

Electrical and microstructural characterization of Gd-doped Ceria/Y-doped Zirconia bi-layer electrolyte prepared by tape casting

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ABSTRACT

GDC-YSZ bi-layer SOFC electrolytes are an interesting manner to protect GDC electrolytes of the low oxygen partial pressure present at anode-electrolyte interface. This oxygen partial pressure condition and high temperatures during the operation of SOFC permit GDC electrolyte reduction injuring the performance of SOFC. In this work, GDC-YSZ bi-layer electrolytes were prepared using double tape casting technique. Single layers of YSZ and GDC electrolytes were also prepared by the same technique for comparison. All samples were sintered at 1600 °C/2 h in air and analyzed by SEM and impedance spectroscopy technique. A good adhesion was established between the layer GDC and YSZ and no cracks were detected despite the differential firing shrinkage. The electrical conductivity of GDC-YSZ bi-layer sample at 350 °C was 7.98×10^{-5} S.cm⁻¹ and for GDC and YSZ single layer samples electrical conductivities were 1.89×10^{-4} S.cm⁻¹ and 4.71×10^{-5} S.cm⁻¹, respectively. These results show that GDC-YSZ bi-layer electrolyte is superior to YSZ single layer electrolyte.

Keywords: GDC-YSZ bi-layer electrolyte; tape casting; SOFC

1. INTRODUCTION

Currently, one of the main goals on solid oxide fuel cells (SOFC) technology is to achieve viable operation at temperatures lower than 1000 °C, in which high cost materials are required to avoid the cell degradation [1-3]. Gadolinia-doped ceria (GDC) exhibits ionic conductivity higher than yttria-stabilized zirconia (YSZ) at temperatures below 800 °C and therefore present great potential for SOFC electrolytes applications [4,5]. However, the oxygen partial pressure at the interface between anode and electrolyte at 800 °C is between 10^{-18} and 10^{-20} atm [6]. In these conditions, it occurs the Ce⁺⁴ reduction since at 800 °C the equilibrium oxygen partial pressure between Ce₂O₃ and CeO₂ phases is 2.5×10^{-20} atm. Consequently, under reducing atmosphere, GDC becomes a mixed conductor resulting in severe degradation of the cell performance [2,7]. Besides that, the reduction of ceria causes expansion of the crystal lattice decreasing the mechanical stability of the electrolyte [8].

An interesting manner to solve the reduction problems of GDC electrolyte for SOFC applications is the utilization of a thin layer of YSZ, which presents negligible electronic conductivity and high chemical stability in reducing environment, between GDC electrolyte and anode forming a bi-layer electrolyte. This electrolyte model has been suggested in order to block the electronic conductivity in the GDC layer, as well as increasing oxygen partial pressure in the GDC-YSZ interface, which improves the chemical stability of the doped ceria [9-13].

Virkar [14] was one of the first researchers to approach the issue of oxygen partial pressure in SOFC with bi-layer electrolytes. He proposed a simplified analytical model for calculating the oxygen partial pressure considering the conduction characteristics of the two layers as main parameters. Chan et al. [15] in a detailed paper, developed a model for bi-layer electrolyte for SOFC showing clearly the influence of the ratio between thickness of two layers, the effect of YSZ blocking layer and how bi-layer electrolyte design can improve the cell performance. Yahiro et al. [8] proposed a bi-layer electrolyte model showing that the deposition of a thin layer of YSZ on yttria-doped ceria (YDC) at anode side led to a significant increase in open circuit voltage and power density with respect to unprotected YDC electrolyte.

Thermal stability of bi-layer electrolyte is ensured by the thermal compatibility between GDC and YSZ. The thermal expansion coefficients for 10 and 5mol% gadolinia-doped ceria is $11.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $10.1 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, respectively, while for YSZ is $9.9 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ [16].

The YSZ layer on the doped ceria electrolyte must be sufficiently thin to minimize its contribution to the total electrical resistance of the electrolyte due to low ionic conductivity of YSZ at intermediate temperatures. Liu et al. [17] produced GDC-YSZ bi-layer electrolyte ($7\mu\text{m}/3\mu\text{m}$) on substrate of anode material using spray coating and obtained values of open circuit voltage close to the theoretical values showing the efficiency of YSZ layer in blocking the electronic conduction generated in the GDC layer.

The literature on GDC-YSZ bi-layer shows that performance improvements occur in relation to unprotected electrolytes. However, it is important to analyze the chemical compatibility between GDC and YSZ. The literature is somewhat controversial about the reactivity between the YSZ and GDC. Jang et al. [18] did not detect the formation of such undesired phases in bi-layer electrolyte sintered at $1400 \text{ }^\circ\text{C}$. Grover et al. [19] showed that formation of phases such as gadolinium zirconate, gadolinium cerate and zirconium cerate occurred in samples sintered at $1400 \text{ }^\circ\text{C}/48 \text{ h}$ from a mixture of CeO_2 , ZrO_2 and Gd_2O_3 . Tompsett et al. [20] found that the reactivity between YSZ and GDC is low and only three days after treatment at $1300 \text{ }^\circ\text{C}$ has been identified some signs of ionic diffusion.

Tape casting technique is indicated to obtain SOFC components because it is an excellent low cost technique to obtain thin flat ceramics [21, 22]. In this work, tape casting technique was used to prepare GDC-YSZ bi-layer electrolyte and single layer electrolytes of GDC and YSZ. Bi-layer electrolyte is discussed in relation to single layers electrolytes from impedance spectroscopy measurements and scanning electron microscopy analysis.

2. MATERIALS AND METHODS

The powder 10 mol% gadolinia-doped ceria (GDC) was prepared mixing appropriate amount of cerium oxide and gadolinium oxide, both of high purity from Aldrich. The powder 8 mol% yttria-stabilized zirconia (YSZ) was from Tosoh. Table 1 shows the amount of organic components used to prepare GDC and YSZ slurries. Ethanol and xylene were used as solvent, phosphate ester (Huntsman) as dispersant, polyvinyl butyral (PVB) Butvar B98 (Solutia) as binder. The plasticizers were triethylene glycol di-2-ethylhexanoate S2075 (Solutia) and polyalkylene glycol UCON 50HB2000 (Dow Chemical).

Table 1: Formulations of GDC and YSZ slurries prepared for single and double tape casting processes

SLURRY	POWDER ^(a)	SOLVENT ^(a)	DISPERSANT ^(b)	BINDER ^(b)	PLASTICIZER ^(c)
GDC	57.4	Ethanol: 5.4 Xylene: 37.2	Phosphate Ester: 0.8	B98: 10.0	S2075: 50.0 UCON: 50.0
YSZ	41.3	Ethanol: 13.1 Xylene: 45.6	Phosphate Ester: 0.8	B98: 20.0	S2075: 50.0 UCON: 50.0

^(a): % in relation to weight of powder + solvent; ^(b): % in relation to weight of powder; ^(c): in relation to weight of binder.

Slurries were vibratory milled in high-density polyethylene jars (Nalgene) and zirconia grinding media (Tosoh). Tape casting was performed in TTC-1200 tape caster (Richard E. Mistler, Inc.) equipped with a single blade. GDC-YSZ bi-layer tapes were prepared by double tape casting. First, YSZ tape ($\sim 40 \mu\text{m}$ thick) was casted and dried in air and then GDC tape ($\sim 370 \mu\text{m}$ thick) was casted on the YSZ layer forming a bi-layer tape as illustrated at Figure 1.

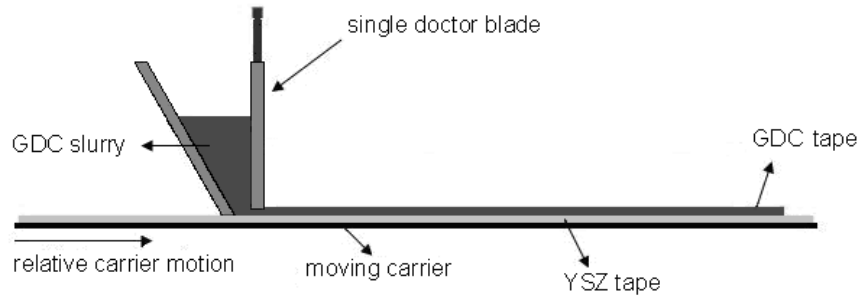


Figure 1: Scheme of double tape casting process used to prepare GDC-YSZ bi-layer tapes.

GDC and YSZ single layers were prepared from the same slurry formulations used for bi-layer tape. Thicknesses of dried GDC and YSZ tapes were measured with a micrometer and 600 and 430 μm , respectively were obtained. Disc samples of 20 mm diameter were cut from the dried tapes and sintered following a firing schedule with a heating rate of 30°C/h up to 600°C, followed by a heating rate of 300°C/h up to 1600°C, with a soak time of 2 h. The sintered samples were characterized by impedance spectroscopy (HP 4192A) in a temperature range of 275 - 425°C, frequency range of 5 Hz - 13 MHz and an applied voltage of 0.5 V. The microstructure was analyzed by scanning electron microscopy (Phillips XL 30 FEG) on polished and thermally etched surfaces (bulk).

3. RESULTS AND DISCUSSION

3.1 Microstructure

Samples cut from the mono-layers of CGD and YSZ were sintered at 1600 °C/2h and both samples showed density higher than 98% of theoretical density and firing shrinkage of 25 and 30%, respectively. Figure 2 shows the SEM micrographs of polished surface and thermally etched samples of GDC and YSZ. The mean grain size was 4 μm for both samples.

Figure 2: SEM micrographs of polished and thermally etched sample of GDC and YSZ sintered at 1600 °C/2h.

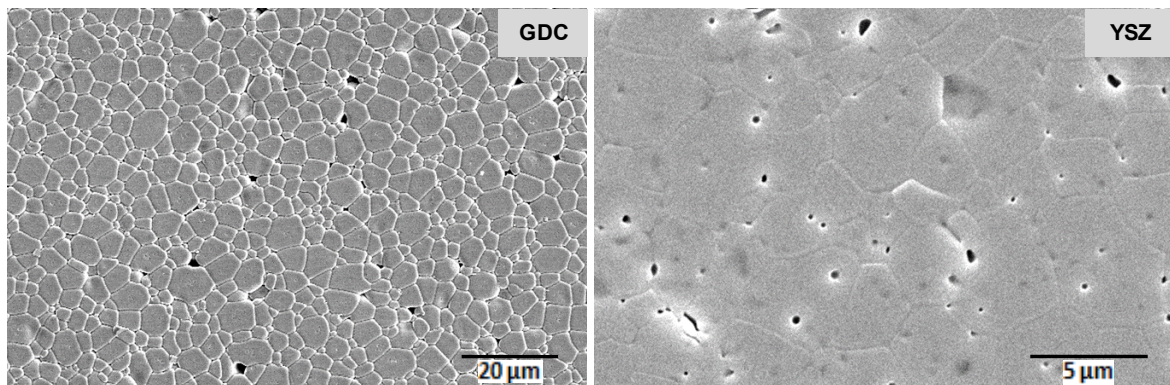


Figure 3 shows the bi-layer tape immediately after casting. Samples were cut from this tape and sintered at 1600 °C/2 h in air. Figure 4 shows SEM micrographs of bi-layer fracture surface of sintered sample.

A good adhesion was established between the layer GDC and YSZ.

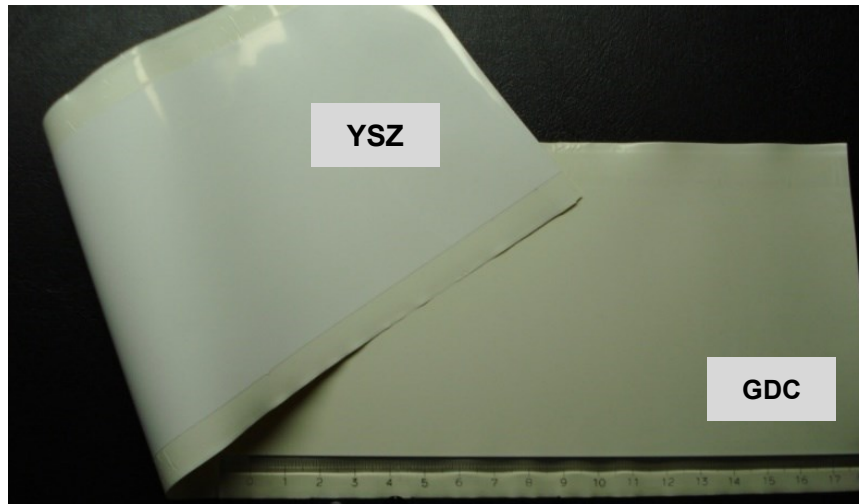


Figure 3: GDC-YSZ bi-layer tape after casting.

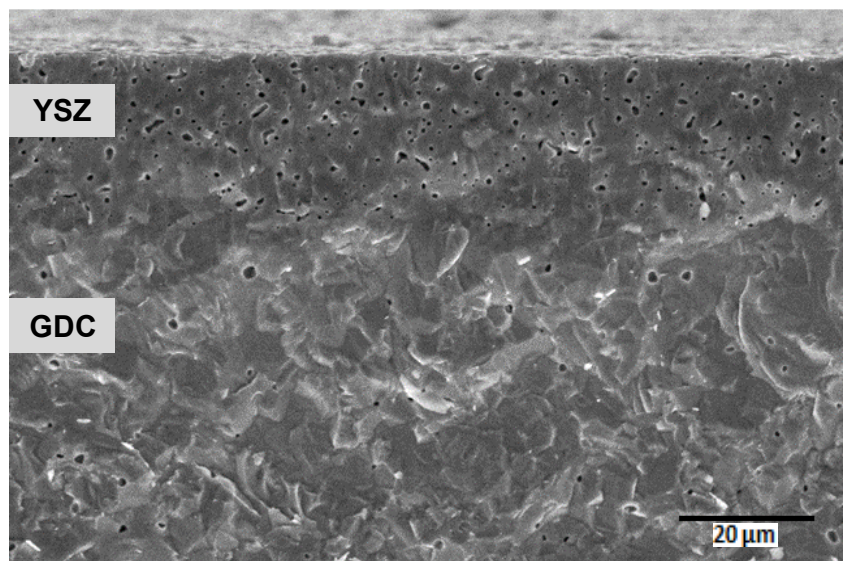


Figure 4: SEM micrographs of fracture surface of the GDC-YSZ bi-layer.

SEM analysis with high magnification of polished and thermally etched surface shows three important features on the interface: i) the presence of secondary phase on the GDC region with about 5.5 μm of thickness, ii) denser layer on the YSZ region just above the secondary phase and iii) YSZ region with large porosity as shown Figure 5. The first two features can be attributed to chemical reaction between GDC and YSZ, as mentioned in the literature [18], generating an interface with peculiar microstructure. The third one can be explained in terms of differential firing shrinkage between GDC and YSZ layers. As mentioned above, single layer of GDC and YSZ showed firing shrinkage of 25 and 30%, respectively, after sintering at 1600 °C/2 h, i.e. there is an important difference between firing shrinkages of materials that compose bi-layer sample. Firing shrinkage of YSZ is larger than GDC, but due to the coupling between two layers, the YSZ layer was prevented from reaching total shrinkage thereby limiting the elimination of porosity. Despite the differential

shrinkage, no cracks were detected in the interface.

A comparison between the fracture surface showed in Figure 4 with polished and thermally etched surface showed in Figure 5, indicates that the GDC layer seems more porous in Figure 5. However, it is easy to note that size and shape of the many holes observed indicate that they were a result of pullout of small grains during the polishing step.

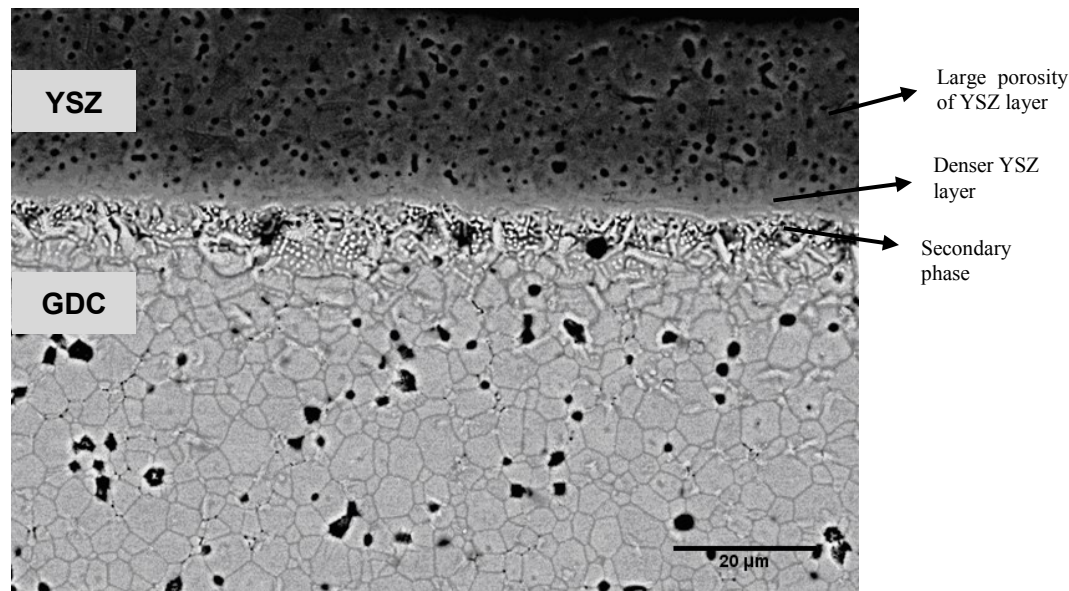


Figure 5: SEM micrographs of polished and etched surface of the GDC-YSZ bi-layer sintered at 1600 °C/2h.

The existence of secondary phase at interface is undesirable because it can reduce the electrical performance of bi-layer electrolyte. Electrical conductivity measurements through impedance spectroscopy of bi-layer samples were done and a comparison with electrical performance of single layer samples was realized.

3.2 Electrical conductivity

The electrical characterization was carried out by impedance spectroscopy. Figure 6 shows the Nyquist plot measured at 400°C for sample GDC-YSZ bi-layer. The numbers marked on the curve correspond to the \log_{10} of frequency. At intermediate frequencies, range there is a well-defined semi-circle with relaxation frequency of 10^3 Hz. At high frequencies range (Figure 6-b) it was observed that exist an overlapping of two or more contributions to total electrical resistivity. The sample used in this measurements is similar to that showed in Figure 5 with one platinum electrode on the YSZ surface and another on the GDC surface. One way to separate the sample contribution and electrode contribution for the impedance spectrum is the comparison between the electrical response of single layer samples, YSZ and GDC, with the response of the bi-layer sample. Figure 7 shows the comparison of all impedance spectra measured at 400°C.

For GDC sample, the semi-circle due to the grain is no longer observed at 400°C. Only the grain boundary contribution, with relaxation frequency of 10^6 Hz, and the electrode response are observed. For YSZ sample it is observed a semi-circle of grain response with relaxation frequency of 10^6 Hz and a small response of grain boundary at 10^4 Hz. The thickness of GDC layer in the bi-layer sample represents approximately 85% of total thickness of sample and comparing GDC-YSZ bi-layer and GDC spectra it is possible identify similarities and to affirm that electrode response appear at 10^3 Hz for both spectra.

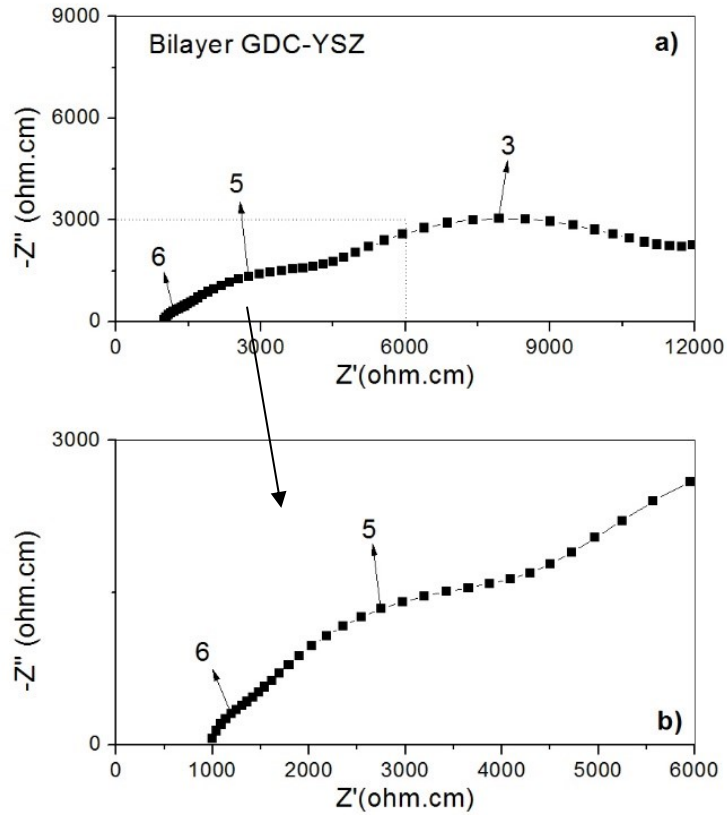


Figure 6: Nyquist plot of GDC-YSZ bi-layer sample measured at 400 °C: (a) complete frequency range; (b) high frequency range.

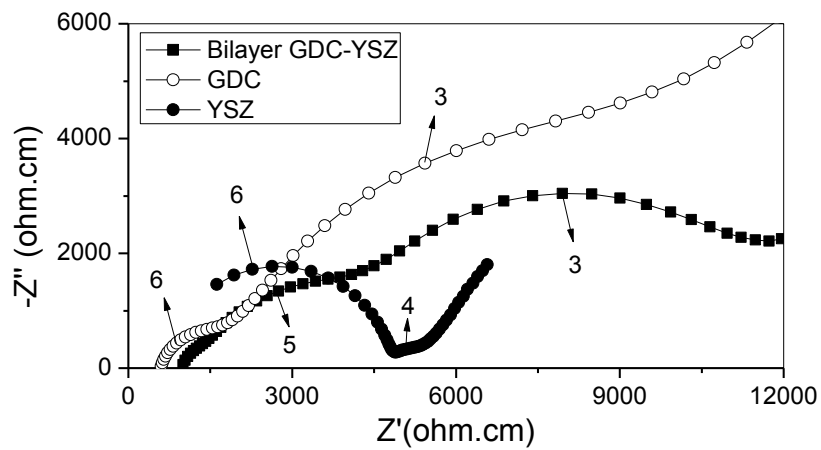


Figure 7: Impedance spectra of GDC and YSZ single layers and GDC-YSZ bi-layer measured at 400°C.

The Arrhenius plots of total electrical conductivity of GDC, YSZ and GDC-YSZ bi-layer samples are shown in Figure 8.

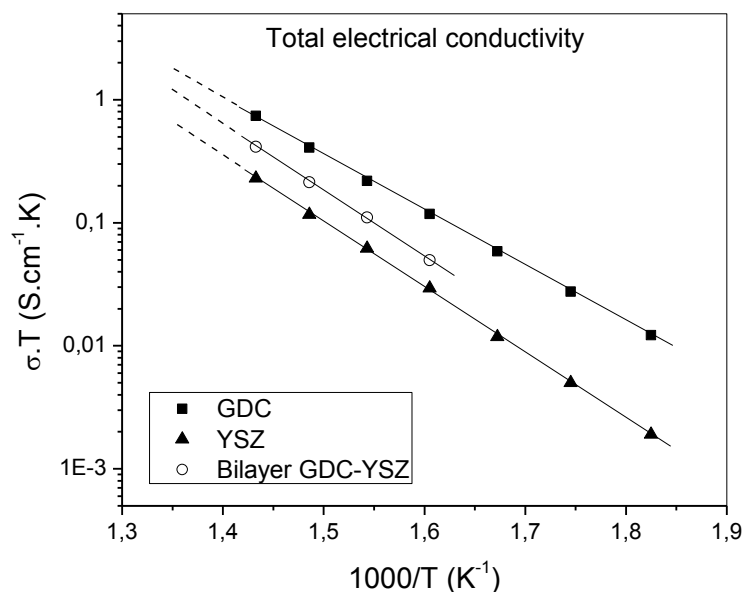


Figure 8: Arrhenius plot of total electrical conductivities for GDC-YSZ bi-layer sample and GDC and YSZ single layer samples sintered at 1600°C/2 h.

Despite the interface between GDC and YSZ, the electrical conductivity of bi-layer sample remained between conductivities of single layer samples. At 350 °C, the electrical conductivity of GDC-YSZ bi-layer was 7.98×10^{-5} S.cm⁻¹, GDC and YSZ single layer was 1.89×10^{-4} S.cm⁻¹ and 4.71×10^{-5} S.cm⁻¹, respectively, that are in agreement with the literature [23]. These results show the advantage of GDC-YSZ bi-layer electrolyte in relation to YSZ single layer.

4. CONCLUSIONS

GDC and YSZ mono-layer and GDC-YSZ bi-layer electrolytes were successfully obtained by the tape casting technique. The interface between the layers showed good adhesion and absence of cracks despite the differential firing shrinkage. Single layer samples of GDC and YSZ showed more densification than corresponding layers at bi-layer sample what can be attributed to the differential firing shrinkages of materials at bi-layer sample. The GDC-YSZ bi-layer sample was more conductive than YSZ single layer. Hence, from an electrical point of view, due to high ionic conductivity, the GDC-YSZ bi-layer electrolyte has a good potential for use in SOFC with advantages over traditional YSZ electrolyte.

5. ACKNOWLEDGEMENT

The authors acknowledge to CAPES and CNPq for the financial support and to Laboratory of Structural Characterization at DEMa/UFSCar for making available its infrastructure.

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