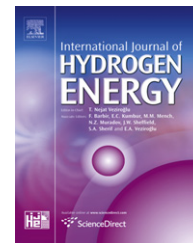




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Optimum cathode configuration for IT-SOFC using $\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-\delta}$ and $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$

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ABSTRACT

Three different cathode configurations using porous layers of $\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-\delta}$ (LBC), LBC–GDC composite in a 50:50 weight ratio, and GDC were prepared and measured by impedance spectroscopy on symmetrical cells. These three cathode configurations were: A) porous GDC + LBC, B) porous GDC + LBC–GDC composite, and C) porous GDC + LBC–GDC composite + LBC. The minimum polarization resistance (R_p) value was obtained with configuration C. The incorporation of both the porous GDC layer and the intermediate layer of LBC–GDC composite, allowed us to solve adherence problems caused by the total expansion mismatch between LBC ($26 \cdot 10^{-6} \text{ K}^{-1}$) and GDC ($12 \cdot 10^{-6} \text{ K}^{-1}$). The R_p values obtained with cell C are comparable to the performance of another cell C prepared with $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF). For example, the R_p values at 600 °C, in air, were 0.071 and 0.065 Ωcm^2 for LBC and BSCF, respectively. These results suggest that configuration C is very promising for developing IT-SOFC cathode with low R_p values.

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1. Introduction

Solid oxide fuel cells (SOFC) are devices that convert chemical energy into electrical energy efficiently and in an environmentally friendly manner. SOFC based on yttria-stabilized zirconia (YSZ), operate at high temperatures (~ 1000 °C), which improves both the ionic conductivity of the solid electrolyte and the electrode reaction kinetic. However, to accelerate the commercialization process of these devices a reduction in cost is required. This would be attained by decreasing the operating temperature to an intermediate range between 500 and 800 °C. However, as temperature decreases a significant increase in the electrode's polarization resistance (R_p) is observed, in particular at the cathode side where the oxygen reduction reaction (ORR) occurs. To achieve

the intermediate temperature range for the SOFC operation, a new cathode material with low R_p must be developed [1]. Among the candidates to be used as cathode materials, cobaltite compounds such as $\text{LnBaCo}_2\text{O}_{5+\delta}$ [2–9], $\text{LnBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ ($\text{Ln} = \text{La, Pr, Nd, Pm, Sm, Gd and Y}$) [10–12], $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) [13–16], and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF) [17–21] are of interest because they exhibit mixed ionic and electronic conductivity.

In the case of the perovskite compounds $\text{LnBaCo}_2\text{O}_{5+\delta}$ ($\text{Ln} = \text{rare earth}$), the highest ionic conductivity and power density values were reported for $\text{Ln} = \text{La}$ [4,5]. The crystal structure of $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3$ is cubic, when the synthesis is performed in air [5,6,8]. Recently, various studies have indicated that $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ shows potential as a candidate for IT-SOFC cathode material [6,8]. The authors have reported R_p

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values of 0.16 and 0.26 Ωcm^2 for $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ and the composite $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ -SDC, respectively [6,8]. Ishihara et al. [2,3] have studied the influence of the Ba content on the cathode performance for the $\text{La}_{1-x}\text{Ba}_x\text{CoO}_{3-\delta}$ system ($0 \leq x \leq 1$) using LSGM as electrolyte. The authors obtained the minimum cathode overpotential at $T = 600^\circ\text{C}$ for the $x = 0.6$ composition.

These cobaltites with the perovskite crystal structure exhibit non negligible oxide ion conductivity, which is sometimes as high as that reported for the electrolyte. However, experimental evidence indicates that if an ionic conductor is mixed with these mixed conductors oxides (MIEC), the cathode performance is improved [7–9,11–13,17,19]. The oxide mixed conductor/ionic conductor ratio is typically expressed in weight percent. The optimum ratio can be strongly affected by the microstructure of each component, the method of preparation, temperature of heat treatment, total expansion and chemical reactivity between the MIEC and the ionic conductor [14,19,22]. For instance, at 600°C , Rp values as low as 0.064, 0.12 and 0.27 Ωcm^2 were obtained for composites prepared with BSCF-SDC (70:30) [13], $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ -GDC (50:50) [11] and LSCF-GDC (40:60) [19], respectively.

Recently, we have found that $x = 0.6$ [23] is the limit of stability for the cubic perovskite phase of the $\text{La}_{1-x}\text{Ba}_x\text{CoO}_{3-\delta}$ system, in air, which concurs with the composition reported by Ishihara et al. [2,3] with the minimum overpotential. Therefore, in this study we have synthesized and then evaluated the cathode performance of the cubic perovskite phase $\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-\delta}$ by impedance spectroscopy measurements using $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ as electrolyte and three different configurations for the electrode of the symmetrical cells. The results are discussed and compared with impedance spectroscopy data obtained with electrodes prepared with BSCF instead of LBC.

2. Experimental

2.1. Sample preparation

$\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-\delta}$ was synthesized by a conventional solid state reaction (SSR) technique. Samples of LBC and BSCF were prepared by mixing commercial powders of La_2O_3 , BaCO_3 , Fe_2O_3 and Co_3O_4 in stoichiometric proportions. The mixtures were ground in an agate mortar and pestle, and then heat treated at 850°C for 20 h, in air. Afterward, samples were ground in an agate mortar once again. LBC and BSFC samples were heat treated at 1150°C and 1100°C , respectively during 24 h, in air, and cooled to room temperature at a rate of $5^\circ\text{C}/\text{min}$. The phase purity of the samples was checked by XRD at room temperature. The obtained products were ball-milled during 30 min using an agate milling media, pressed into pellets and sintered at 1200°C during 4 h, in air, and cooled to room temperature at $5^\circ\text{C}/\text{min}$. The $\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-\delta}$ - $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ composite was prepared mixing commercial GDC powder from Praxair Specialty Ceramics and LBC in a 50:50 weight ratio in agate mortar with pestle in presence of isopropanol.

2.2. Basic characterization

X-Ray diffraction (XRD) data were collected at room temperature with a Philips PW1700 diffractometer using $\text{Cu K}\alpha$ radiation and a graphite monochromator from $2\theta = 20$ – 110° with a counting time of 12 s per 0.02° . The crystal structures of the samples were analyzed by the Rietveld method using the FullProf Program [24].

Reactivity tests were carried out on samples obtained by mixing LBC and GDC or Pt powders in a 50:50 weight ratio and heat treated in air in the temperature range $800 \leq T \leq 1100^\circ\text{C}$ during 6 h. After the heat treatment, the mixture was quenched to room temperature and analyzed by X-ray diffraction.

The total expansions of LBC, LBC-GDC, BSCF and GDC were measured on cylindrical samples ($\varnothing \sim 5.5$ mm, $h \sim 9$ mm) heat treated at 1200, 1000, 1100 and 1350°C , respectively, during 4 h, in air. Thermal expansion measurements were carried out from room temperature to 900°C using a dilatometer LINSEIS L75PT Series. All the samples were heated at 900°C at $5^\circ\text{C}/\text{min}$ and, after a 1 h dwell, were cooled to room temperature and then heated once again at 900°C at a rate of $1^\circ\text{C}/\text{min}$, in air.

Pellets of LBC and LBC-GDC for electrical conductivity measurements ($\varnothing \sim 14$ mm, thick ~ 1.2 mm) were heat treated at 1100 and 1000°C respectively, during 4 h, in air, and then cooled to room temperature at a rate of $5^\circ\text{C}/\text{min}$. The variations of the electrical conductivity with temperature were measured with a four probe dc method using the van der Pauw technique [25]. Measurements were performed in the temperature range $25 \leq T \leq 900^\circ\text{C}$ in static air during a heating/cooling cycle with a rate of 1°C min^{-1} .

2.3. Electrochemical characterization

The polarization resistance of the three cathode configurations was investigated in air by impedance spectroscopy measurements on symmetrical cells using disks of GDC as electrolyte. Both sides of the electrolytes were polished before spraying the inks to form the electrode. The inks were prepared mixing the corresponding ceramic powders with ethanol, α -terpineol, polyvinyl butyral, and polyvinyl pyrrolidone in a 40:40:27:2:1 ratio. Inks containing LBC, LBC-GDC composite and GDC were sprayed on dense GDC to form three different cathode configurations: A) a porous layer of GDC plus a single porous layer of LBC, B) a porous layer of GDC plus a porous composite layer of LBC-GDC in a 50:50 weight ratio and, C) a porous layer of GDC plus a porous composite layer of LBC-GDC and finally a porous layer of LBC. After deposition, the porous GDC layer was heat treated at 1300°C during 1 h, while the LBC-GDC and LBC porous layers were heat treated at 1050°C . On the other hand, the BSCF and BSCF-GDC composite layers were calcined at 950°C [15].

The impedance spectroscopy measurements were performed in a temperature range between 400 and 700°C in static air by steps of 50°C . The data acquisition was performed by an Autolab system PGSTAT-30 coupled to a module FRA2 in a frequency range of $10^{-3} \leq f \leq 1$ MHz. An ac signal of 50 mV was applied to the cell, under zero DC polarization. Platinum grids, slightly pressed on the porous electrodes using a mullite

tube, were used as current collectors. Impedance diagrams were analyzed using Z-view2 software [26].

2.4. Microstructure

The microstructure and thickness of the porous layers and interfaces were characterized by scanning electron microscopy (SEM) using a Philips 515 and a SEM-FEG FEI Nova Nano Sem 230 microscopes.

3. Results and discussion

3.1. XRD data and chemical compatibility

The analysis of the XRD data indicated that the $\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-\delta}$ sample was single phase and its crystal structure was cubic with lattice parameter $a = 3.9168$ (5) Å. The refinement of the crystal structure was performed using the cubic space group $Pm\bar{3}m$, with La/Ba at position (0,0,0)(2a), Co at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (1b), and oxygen at $(0, \frac{1}{2}, \frac{1}{2})$ (3c). Similarly, the crystal structure of the BSCF sample was also refined using the cubic space group $Pm\bar{3}m$ resulting in the lattice parameter $a = 3.9975$ (5) Å [16,27].

To investigate the chemical reactivity between the cathode and the electrolyte or the Pt current collectors, mixtures of LBC with GDC and LBC with Pt in a 50:50 weight ratio were heat treated at 800–1100 °C during 6 h, in air. Fig. 1 shows the XRD patterns of the mixture LBC + GDC at 25 °C and after the heat treatments. At $T = 1000$ °C, all the reflections could be assigned to LBC and GDC, which indicates that LBC is chemically compatible with GDC below 1000 °C. On the other hand, at $T = 1100$ °C, additional peaks corresponding to the formation of BaCeO_3 [28] and CoO can be observed. Due to the formation of BaCeO_3 , the Ba content of the LBC phase tends to decrease and the Gd content of the GDC phase tends to increase. This behavior is revealed by the shift of the LBC reflections to higher angles and of the GDC peaks to lower angles. The presence of BaCeO_3 was also noticed by Kim et al. [10] and Gu et al. [8] with the mixtures of $\text{GdBaCo}_2\text{O}_{5+\delta} + \text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ and $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta} + \text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ heat treated at 1100 °C, respectively.

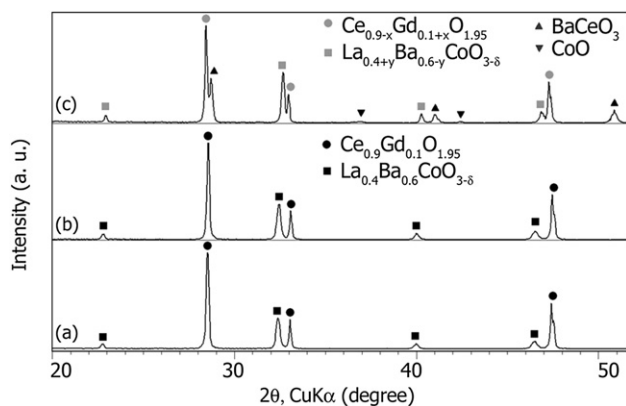


Fig. 1 – XRD patterns of the LBC and GDC mixtures at (a) 25 °C and (b) calcined at 1000 °C and (c) 1100 °C in air.

No chemical reaction was found between LBC and Pt in the temperature range 900–1100 °C. Chemical compatibility of BSCF with GDC and SDC has been already studied [13,15]. Nevertheless, the stability of the cathode material phase was checked by XRD for the three cell configurations before and after impedance measurements. Our observations indicate that the LBC cubic phase remains stable during these measurements.

3.2. Total expansion measurements

Fig. 2 shows the $\Delta L/L_0$ vs T curves, where ΔL is the length change and L_0 the initial length of the sample, for LBC, the LBC–GDC composite, and GDC. The total expansion values obtained for the temperature range $30 \leq T \leq 900$ °C were $26 \cdot 10^{-6} \text{ K}^{-1}$ and $17 \cdot 10^{-6} \text{ K}^{-1}$ for LBC and LBC–GDC, respectively. In addition, the total expansion values obtained for GDC and BSCF were $12 \cdot 10^{-6} \text{ K}^{-1}$ and $18 \cdot 10^{-6} \text{ K}^{-1}$, respectively, which are similar to the values reported in the literature [27]. Clearly, the incorporation of GDC to form the composite LBC–GDC led to a significant reduction of the total expansion with respect to the value obtained for LBC alone. Similar behavior was found for other composites prepared with the cobaltites $\text{LnBaCo}_2\text{O}_{5+\delta}$ or $\text{LnBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{and Gd}$) and GDC or SDC [7–9,11,12]. The $\Delta L/L_0$ vs T curve for LBC exhibits a slope change above $T \sim 400$ °C. For these oxides, the expansion at the low temperature range (30–400 °C) is related to the thermal expansion, while the expansion at the high temperature range ($T > 400$ °C) is caused by both thermal and chemical contributions, simultaneously, the latter being related to the expansion caused by the removal of oxygen atoms from the crystal structure [4,27]. The $\Delta L/L_0$ vs T curve for the LBC–GDC composite, shows the presence of hysteresis during the cooling/heating cycle. This behavior was confirmed on pellets prepared at temperatures as low as 900 °C.

3.3. Electrical conductivity

Fig. 3 shows the variations of the electrical conductivity (σ) with temperature for LBC and LBC–GDC composite between

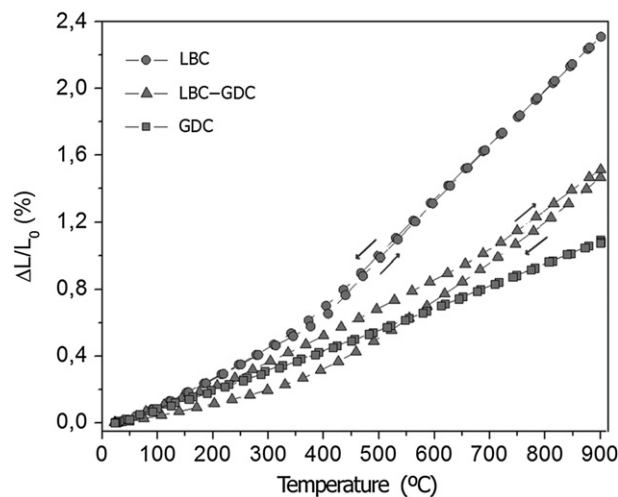


Fig. 2 – Thermal expansion curves for LBC, GDC, and LBC–GDC composite in the temperature range of 30–900 °C in air.

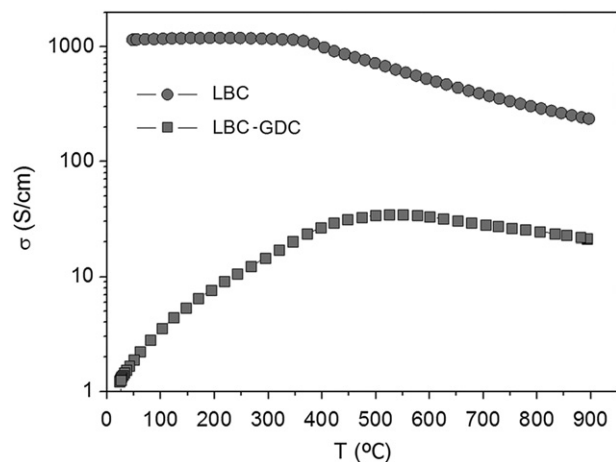


Fig. 3 – Variations of the electrical conductivity with temperature for LBC and LBC–GDC composite in the range $20 \leq T \leq 900$ °C, in air.

30 and 900 °C, in air. The mixing of GDC and LBC to form the composite reduces the σ values in the whole temperature range, compared to LBC. The difference is remarkable at low temperatures, where σ decreases almost three orders of magnitude, for instance, at 100 °C, it changes from 1200 S cm^{-1} for LBC to 1 S cm^{-1} for the composite. As the temperature increases, the electrical conductivity of LBC decreases, reaching a value of $\sigma = 150 \text{ S cm}^{-1}$ at 900 °C. This behavior is mainly due to the formation of oxygen vacancies above $T \sim 400$ °C, which is accompanied by the reduction of the high-valence-state Co^{4+} to Co^{3+} and thereby, the diminution of the hole concentration [4]. Simultaneously, the electrical conductivity of the composite material increases, reducing the difference observed at low temperature. Similar results were observed for $\text{LnBaCo}_2\text{O}_{5+\delta}$ /SDC composites ($\text{Ln} = \text{Pr}, \text{Gd}$) [7,9].

3.4. Cell configuration

During the preparation of the cells, adherence difficulties were found between LBC and dense GDC due to the large difference between the total expansion of $\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-\delta}$ and GDC. In order to overcome this problem, the temperature of the heat treatment, for the cathode, had to be increased, however, in this case, chemical reactivity between LBC and GDC was observed. The solution to this inconvenient was the introduction of a porous layer of GDC, approximately $20 \mu\text{m}$ thick, between the electrode and the dense electrolyte. Those symmetrical cells prepared with the extra GDC porous layer showed very good adhesion due likely to the rough surface of the porous GDC layer, which increases the number of interlocked points between electrode and electrolyte. In addition, an intermediate layer of composite LBC–GDC in a weight ratio of 50:50 was incorporated on the porous GDC in order to reduce the expansion mismatch between LBC and GDC. In Fig. 4, a schematic of the three symmetrical cells used during impedance spectroscopy measurements is shown. These configurations are:

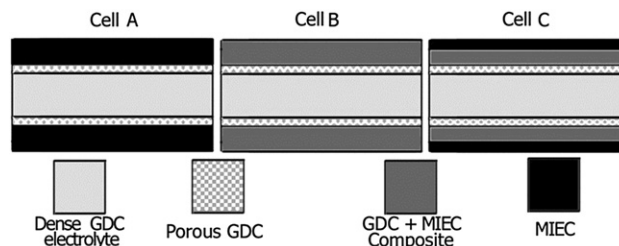


Fig. 4 – Schematic for the three cell configurations.

- porous LBC/porous GDC/dense GDC/porous GDC/porous LBC
- porous LBC–GDC composite/porous GDC/dense GDC/porous GDC/porous LBC–GDC composite.
- porous LBC/porous LBC–GDC composite/porous GDC/dense GDC/porous GDC/porous LBC–GDC composite/porous LBC.

The arrangement of the layers that form cell C is usually known as graded cathode and has been used to reduce the expansion differences between the cobaltites and the electrolytes yttria-stabilized zirconia (YSZ) [20,21] or $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.8}$ (LSGM) [4,10]. The porous GDC layer is usually introduced between YSZ and the cobaltite to avoid the chemical reaction at the cobaltite/YSZ interface.

Fig. 5 shows SEM micrographs of the top-view of the electrode and the cross-section of two cells with configuration C using LBC and BSCF. SEM images show good bonding, continuous contact at the interfaces and no delamination. The size of LBC and BSCF ceramic grains is larger than $1 \mu\text{m}$, while the size of the GDC particles forming the composite is between 0.1 and $0.5 \mu\text{m}$. Noteworthy, the GDC particles are located on the surface of the LBC ceramic grains, as is clearly observed in Fig. 5c. The thicknesses of the GDC, GDC + LBC and LBC porous layers were estimated, from SEM observations, to be approximately 20 , 40 and $25 \mu\text{m}$, respectively.

3.5. Electrochemical characterization

It is well known that the use of composites increases the performance of the cathode. One of the most important parameters that affect these electrodes is the weight ratio MIEC/electrolyte, whose optimum value may be different for composites with different composition or even for composites with the same composition but different microstructure, which is usually controlled with the preparation method [19]. Thus, it is possible to find previous studies on composites electrochemical performance using wt % ratios MIEC/electrolyte varying from 70:30 to 30:70 [7–9,11–13,17,19,22]. In particular, Gu et al. [8] have obtained an optimum ratio of 50:50 wt% for the composite $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}\text{–Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ containing $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ prepared by the solid state reaction method. Similarly, Kim et al. [12] also found that the optimal ratio for the composite $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}\text{–GDC}$ with the cobaltite $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ prepared by the solid state reaction method was 50:50. Based on these results, the

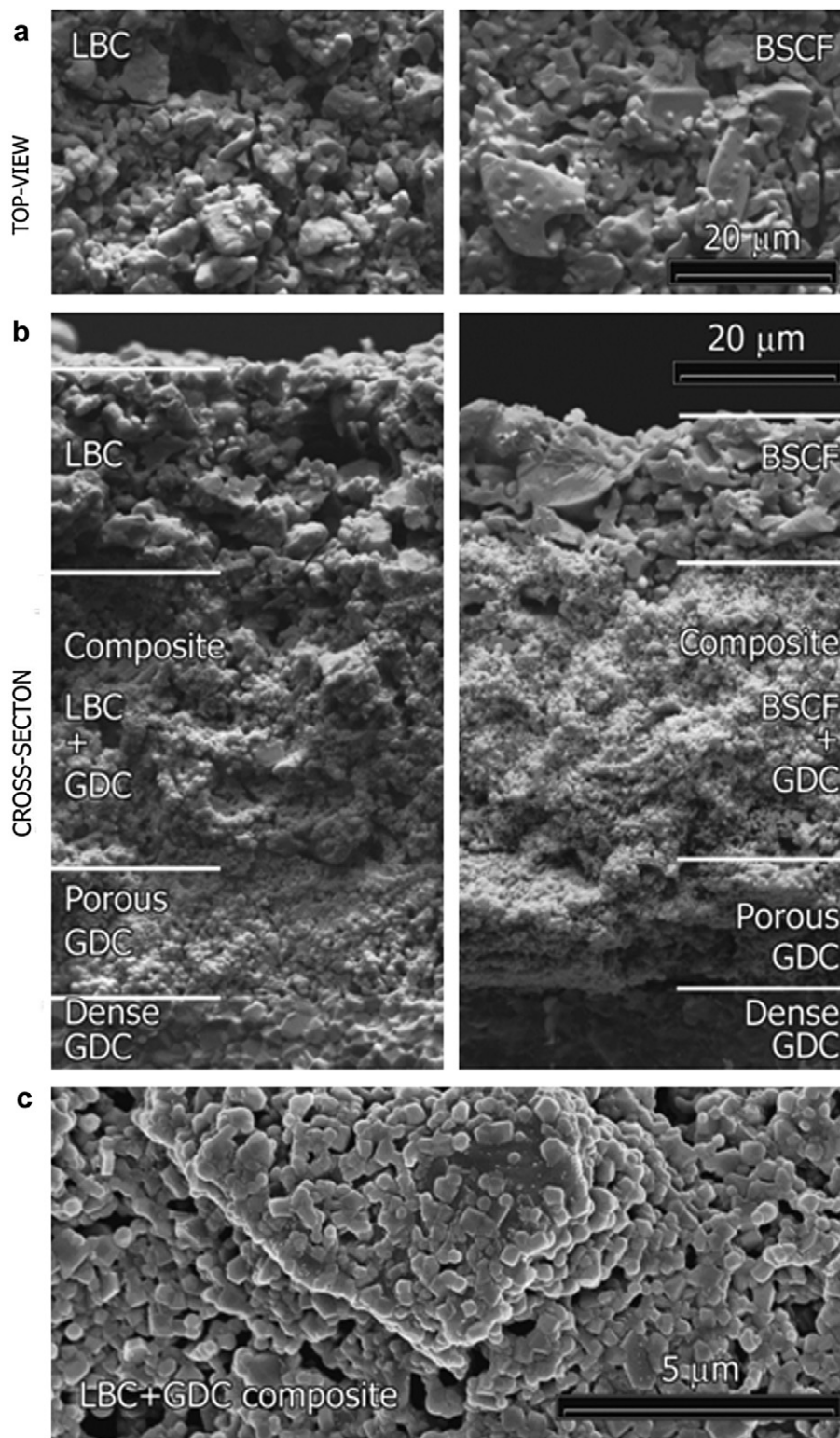


Fig. 5 – SEM micrographs of cell C prepared with LBC and BSCF: a) Top-view of the electrode for both cells. b) SEM micrograph of the cross-section of both cells C. c) SEM micrograph of the LBC–GDC composite.

wt% ratio 50:50 was chosen in the present work for the LBC–GDC composite.

Fig. 6 shows the impedance diagrams measured at 600 °C, in air, for the three cells prepared with LBC. The R_p values

obtained for each electrode were 0.140, 0.125 and 0.071 $\Omega \text{ cm}^2$ for cells A, B and C, respectively, revealing that configuration C provides the lower R_p value for the temperature range $400 \leq T \leq 700$ °C. For comparison, we have tested a cell with

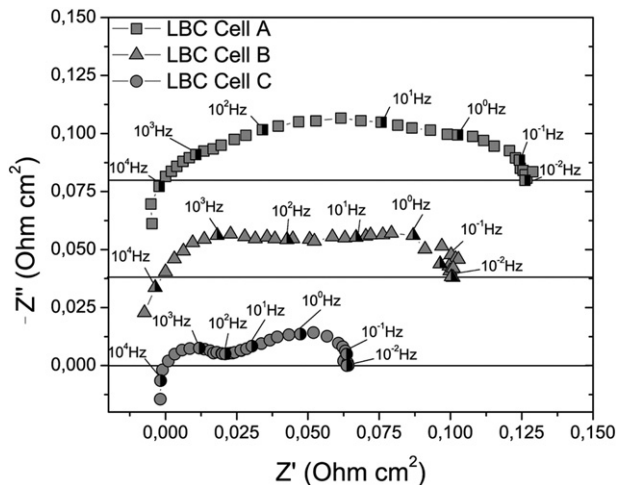


Fig. 6 – Impedance arcs measured, in air, at 600 °C for cells A, B and C prepared with LBC as oxide mixed conductor. Ohmic resistance values were eliminated from the graph for better visualization of the electrode polarization resistance.

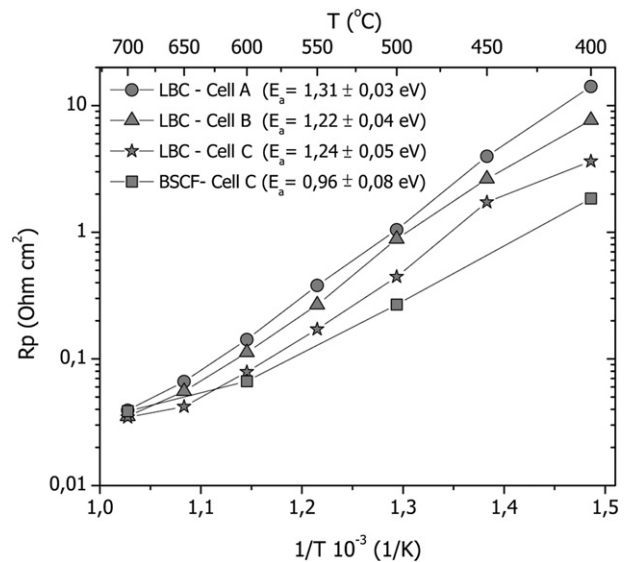


Fig. 7 – Arrhenius plots of the polarization resistance of cells A, B and C prepared with LBC and cell C prepared with BSCF.

configuration C, using BSCF instead of LBC [1,13] as MIEC. In this case, a polarization resistance value of 0.065 Ωcm^2 , at 600 °C, was obtained.

These results indicate that the incorporation of the composite LBC–GDC in the cathode improves the performance of the cell. The composite LBC–GDC has some characteristics in common with the composite BSCF–SDC used by Wang et al. [13]. For example, like BSCF, $\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-\delta}$ has cubic symmetry and oxide ion conductivity higher than the double perovskites $\text{LnBaCo}_2\text{O}_{5+\delta}$ ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}$) [5], whose crystal structure is not cubic. Also, the microstructure of the composite (Fig. 5c) shows that small GDC particles of 0.1–0.5 μm in size are attached all over the surface of bigger LBC ceramic grains ($>1\ \mu\text{m}$). However, no evidence of chemical reaction between LBC and GDC could be detected to fully support the model suggested by Wang et al. [13], although more research is needed either to confirm or rule out this option.

Finally, we think that the porous LBC top layer in cell C improves the contact of the cathode with the current collector (Pt mesh). Fig. 3 shows the variations of the electrical conductivity at the temperature range $20 \leq T \leq 900\ \text{°C}$ for LBC and the composite LBC–GDC, in air. Clearly, the electric conductivity of the composite material results more than one order of magnitude lower than that obtained for LBC. The effect of the current collector and the preparation method on the cathode performance was recently studied by Guo et al. [14]. They showed that a LaCoO_3 layer deposited on the BSCF cathode as current collector reduces R_p , in agreement with our results.

Fig. 7 shows the Arrhenius plots of the polarization resistance for cells with configuration A, B and C and BSCF with configuration C. The activation energy (E_a) values calculated from the R_p vs. $1/T$ data were 1.31, 1.22 and 1.24 eV for cells A, B and C, respectively. Systematically, the lowest R_p values

were obtained with cell C prepared with LBC and BSCF. The R_p values at 600 °C, in air, were 0.071 and 0.0658 Ωcm^2 for cell C with LBC and BSCF, respectively, which is low for cathodes produced by SSR [13,18]. Impedance measurements as a function of time show that the R_p value obtained with the cell configuration C prepared with LBC slightly increases with time. R_p increased about ~ 1.3 times its initial value after 2 days. Similar behavior was also observed by Amin et al. [6] for electrodes prepared with $\text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$. On the other hand, no drift with time was observed for the R_p value of the cell C prepared with BSCF. The low polarization resistance values obtained with the cell configuration C are promising for IT-SOFC applications.

4. Conclusions

The cubic perovskite $\text{La}_{0.4}\text{Ba}_{0.6}\text{CoO}_{3-\delta}$ (LBC) was used to test the performance of three different electrodes configurations through impedance spectroscopy measurements on symmetrical cells. Systematically, the lowest polarization resistance values were found with the graded electrode consisting of: porous LBC/LBC–GDC composite/porous GDC/dense GDC/porous GDC/LBC–GDC composite/porous LBC. The GDC porous layer was crucial to get good adherence between the electrode and the electrolyte due to the rough surface of the porous GDC which increases the contact points for adhesion resulting in better interlocking. In addition, the intermediate layer of the 50% wt LBC–GDC composite helped to reduce the difference in the expansion coefficients between LBC and GDC leading to a better adherence of the electrode and also a higher surface area for oxygen reduction. Finally the top layer of LBC, whose electrical conductivity is higher than that of the composite layer improves the current collection at the electrode. R_p values as low as 0.071 and

0.065 Ωcm^2 were measured with the cell configuration C for LBC and BSCF at 600 °C, in air. These results are promising for IT-SOFC applications.

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REFERENCES

- [1] Zhou W, Ran R, Shao Z. Progress in understanding and development of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ -based cathodes for intermediate-temperature solid-oxide fuel cells: a review. *J Power Sources* 2009;192:231–46.
- [2] Ishihara T, Fukui S, Nishiguchi H, Takita Y. La-doped BaCoO_3 as a cathode for intermediate temperature solid oxide fuel cells using a LaGaO_3 base electrolyte. *J Electrochem Soc* 2002; 149:A823–8.
- [3] Ishihara T, Fukui S, Nishiguchi H, Takita Y. Mixed electronic-oxide ionic conductor of BaCoO_3 doped with La for cathode of intermediate-temperature-operating solid oxide fuel cell. *Solid State Ionics* 2002;15-153:609–13.
- [4] Kim JH, Manthiram A. $\text{LnBaCo}_2\text{O}_{5+\delta}$ oxides as cathodes for intermediate-temperature solid oxide fuel cells. *J Electrochem Soc* 2008;155:B385–90.
- [5] Kim J-H, Mogni L, Prado F, Caneiro A, Alonso JA, Manthiram A. High temperature crystal chemistry and oxygen permeation properties of the mixed ionic-electronic conductors $\text{LnBaCo}_2\text{O}_{5+\delta}$ (Ln = Lanthanide). *J Electrochem Soc* 2009;156:B1376–82.
- [6] Amin R, Karan K. Characterization of $\text{LaBaCoO}_{3-\delta}$ as a SOFC cathode material. *J Electrochem Soc* 2010;157:B285–91.
- [7] Chen D, Ran R, Shao Z. Assessment of $\text{PrBaCo}_2\text{O}_{5+\delta}+\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ composites prepared by physical mixing as electrodes of solid oxide fuel cells. *J Power Sources* 2010;195:7187–95.
- [8] Gu H, Chen H, Gao L, Guo L. Electrochemical properties of $\text{LaBaCo}_2\text{O}_{5+\delta}-\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ composite cathodes for intermediate-temperature solid oxide fuel cells. *Electrochim Acta* 2009;54:7094–8.
- [9] Li N, Wei B, Lü Z, Huang X, Su W. $\text{GdBaCo}_2\text{O}_{5+\delta}-\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ composite cathodes for intermediate temperature SOFCs. *J Alloys Compd* 2011;509:3651–5.
- [10] Kim J-H, Prado F, Manthiram A. Characterization of $\text{GdBa}_{1-x}\text{Sr}_x\text{Co}_2\text{O}_{5+\delta}$ ($0 < x < 1$) double perovskite as cathode for solid oxide fuel cells. *J Electrochem Soc* 2008;155:B1023–8.
- [11] Kim JH, Cassidy M, Irvine JTS, Bae J. Advanced electrochemical properties of $\text{LnBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ (Ln = Pr, Sm and Gd) as cathode materials for IT-SOFC. *J Electrochem Soc* 2009;156:B682–9.
- [12] Kim JH, Cassidy M, Irvine JTS, Bae J. Electrochemical investigation of composite cathodes with $\text{SmBa}_{0.5}\text{Sr}_{0.5}\text{Co}_2\text{O}_{5+\delta}$ cathodes for intermediate temperature-operating solid oxide fuel cell. *Chem Mater* 2010;22:883–92.
- [13] Wang K, Ran R, Zhou W, Gu H, Shao Z, Ahn J. Properties and performance of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}+\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ composite cathode. *J Power Sources* 2008;179:60–8.
- [14] Guo Y, Zhou Y, Chen D, Shi H, Ran R, Shao Z. Significant impact of the current collection material and method on the performance of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ electrodes in solid oxide fuel cells. *J Power Sources* 2011;196:5511–9.
- [15] Dua Z, Yang M, Yan A, Hou Z, Dong Y, Chong Y, et al. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ as a cathode for IT-SOFCs with a GDC interlayer. *J Power Sources* 2006;160:57–64.
- [16] Zhao H, Shen W, Zhu Z, Li X, Wang Z. Preparation and properties of $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ cathode material for intermediate temperature solid oxide fuel cells. *J Power Sources* 2008;182:503–9.
- [17] Dusastre V, Kilner JA. Optimisation of composite cathodes for intermediate temperature SOFC applications. *SolidState Ionics* 1999;126:163–74.
- [18] Baqué L, Caneiro A, Moreno MS, Serquis A. High performance nanostructured IT-SOFC cathodes prepared by novel chemical method. *Electrochem Comm* 2008;10:1905–8.
- [19] Leng Y, Chan SH, Liu Q. Development of LSCF–GDC composite cathodes for low-temperature solid oxide fuel cells with thin film GDC electrolyte. *Int J Hydrogen Energy* 2008;33:3808–17.
- [20] Jung HG, Sun YKS, Jung HY, Park JS, Kim HR, Kim GH, et al. Investigation of anode-supported SOFC with cobalt-containing cathode and GDC interlayer. *SolidState Ionic* 2008;179:1535–9.
- [21] Xu X, Xia C, Xiao G, Peng D. Fabrication and performance of functionally graded cathodes for IT-SOFCs based on doped ceria electrolytes. *SolidState Ionics* 2005;176:1513–20.
- [22] Kao WX, Lee MC, Chang YC, Lin TN, Wang CH, Chang JC. Fabricating and evaluation of the electrochemical performance of the anode-supported solid oxide fuel cell with the composite cathode of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ -Gadolinia-doped ceria oxide/ $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$. *J Power Sources* 2010; 195:6468–72.
- [23] Setevich C, Mogni L, Caneiro A, Prado F. Characterization of the $\text{La}_{1-x}\text{Ba}_x\text{CoO}_{3-\delta}$ ($0 \leq x \leq 1$) system as cathode material for IT-SOFC. *J Electrochem Soc* 2012;159:B73–80.
- [24] Rodríguez-Carvajal J. Fullprof: a program for Rietveld refinement and profile matching analysis of complex powder diffraction patterns, Laboratoire Léon Brillouin (CEA-CNRS).
- [25] Montgomery HC. Method for measuring electrical resistivity of anisotropic materials. *J Appl Phys* 1971;42:2971–5.
- [26] Johnson D. Zview version 2.9b. Copyright. Scribner Associates, Inc; 1990–2005.
- [27] Wei B, Lu Z, Huang X, Miao J, Sha X, Xin X, et al. Crystal structure, thermal expansion and electrical conductivity of perovskite oxides $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ($0.3 < x < 0.7$). *J Euro Ceram Soc* 2006;26:2827–32.
- [28] Knight KS, Bonanos N. A high-resolution neutron powder diffraction study of neodymium doping in barium cerate. *SolidState Ionic* 1995;77:189–94.