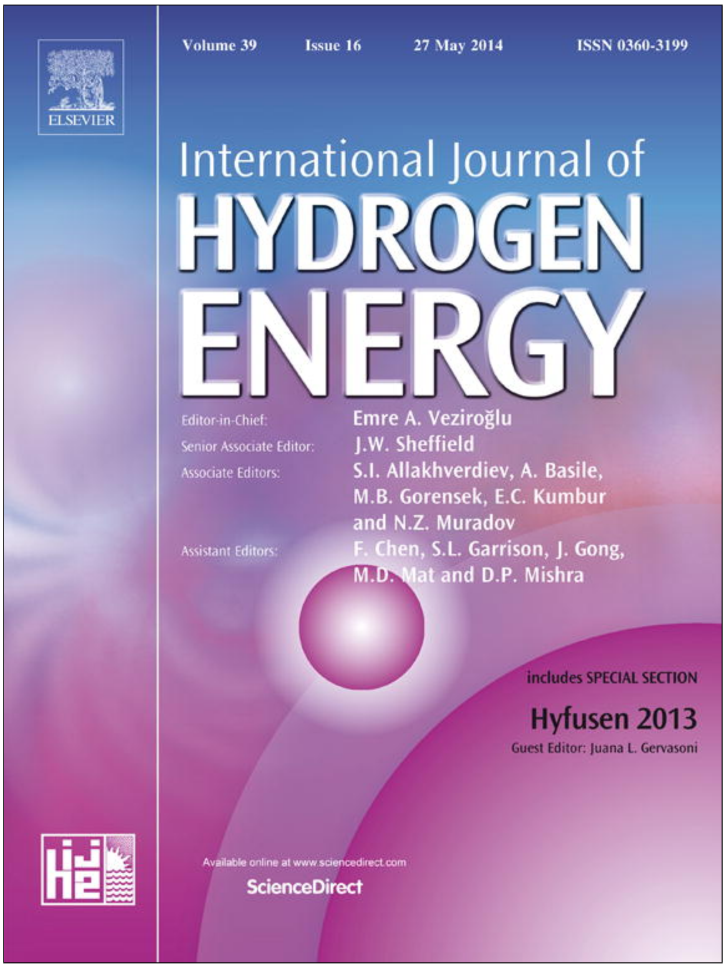
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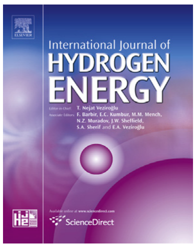

Effects of the electrode configuration, phase relationship and microstructure on the polarization resistance of $La_{0.3}Ba_{0.7}CoO_{3-\delta}$ as cathode material for IT-SOFC

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ABSTRACT

The polarization resistance of $La_{0.3}Ba_{0.7}CoO_{3-\delta}$ (LBC7) as cathode material was studied by impedance spectroscopy measurements in the temperature range of $450 \le T \le 750$ °C, in air, on samples prepared by the solid state reaction (SSR) method and a wet chemical (WC) route, using symmetrical cells with single-layer and graded composition electrodes. While the LBC7 sample prepared by the SSR method and cooled at a rate of 10 °C/min turned out to be single phase with cubic symmetry, the sample prepared by the WC route is a mixture of the cubic phase and the 2H hexagonal phase. The lowest polarization resistance at 600 °C, $Rp \sim 0.06\ \Omega\ cm^2$, was obtained for the graded composition electrodes. Our results suggest that the electrode configuration is a key factor in order to reduce the polarization resistance of the LBC7 electrode material.

1. Introduction

The development of intermediate solid oxide fuel cells (IT-SOFC) requires the finding of an appropriate assemblage of materials able to reduce the working temperature of this electrochemical device at the temperature range $500 \le T \le 800$ °C. In particular, perovskite oxides exhibiting oxide ion and electronic conductivity, simultaneously, have been proposed as cathode materials. These compounds reduce the polarization resistance values of the cathode by increasing the area where the oxygen reduction reaction takes place from the triple phase boundary (gas-electrode-electrolyte) to the whole surface of the electrode [1,2]. Among the perovskite oxides, the solid solutions $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$, $La_{1-x}Ba_xCo_{1-y}Fe_yO_{3-\delta}$ and $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ [2–5] have been extensively investigated as cathode materials due to their low polarization resistance values. In particular, Shao and Haile [6] have reported a very promising performance of the cubic perovskite $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) in a cell prepared with $Ce_{0.9}Sm_{0.1}O_{2-\delta}$ (SDC) as electrolyte ($Rp = 0.05\ \Omega\ cm^2$ at 600 °C). However, several studies [7,8] have

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shown that the cubic phase of the $Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O_{3-\delta}$ compounds is metastable, transforming to a mixture of the cubic and a hexagonal phase when annealed at temperatures below 900 °C during several days. More recently, we have reported a good performance of the $La_{1-x}Ba_xCoO_{3-\delta}$ compounds [3] as cathode materials obtaining the best values for $x = 0.7$ ($Rp = 0.065\ \Omega\ cm^2$ at 600 °C). Like BSCF, the crystal structure of this compound is initially cubic and then transforms to a mixture of phases when heat treated below 900 °C during long periods of time, which could be an issue for the long term cathode behavior while the crystal structure of the electrode material is out of equilibrium at a given temperature.

In addition to the phase composition, the performance of the cathode material may be affected by other causes such as the microstructure and the chosen configuration. The microstructure of the cathode is related with the surface area where the oxygen reduction reaction takes place [9], while the use of composites or graded composition electrodes tend to decrease the polarization resistance [10,11]. Aiming to investigate the effects of the secondary phase, the microstructure and the configuration of the electrode on the polarization resistance of cathodes prepared with GDC as electrolyte and $La_{0.3}Ba_{0.7}CoO_{3-\delta}$ (LBC7) as electrode, we have prepared three cells varying the synthesis method of the cathode material LBC7 and the configuration of the electrode. We have found that the configuration of the electrode, in this case consisting of three layers: porous GDC/composite GDC + LBC7/porous LBC7, is the most relevant in order to obtain low polarization resistance values.

2. Experimental

The $La_{0.3}Ba_{0.7}CoO_{3-\delta}$ (LBC7) sample was synthesized using both the solid-state reaction (SSR) and a wet chemical (WC) method. For SSR, required amounts of La_2O_3, previously dried overnight at 1000 °C, in air, $BaCO_3$ and Co_3O_4 were mixed and ground with a mortar and pestle and heat treated at 850 °C for 8 h, in air. Subsequently, the powders were ball milled during 15 min using an agate milling media, pressed into pellets and sintered at 1100 °C for 24 h, in air. Two different cooling rates, 10 °C/min and 1 °C/min, were used to cool down the samples to room temperature. Afterwards, the sample cooled at 10 °C/min was annealed at 750 °C for 10 days. For the WC method, stoichiometric amounts of La_2O_3, $BaCO_3$ and $Co(CH_3COO)_2 .4H_2O$ were dissolved in acetic acid. With the addition of water and small amounts of hydrogen peroxide, the mixture was refluxed at $T \sim 80$ °C until a clear blue solution was obtained. Then the solvents were evaporated until a dark gel was formed. This gel was fired at 400 °C for 2 h and then heat treated at 750 °C for 24 h, in air.

X-Ray diffraction (XRD) data were collected at room temperature with a Philips PW1700 diffractometer using Cu Kα radiation and a graphite monochromator from $2\theta = 10$ to 80° with a counting time of 10 s per 0.02°. The crystal structures of the LBC7 samples were analyzed by the Rietveld method using the FullProf Program [12].

The polarization resistance of the LBC7 electrodes was studied by impedance spectroscopy measurements on electrochemical cells using GDC as electrolyte and a symmetrical configuration, in air. Commercial $Ce_{0.9}Gd_{0.1}O_{1.95}$ powder from Praxair Specialty Ceramics was pressed into 12.5 mm diameter disks, applying a uniaxial pressure of 500 kg/cm², and calcined at 1350 °C during 4 h, in air. After sintering, the electrolyte disks were approximately 9.8 mm in diameter and around 0.5 mm thick. Both sides of the electrolytes were cleaned with solvent before spraying the electrodes. The inks for electrode deposition were prepared mixing the corresponding ceramic powders with ethanol, α-terpineol, polyvinyl butyral, and polyvinyl pyrridone in appropriate ratio. Two electrode configurations were tested using symmetrical cells. One electrode configuration consist of a single layer of porous LBC7 obtained by the WC route, sprayed onto dense GDC electrolite and heat treated at 750 °C for 1 h, in air. The other was a graded composition electrode formed by three layers: one of porous GDC sprayed on the dense electrolyte, and then heat treated at 1300 °C during 1 h, one layer of the composite LBC7+GDC in a weight ratio of 50:50 also sprayed onto the previous layer, and finally a pure LBC7 layer sprayed onto the composite layer. The triple-layer electrode cells were

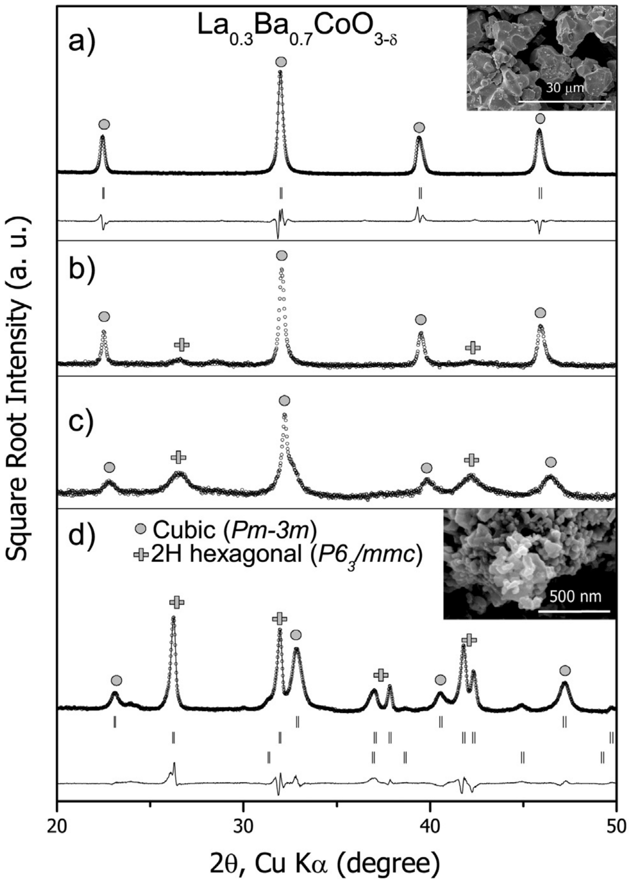

Fig. 1 – XRD patterns of LBC7 samples prepared by: a) SSR method, cooled at a rate of 10 °C/min; b) SSR method, cooled at a rate of 1 °C/min cooling rate; c) SSR method, cooled at a rate of 10 °C/min, plus a heat treatment at 750 °C for 10 days; d) WC route. The experimental data (○), calculate profile (—), peak position (|) and difference between experimental and calculated profiles obtained from Rietveld analysis, are also included. SEM micrographs show the microstructure of the samples prepared by the SSR and WC methods.

fabricated using LBC7 material prepared by the SSR method and the WC route and heat treated at 1000 °C and 750 °C, respectively, for 1 h, in air.

The impedance spectroscopy measurements were performed at the temperature range $400 \leq T \leq 750$ °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 1 MHz and 10^{-3} Hz. An ac signal of 50 mV was applied to the cell, under zero DC polarization. Gold grids, slightly pressed on the porous electrodes using a mullite tube, were used as current collectors. Impedance diagrams were analyzed using Z-view2 software [13].

The microstructure and thickness of the porous layers and interfaces were characterized by scanning electron microscopy (SEM) using a Jeol microscope JSM-6010LA.

3. Results and discussion

The XRD data of the LBC7 materials prepared by the SSR method and the WC route were analyzed using the Rietveld method. The crystal structure of the SSR sample cooled at a rate of 10 °C/min was refined with a single cubic perovskite phase (SG *Pm*-3*m*), whereas the crystal structure of the WC sample was refined using a mixture of phases of a 2H hexagonal phase (SG P $6_3/mmc$), a cubic perovskite (SG *Pm*-3*m*) and a small amount of CoO. The lattice parameter of the cubic phase decreases from $a = 3.954$ Å for the SSR sample, to $a = 3.851$ Å for the WC sample, which exhibits a larger fraction of a hexagonal phase. This behavior is caused by the migration of the Ba cations from the cubic perovskite, which remains with higher La content, to the hexagonal phase. Fig. 1(a) and (d) shows the experimental data, calculated patterns, the position of the allowed reflections, and the difference between observed and calculated profiles of the SSR and WC samples cooled at a rate of 10 °C/min. The two insets in Fig. 1 are SEM micrographs displaying the microstructure of these samples. The ceramic grains size of the as prepared SSR material is larger than 5 μm, while for the WC material the particle size is lower than 0.5 μm. Additionally, Fig. 1(b) shows the XRD patterns of LBC7 samples prepared by the SSR method cooled at 1 °C/min, while Fig. 1(c) displays the XRD of the LBC7 sample cooled at a rate of 10 °C/min with an extra heat treatment at 750 °C for 10 days, in air. Clearly, extra peaks corresponding to the 2H hexagonal phase show up for the sample cooled at a rate of 1 °C/min (Fig. 1(b)). These extra peaks are even more intense in the case of the SSR sample heat treated at 750 °C during 10 days. The evolution of the phases coexisting in the SSR sample with the heat treatment time shows that the cubic phase is metastable at temperatures below 900 °C and suggests a slow kinetics towards equilibrium. On the other hand, the LBC7 material synthesized at low temperature, $T = 750$ °C, using a WC route, exhibits a larger fraction of the 2H hexagonal phase. This result is revealed by the increase of the relative intensity of the 2H hexagonal phase reflections when compared to the cubic phase reflections. This behavior suggests the phase relationship in this sample is closer to equilibrium. Therefore, the use of this LBC7 material as electrode

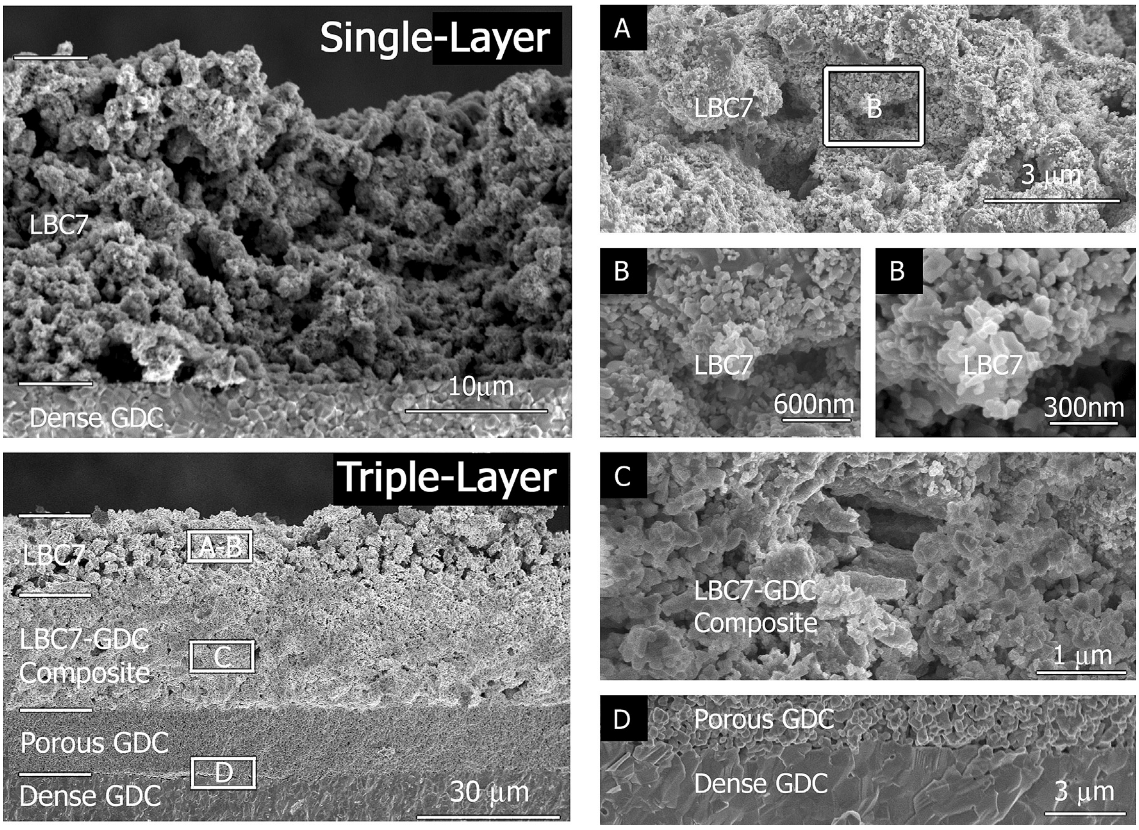

Fig. 2 – SEM micrographs of the cross-section of the LBC7 electrodes prepared by the WC route with the single and triple-layer configuration. A–D display closer views of the triple-layer electrode.

will let us test the effect of this secondary phase on its electrochemical response. The crystal structure behavior of the LBC7 samples is closely related to their oxygen content. In particular, perovskite phases with Ba in the A site and Co in the B site usually exhibit large oxygen nonstoichiometry, which is charge compensated adjusting the oxidation state of Co cations [14]. For instance, $La_{0.2}Ba_{0.8}CoO_{3-\delta}$ (LBC8) is obtained as a single cubic perovskite phase when prepared in a slightly reduced atmosphere such as pure argon at 1100 °C [3], or as a single 2H hexagonal phase when it is synthesized in a more oxidizing atmosphere such as pure oxygen at 38.0 MPa and 700 °C [15]. In the case of the LBC7 material synthesized by SSR, the overall oxygen content decreases with temperature revealing that oxygen atoms are removed during heating and incorporated during cooling [3]. Thereby, fast cooling rates help maintain the cubic phase, which is stable at high temperature, while slow cooling rates and heat treatments below 900 °C allow the incorporation of oxygen atoms and the formation of the secondary 2H hexagonal phase. Similar behavior is observed for the BSCF cathode material [7].

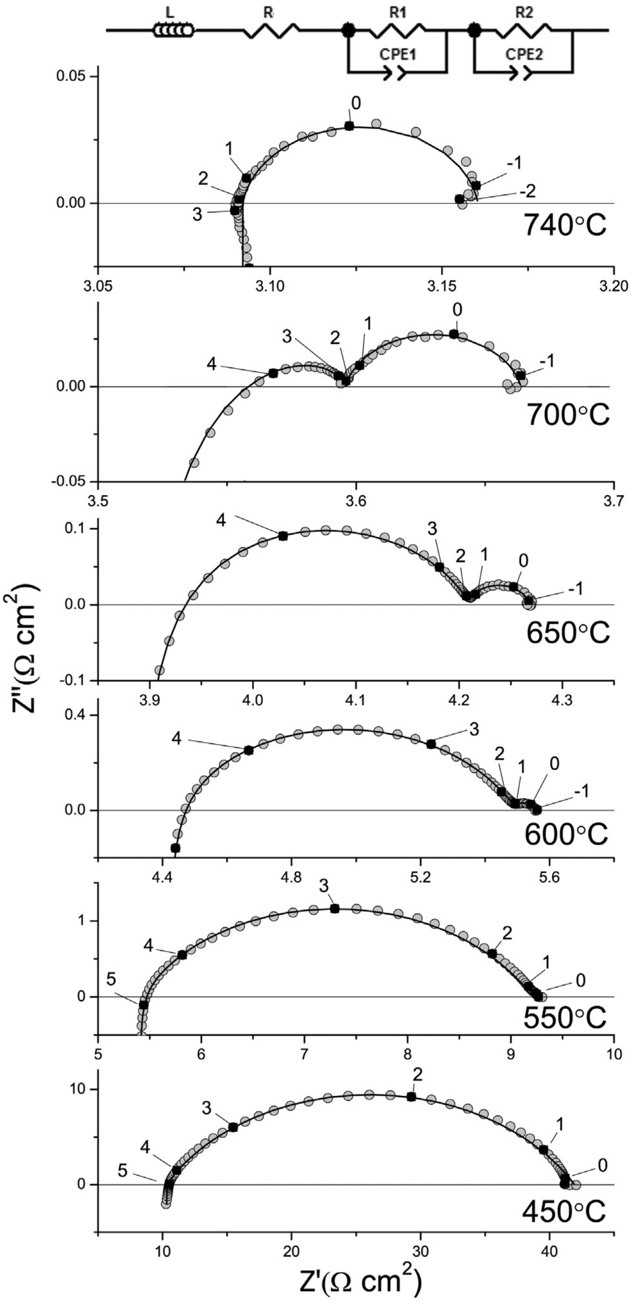

Fig. 3 – **Variation of the impedance diagrams with temperature, in air, for a single-layer LBC7 electrode prepared by the WC method. The solid line corresponds to the fit of the experimental data using the equivalent circuit displayed at the top of the figure. The logarithm of the frequency is indicated in the figure.**

The polarization resistance of LBC7 electrodes was studied by means of impedance spectroscopy measurements in the temperature range 450 ≤ T ≤ 750 °C, in air. Symmetrical cells prepared with SSR and WC samples and two different electrode configurations were measured. Those cells consisting of a porous monolayer electrode deposited on a dense GDC pellet could be prepared only with LBC7 obtained by the WC route. For the SSR material we have found severe adherence problems. In the case of the graded composition electrodes [11], consisting of three porous layers with the configuration GDC/GDC + LBC7/LBC7, the cells were fabricated with the LBC7 material obtained by the two preparation methods, SSR and WC. Fig. 2 shows SEM micrographs of the electrode cross section of the two types of cells prepared with LBC7 by the WC synthesis method. The micrographs show that the microstructure is homogeneous and uniformly distributed, had good connectivity between grains, continuous contact at the interfaces and no delamination. The thickness of the single-layer electrode prepared with the WC material is around 25 μm, while the size of the ceramic particles is in the range of 50–300 nm. The total thickness of the triple-layers electrode was around 55 μm, while the thickness for each layer was estimated from the electrode zone marked in Fig. 2 to be 15, 25 and 15 μm for the porous GDC, the composite LBC7+GDC and the LBC7 cathode, respectively. Fig. 2(A)–(D) magnify the areas indicated with A,B,C and D in the cross section of the graded electrode.

Fig. 3 shows the variation of the impedance spectra as a function of temperature (450 ≤ T ≤ 740 °C), in air, for a cell with a single-layer electrode consisting of LBC7 prepared by the WC method. Systematically, the impedance of the symmetrical cells becomes positive at high frequency denoting an inductive contribution from the device and leads. The impedance data reveal the presence of two impedance arcs in the Nyquist plane each of them associated to a different process. At low temperatures, only one broad impedance arc is observed, labeled high frequency (HF) arc. As the temperature increases, the polarization resistance associated to the HF contribution, decreases becoming negligible at 700 °C, while a second arc (LF) clearly appears on the low frequency side. This LF arc shows little variation with temperature and is not detected at low temperatures, being negligible with respect to the HF contribution. Based on these observations the impedance diagrams were reproduced with an equivalent circuit consisting of a pure resistance in series with an inductance and two elements (R_i,CPE) formed by a resistance R_i in parallel with a constant phase element $CPE = 1/B(j\omega)^p$; where B is a constant and p a parameter that may vary from $p = 1$ for a pure capacitor, to $p = -1$ for a pure inductance (see Fig. 3).

In Fig. 4 we compare the impedance spectra at $T = 600$ °C for three different cells whose electrodes were prepared with LBC7. Fig. 4(a) and (b) shows the impedance data for the single-layer and triple-layer electrodes, respectively, fabricated with the LBC7 material obtained by the WC method. In both cases, the experimental data consist of the two arcs assigned to the HF and LF processes. However, the polarization resistance of the single-layer electrode cell was found to be more than one order of magnitude higher than the value obtained with the triple-layer electrode cell. The strong diminution of the polarization resistance is concentrated in the HF process, while the LF arc, usually associated to the gas phase diffusion in the electrode [16], remains almost constant. The capacitance values calculated for the HF process at 600 °C vary from 1×10^{-5} F/cm^2 for the three layer electrode to 4.4×10^{-5} F/cm^2 for the one layer electrode, while the apex frequency changes from 20 kHz to 3 kHz. These values of capacitance have been reported for interfacial polarization at the electrode/electrolyte interface [10]. Fig. 4(c) displays the impedance spectra obtained for the graded composition electrode fabricated with the LBC7 material prepared by the SSR method. These impedance data also consist of two complex arcs with a total polarization resistance value of approximately $Rp \sim 0.06$ Ω cm^2, which is similar to the value obtained for the graded composition electrode prepared by the WC method. However, for the WC material, the frequency ranges for the HF and LF contributions are well separated, while for the SSR electrode both contributions overlap.

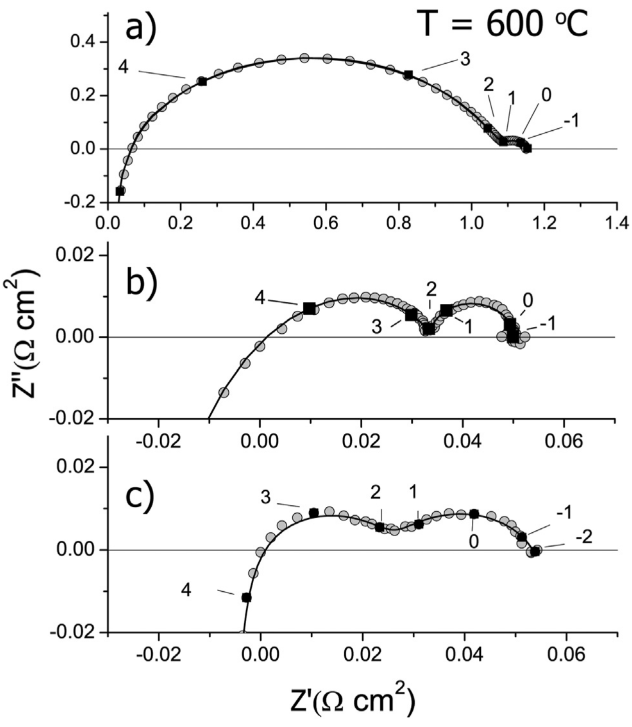

Fig. 4 – Complex impedance spectra of LBC7 electrodes at 600 °C, in air. a) Single-layer electrode prepared by the WC route. b) Graded composition electrode prepared by the WC route c) Graded composition electrode prepared by the SSR method. The logarithm of the frequency is indicated in the figure.

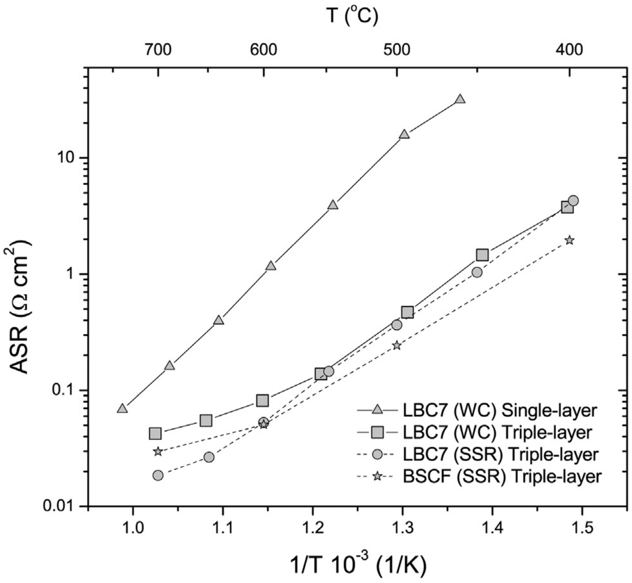

Fig. 5 – Arrhenius plot of the polarization resistance for LBC7 and BSCF electrodes prepared by the WC or SSR routes using single-layer and graded composition electrodes.

Fig. 5 shows the Arrhenius plot of the total area specific polarization resistance (ASR) obtained for electrodes prepared with LBC7 by the WC route using single-layer and triple-layer configurations. For comparison, we have added the experimental data obtained for graded composition electrodes of BSCF and LBC7 prepared by the SSR method [11]. The calculated activation energy values for the LBC7 electrodes were 1.6 and 1.0 eV, for the single-layer and the graded composition electrode prepared by the WC route, respectively. The values obtained for the graded composition electrodes of LCB7 and BSCF prepared by the SSR method were 1.2 and 0.9 eV. Systematically, lower polarization resistance values were obtained with the graded composition cathodes and small differences were detected as a consequence of variations in the synthesis method or the material composition. Noteworthy, the presence of the 2H hexagonal phase is a variable that seems to barely affect the polarization resistance of the electrode. The good performance of the graded composition electrode can be explained by several reasons, such as, the good adherence between electrode and electrolyte, due to the porous GDC layer, the lower expansion coefficient of the composite layer, a more efficient current collection of the top layer of pure cathode material and the raise of the electrode-electrolyte interface area by the incorporation of the composite layer.

4. Conclusions

In this paper, we have studied the electrochemical response of $La_{0.3}Ba_{0.7}CoO_{3-\delta}$ as cathode material by impedance spectroscopy measurements on symmetrical cells using GDC as electrolyte. The LBC7 material was prepared by the SSR and WC routes, obtaining samples with different microstructure and phase relationship. Also, we prepared cells with different electrode configurations consisting of a single layer or three layers. In all cases, the impedance spectroscopy data consist of two arcs located at the high (HF) and low (LF) frequency range. The polarization resistance of the single-layer electrode prepared by the WC method was found to be more than one order of magnitude higher than the value obtained for the three-layer electrode fabricated with the same preparation method. The strong diminution of the polarization resistance is concentrated in the HF process. The lower polarization resistance values were obtained for the graded electrodes. For instance, the value of Rp at 600 °C was approximately 0.06 Ω cm^2. Our results show that the use of graded electrodes for the LBC7 cathode material is responsible for the low polarization resistance values obtained.

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