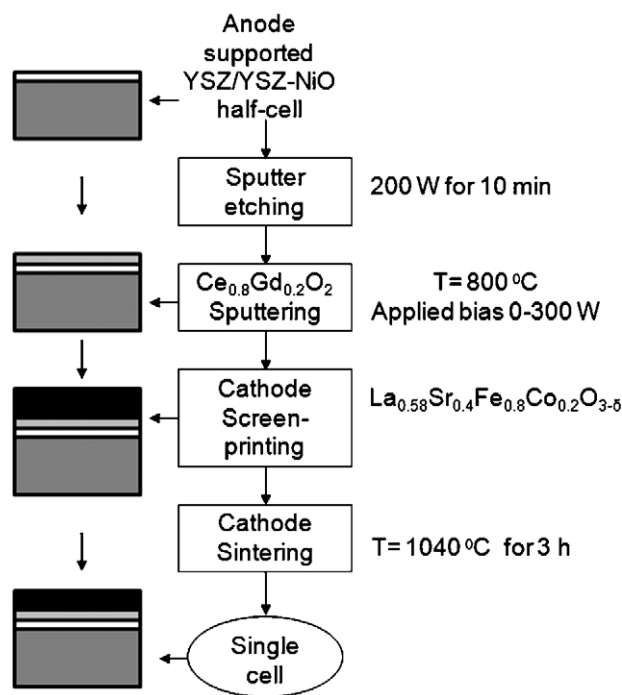


Fig. 1. Flow chart of the experimental procedure followed for fuel cell preparation. On the left side a schematic drawing (not in scale) displays the fuel cell configuration.

in the electrochemical tests, which showed that the performance of solid oxide fuel cell having bias sputtered interlayers is increased.

2. Experimental

Half cells comprised of Ni/yttria-stabilized (8 mol%) zirconia (Ni/YSZ) anode support, Ni/YSZ anode functional layer, and YSZ electrolyte were used as substrates for the deposition of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (GDC) interlayers. Substrates, with 50 mm × 50 mm total area, were produced by warm pressing Ni/YSZ anode support (1.5 mm thickness), followed by vacuum slip casting of both the anode functional layer and the electrolyte. After co-sintering at 1400 °C, the final thickness of each cast layer was ~10 μm. Further details of solid oxide fuel cell production are described elsewhere [3,6].

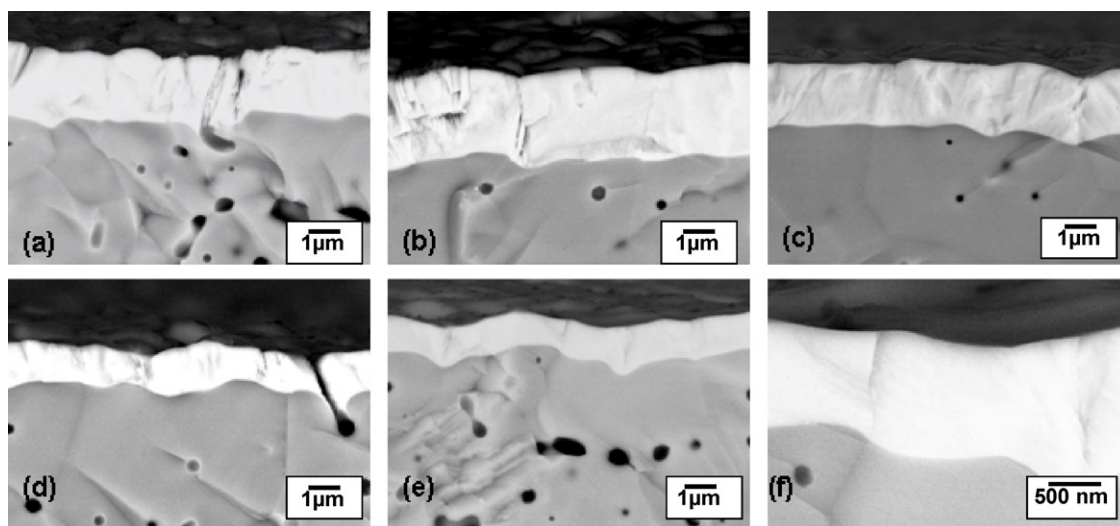


Fig. 2. Back scattering scanning electron micrographs of the cross section of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ interlayers (brighter regions) deposited onto yttria-stabilized zirconia electrolyte (darker regions) with different applied bias power: (a) 0 W, (b) 10 W, (c) 50 W, (d) 100 W, (e) 300 W, and (f) 300 W with higher magnification.

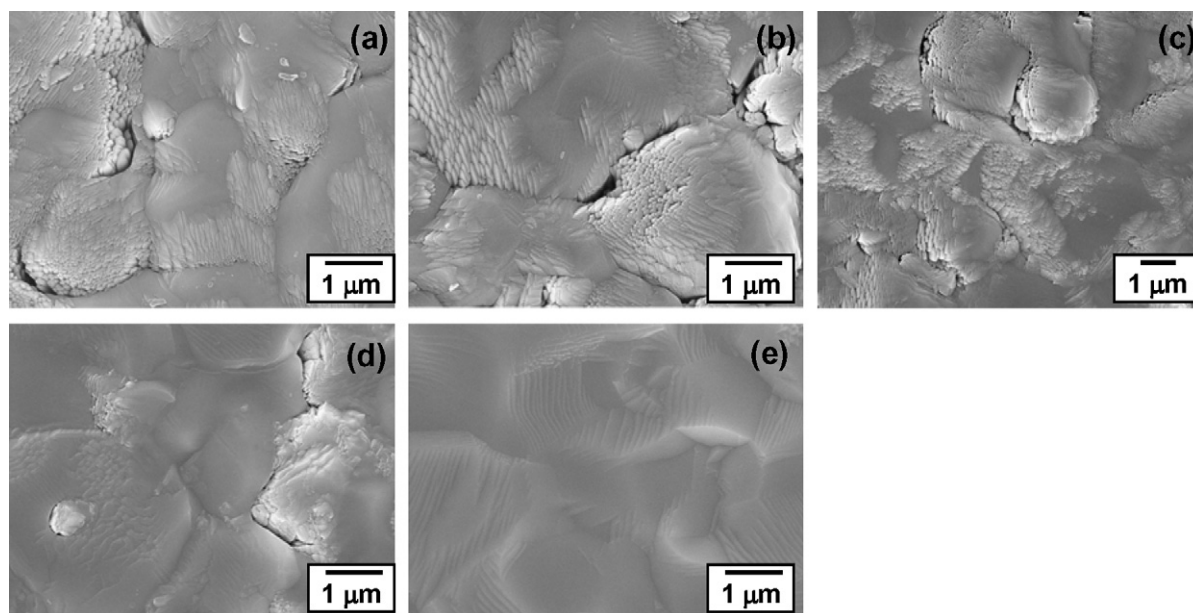


Fig. 3. Scanning electron micrographs of the surface of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ interlayers deposited with different applied bias power: (a) 0 W, (b) 10 W, (c) 50 W, (d) 100 W, and (e) 300 W.

$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ coatings were carried out in a physical vapor deposition system CS 400ES (Von Ardenne Anlagentechnik, Germany). Before loading into the deposition system, the surface of substrates were cleaned with organic solvents and dried. Subsequent conditioning of the surfaces was performed under vacuum into the deposition system by sputter-etching (200 W for 10 min). After transferring to the sputtering chamber, specimens were heated to the deposition temperature (800 °C) at a rate of 3 °C min⁻¹. Gadolinia-doped ceria interlayers were grown by reactive magnetron dc-sputtering by using a metallic target with nominal composition of 80 at.% Ce and 20 at.% Gd (99.7% purity) under 16 standard cubic centimeters (sccm) oxygen flow. During the deposition, the pressure on the chamber was kept at 5×10^{-3} mbar and dc-sputtering energy set to 500 W. High-frequency bias voltage was applied to the metallic sample holder by controlling a fixed bias power, ranging from 0 to 300 W. The interlayer growth rate dependence on the applied bias was firstly studied by fixing the total energy of the deposition process to 2 kWh. By assuming a linear growth rate, GDC layers with $\sim 1 \mu\text{m}$ thickness were fabricated by adjusting the deposition time for each applied bias (0, 50, 100, and 300 W).

Microstructural analyses of both fractured cross sections and surfaces of the deposited interlayers were performed in a field emission gun electron scanning microscope (FEG-SEM, Zeiss Ultra 55), using both back scattered and secondary electrons. Interlayers have been analyzed by energy dispersive X-ray spectroscopy, which demonstrated that the deposited GDC have composition close to the nominal $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$. The desired fluorite structure has been previously proved by X-ray diffraction [9].

$\text{La}_{0.58}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ (LSFC) cathode was screen printed onto the GDC interlayer by using conventionally prepared ceramic suspensions. Details concerning the preparation of both LSFC powder and suspension are reported elsewhere [9]. After the screen printing depositions, single cells were heat treated at 1040 °C for 3 h in air. Final thickness of cathode layer was $\sim 60 \mu\text{m}$ and the active area of the single cells $\sim 40 \text{ mm} \times 40 \text{ mm}$. Fig. 1 displays a diagram of the experimental procedure for fuel cells preparation and a schematic drawing of fuel cell configuration.

Electrochemical tests were performed in an alumina housing placed in a resistive furnace [9,10]. Gas tightness was obtained by a

gold sealant, and electrical contact was assured by Ni and Pt meshes used at the anode and the cathode sides, respectively. After the controlled reduction of the anode, hydrogen (3 vol.% H_2O) was flown into the chamber at 1000 ml min⁻¹ using mass flow controllers. Polarization curves were collected by direct current measurements using a current-control power supply type Gossen 62N-SSP500-40 (Gossen-Metrawatt GmbH, Germany), and a computer-controlled data acquisition system. For all single cells prepared with different applied bias power, at least two nominally identical cells were measured.

3. Results and discussion

The microstructure of sputtered GDC interlayers, deposited onto anode-supported half cells at 800 °C with different applied bias power, were investigated in a FEG-SEM. Figs. 2 and 3 display cross section and surface micrographs of GDC interlayers, respectively. In Fig. 2, backscattered electrons were used for phase contrast, and the

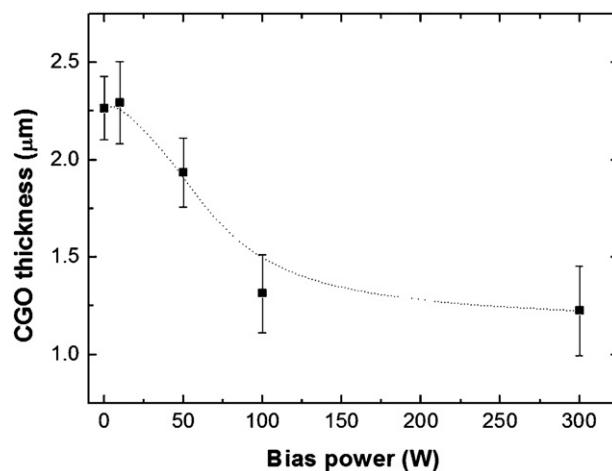


Fig. 4. Applied bias dependence of the thickness of the $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ interlayer. Values correspond to the average of ~ 15 measurements in different regions along the cross section of samples, error bars are the standard deviation, and the dotted line is guide to the eye.

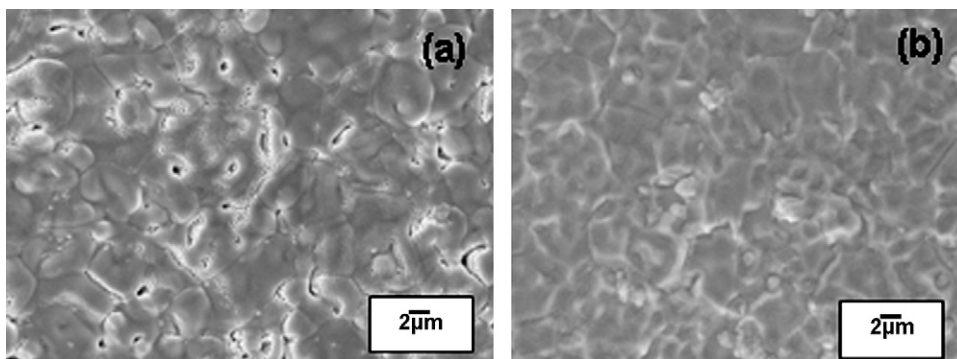


Fig. 5. Scanning electron micrographs of the surface of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ interlayers deposited with (a) 10 W and (b) 300 W applied bias power, after sintering at 1080 °C for 3 h.

GDC layer is clearly defined as the brighter regions on the top of the YSZ electrolyte. Zero bias sputtered GDC layers (Fig. 2a and 3a) show similar features of previously studied ones deposited using the same experimental conditions and apparatus [9,10]. The unbiased layers exhibit homogeneous cross sections and surfaces; however, a considerable portion of the deposited GDC is comprised of regions displaying a columnar microstructure (Fig. 3). The columnar structure is typically found in sputtered films [9,11] and associated with remnant islands, formed in the initial growth stage, that did not attain the coalescence stage completely, limiting the continuity of the deposited layer [11].

Increasing the applied bias power (Figs. 2b–d and 3b–d) results in a progressive change of the microstructural properties of

GDC interlayers. At low bias, up to 10 W, samples have similar microstructure than that of unbiased depositions. However, for applied bias of 50 W and higher a clear reduction of regions displaying columnar structure is inferred from both cross section and surface images. For the highest applied bias (300 W) the microstructure of the GDC layer is rather homogeneous and denser than the ones grown at lower bias (Fig. 2e and f). Such a bias power dependence on the microstructural properties is mirrored on the growth rate of the interlayers.

The variation of the thickness of the GDC layers with the applied bias was determined in samples sputtered with fixed total energy of 2 kWh, as shown in Fig. 4. Low bias (10 W) had no appreciable effect on the growth rate, but increasing the applied bias decreased signif-

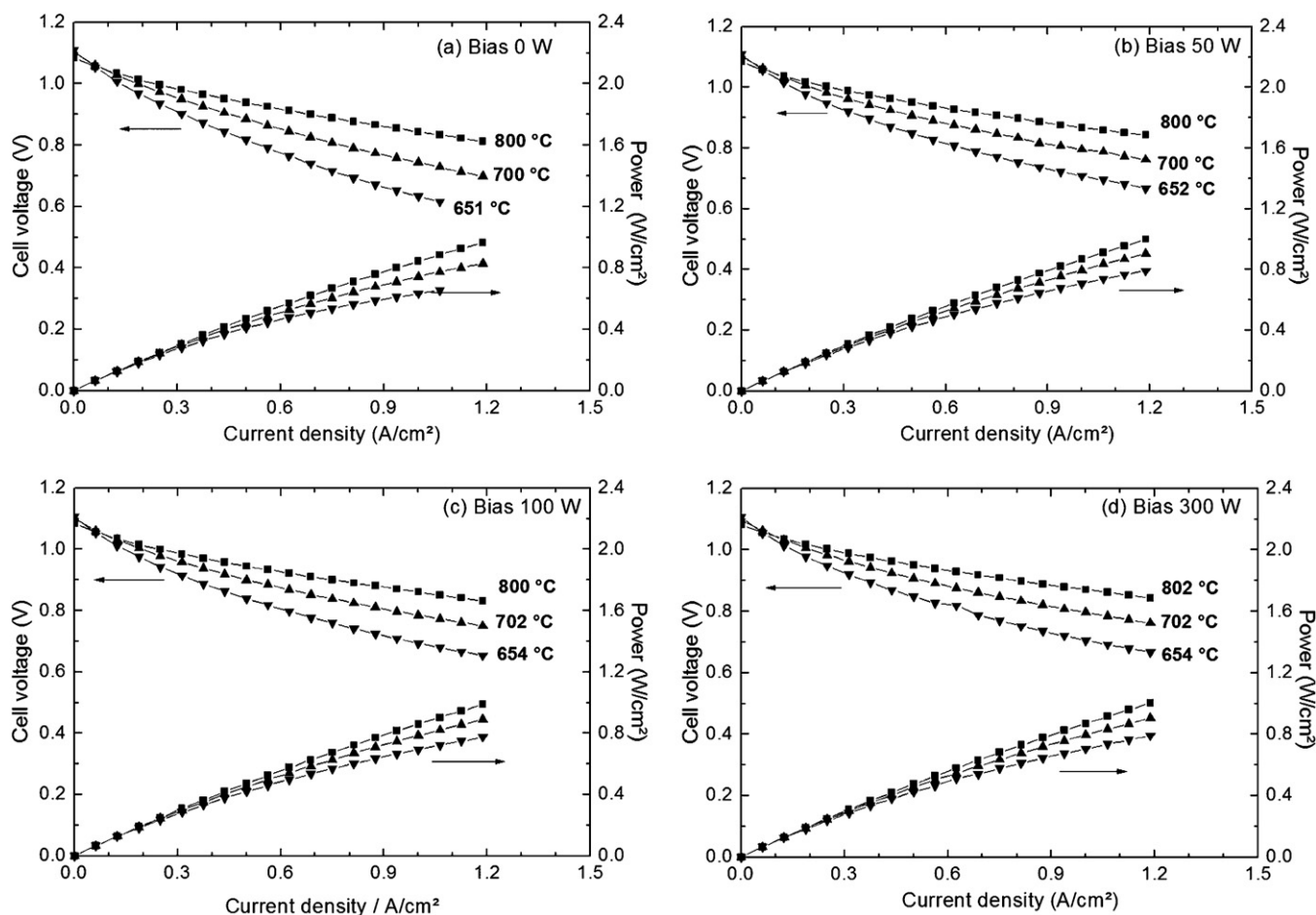


Fig. 6. Cell voltage (left y-axis) and power density (right y-axis) curves measured in the 650–800 °C range for single cells with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ interlayer sputtered with applied bias power: (a) 0 W, (b) 50 W, (c) 100 W, and (d) 300 W.

icantly the thickness of the GDC layers. For 100 W bias, the thickness was reduced to approximately half of the value measured for unbiased sample, and depositions carried out at 300 W bias maintained similar growth rate of the one at 100 W ($\sim 25 \text{ nm min}^{-1}$). The slower growth rate of biased depositions can be attributed either to the fact that the applied bias converts the substrate in a secondary sputtering target, which promotes the re-sputtering of particles loosely attached to the surface of the film or, more likely, to the higher compactness of interlayers deposited over the same area [11].

The microstructure of deposited GDC interlayers was investigated after a heat treatment simulating the cathode sintering. The deposited GDC barriers were sintered at 1080°C for 3 h in air and analyzed by FEG-SEM. Fig. 5 shows the sintered surface of interlayers sputtered with 10 and 300 W applied bias. A rough visual inspection of both Figs. 3 and 5 suggests coarsening of the sintered GDC grains. However, samples deposited with low applied bias power (10 W, Fig. 5a) retain residual porous regions after sintering that are probably related to the former columnar regions (Fig. 3b), while the 300 W biased sample maintains a rather dense microstructure.

The combined results of the microstructural characterization revealed that applied biases $\geq 50 \text{ W}$ play a significant role on the microstructure of sputtered layers, lowering the growth rate and favoring the formation of compact and continuous GDC interlayers.

Such findings are relevant for the performance of SOFC, and the electrochemical properties of single cells with sputtered GDC

interlayers with final thickness adjusted to $\sim 1 \mu\text{m}$ were studied. Fig. 6 shows typical polarization curves of single cells with GDC interlayers deposited with 0, 50, 100, and 300 W bias, measured in the $650\text{--}800^\circ\text{C}$ range. The polarization curves exhibit characteristic features of SOFC: the open circuit voltage is $\sim 1.1 \text{ V}$; the ohmic drop polarization is the most significant one in the measured current range; and a clear increase of the performance is observed with increasing measuring temperature. The measured power outputs are within the range of state-of-the-art anode support SOFC, reaching $\sim 1 \text{ W cm}^{-2}$ at 800°C and 800 mV [6,9,10].

In order to better analyze the effect of applied bias on the performance of fuel cells, Fig. 7a shows the polarization curves measured at 800°C for samples with GDC interlayer deposited with different applied bias. Fig. 7a displays an evident enhancement of the polarization curves of samples with bias-deposited interlayers. Such an enhancement is clearly observed in Fig. 7b, which shows the temperature dependence of both the average current density values at 900 mV extracted from the polarization curves of nominally identical samples (left y-axis). The temperature dependence of the fuel utilization (FU) was calculated and the results for the sample with GDC interlayer deposited with 300 W applied bias are shown in Fig. 7b (right y-axis). Fuel cell tests have been performed with fuel flow well in excess and typical FU values are within $\sim 5\text{--}10\%$ range. Current density values at 900 mV and 800°C reach $\sim 0.8 \text{ A cm}^{-2}$ for samples deposited with 300 W applied bias while the unbiased sample delivers $\sim 0.7 \text{ A cm}^{-2}$, corresponding to power outputs of ~ 0.7 and 0.6 W cm^{-2} , respectively. All single cells having bias sputtered GDC interlayers have higher performance than the unbiased one in the whole temperature range investigated. However, a direct correlation between the applied bias and the current density was not evident. In comparison to zero bias, samples having GDC interlayers sputtered with 300 and 100 W bias display an increase of $\sim 15\%$ of the current density, and 100 W biased depositions have $\sim 10\%$ higher current densities. The observed behavior may be attributed to small differences of the interlayer thickness that are possibly related to the positioning of the samples in the sputtering chamber. New experiments are underway to further investigate this point.

4. Conclusions

The influence of applied bias on the properties of magnetron sputtered gadolinia-doped ceria diffusion barrier layers was studied. The applied bias had a clear effect on the microstructure and growth rate of the interlayer. Increasing bias power, in the $50\text{--}300 \text{ W}$ range, progressively inhibited the columnar structure and favored a more continuous and denser microstructure. Such features resulted in more effective barriers against strontium diffusion that prevented the formation of resistive phases at the cathode/electrolyte interface. Therefore, anode-supported single solid oxide fuel cells having bias sputtered interlayers were found to have enhanced electrochemical properties, as evidenced by an appreciable increase of the current density. The experimental data indicated that the applied bias is a useful feature of the sputtering process that improves the quality of ceria-based diffusion barrier interlayers for intermediate temperature solid oxide fuel cells.

Acknowledgements

FCF is thankful for the Brazilian agencies FAPESP (2007/08686-8) and CNPq (306422/2007-7). F. Vondahlen and W. Herzhof are thanked for helping us with PVD depositions and samples supply/cathode depositions, respectively.

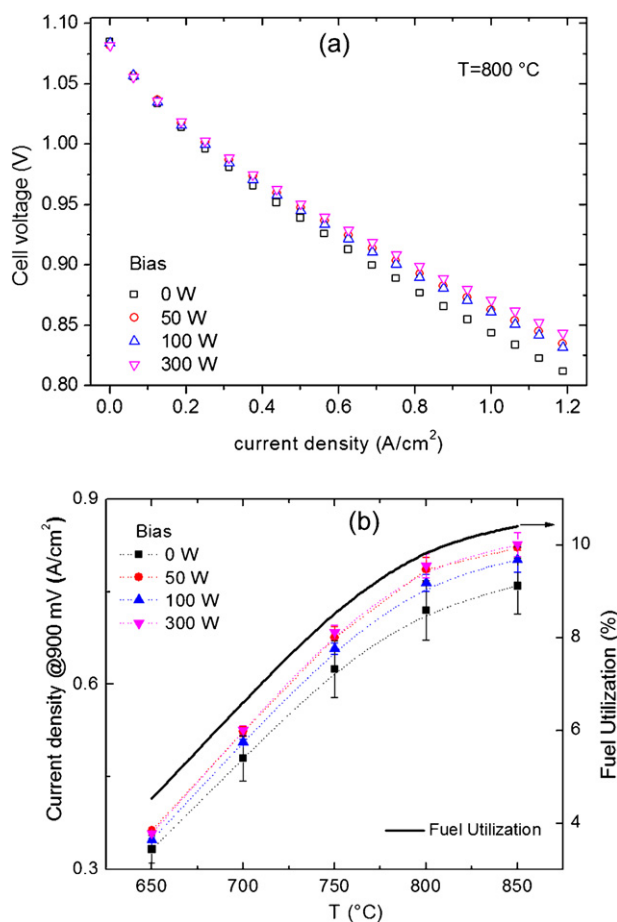


Fig. 7. (a) Polarization curves measured at 800°C for single cells with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ interlayers sputtered with different applied bias power. (b) Temperature dependence of the average current density at 900 mV for single cells with $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ interlayers sputtered with different applied bias power (left y-axis) and temperature dependence of fuel utilization calculated for the sample with interlayer deposited with 300 W applied bias (right y-axis).

References

- [1] S.C. Singhal, K. Kendall, High-temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications, 1st ed., Elsevier, New York, 2004.
- [2] B.C.H. Steele, A. Heinzel, *Nature* 414 (2001) 345–352.
- [3] H.P. Buchkremer, U. Diekmann, D. Stöver, Proc. of 2nd European Solid Oxide Fuel Cell Forum, 1996, pp. 221–228.
- [4] D.J.L. Brett, A. Atkinson, N.P. Brandon, S.J. Skinner, *Chem. Soc. Rev.* 37 (2008) 1568–1578.
- [5] L. Blum, W.A. Meulenber, H. Nabielek, R. Steinberger-Wilckens, *Int. J. Appl. Ceram. Technol.* 2 (2005) 482–492.
- [6] F. Tietz, Q. Fu, V.A.C. Haanappel, A. Mai, N.H. Menzler, S. Uhlenbruck, *Int. J. Appl. Ceram. Technol.* 4 (2007) 436–445.
- [7] E.V. Tsipis, V.V. Kharton, *J. Solid State Electrochem.* 12 (2008) 1367–1391.
- [8] S.P. Simner, J.P. Shelton, M.D. Anderson, J.W. Stevenson, *Solid State Ionics* 161 (2003) 11–18.
- [9] S. Uhlenbruck, N. Jordan, D. Sebold, H.P. Buchkremer, V.A.C. Haanappel, D. Stöver, *Thin Solid Films* 515 (2007) 4053–4060.
- [10] N. Jordan, W. Assenmacher, S. Uhlenbruck, V.A.C. Haanappel, H.P. Buchkremer, D. Stöver, W. Mader, *Solid State Ionics* 179 (2008) 919–923.
- [11] B.N. Chapman, *Glow Discharge Processes: Sputtering and Plasma Etching*, John Wiley and Sons, New York, 1980.