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<th>Journal:</th>
<th>Journal of Materials Chemistry A</th>
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<tr>
<td>Manuscript ID</td>
<td>TA-ART-05-2018-004338.R1</td>
</tr>
<tr>
<td>Article Type:</td>
<td>Paper</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>31-Jul-2018</td>
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<tr>
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Journal of Materials Chemistry A

ARTICLE

An insight into the electrochemical performance of La_{0.5-x}Pr_{x}Ba_{0.5}CoO_{3-δ} as cathodes for solid oxide fuel cells: study of the O\textsubscript{2}-reduction reaction.

D. Garcés \textsuperscript{a}, H. Wang \textsuperscript{b}, S. A. Barnett \textsuperscript{b}, A. G. Leyva \textsuperscript{a,c}, F. Napolitano \textsuperscript{d,e}, R. O. Fuentes \textsuperscript{a,c}, H. Troiani \textsuperscript{d,e}, L. V. Mogni \textsuperscript{a,d,e}

New LT-SOFC cathodes with La\textsubscript{0.5-x}Pr\textsubscript{x}Ba\textsubscript{0.5}CoO\textsubscript{3-δ} (0 ≤ x ≤ 0.5) compositions were studied. The La-rich compounds exhibit an inter-growing cubic and tetragonal structure whereas the Pr-rich show a tetragonal structure. Cathode polarization resistances, estimated from electrochemical impedance (EIS), take values around 0.15 and 0.04 Ωcm\textsuperscript{-2} in air at 600 and 700 °C, respectively. The O\textsubscript{2}-reduction mechanism and its kinetic coefficients, O-ion diffusion (D\textsubscript{chem}), and O-surface exchange (k\textsubscript{surf}), were studied by applying the ALS model for macro homogenous porous electrodes to the EIS data, in combination with microstructural parameters obtained from three-dimensional tomography using focused ion beam-scanning electron microscopy (3D FIB-SEM). The diffusion coefficients for samples with mixing of phases take values of D\textsubscript{chem} ~ 10\textsuperscript{-6} cm\textsuperscript{2}/s, at 700 °C in air, whereas the pure tetragonal phases present lower values D\textsubscript{chem} ~ 10\textsuperscript{-4} cm\textsuperscript{2}/s. On the contrary the k\textsubscript{surf} for all samples takes values ranging between 0.4 and 1.10\textsuperscript{4} cm/s at 700 °C in air. In addition, the origin of time evolution of polarization at 700 °C in air was evaluated by combining the EIS spectra as a function of time and the ex-situ sample characterization of fresh and tested samples by 3D FIB-SEM tomography and inductively coupled plasma-optical emission spectrometry (ICP-OES). Little changes of microstructures were detected, whereas an increasing of the amount of a water-soluble Ba surface species in comparison with total cation surface segregation was observed for all samples after the ageing. This may constitute the main reason causing the polarization resistance degradation. However, the analysis of time evolution shows, that contrary to the situations reported for SrO segregation in Sr-based perovskites, the D\textsubscript{chem} is the coefficient mainly affected for compositions with inter-grown phases. At the same time, both D\textsubscript{chem} and k\textsubscript{surf} decreases with time when only the tetragonal phase is present.

Introduction

The large-scale commercialization of SOFCs is currently constrained by a combination of cost and durability issues. In order to address these concerns, much effort has been focused on developing low-temperature SOFCs (LT-SOFCs), with cell operating temperature < 700 °C [1]. One of the major concerns to achieve this goal is the development of cathode materials with low polarization resistance and good stability over time.

Cobaltites with the perovskite structure such as, the Strontium-Barium cobaltites Ba\textsubscript{0.5}Sr\textsubscript{0.5}CoO\textsubscript{3-x}Fe\textsubscript{2-x}O\textsubscript{3.5} (BSCF) [2], are promising cathode materials for LT-SOFCs. Despite the good performance of Sr-containing perovskites, a significant problem is the long-term instability due to Sr-surface segregation [3]. Yildiz’s group pointed out, from the study of thin film electrodes, that the cation surface segregation increases due to the size mismatch between the dopant and host cations, being more important the Ba surface segregation than Sr and Ca surface enrichment for (La,M)MnO\textsubscript{3} with M = Ba, Sr or Ca electrodes [4]. However, there is not enough information about Ba-segregation in Ba-cobaltites porous electrodes. In these perovskites, the Ba plays a key role since its large cation radii mismatch also distorts the cubic crystal structure promoting the oxygen vacancy formation and migration [5], thus reducing the R\textsubscript{p} due to the improvement of the O-surface exchange and the O-ion diffusion. However, the same structural distortion, also induces a slow segregation of a hexagonal perovskite phase [6–8] which deteriorates the O\textsubscript{2} reduction kinetics with time [9]. Recent works have shown that La\textsubscript{0.5}Ba\textsubscript{0.5}CoO\textsubscript{3-δ} is a promising cathode material for LT-SOFCs because of its low cathode polarization resistance [10–12]. Besides, in this oxide we did not observe the hexagonal phase formation suggesting that La\textsuperscript{3+} ions play an important role in stabilizing the cubic phase because of its charge and ionic radii.

With these ideas, in this work, the La content of the perovskite oxide La\textsubscript{0.5}Ba\textsubscript{0.5}CoO\textsubscript{3-δ} is partially substituted with Pr as La\textsubscript{0.5-x}Pr\textsubscript{x}Ba\textsubscript{0.5}CoO\textsubscript{3-δ} (LPBC), with 0 ≤ x ≤ 0.5 to improve even more the cathode performance mainly due to the property of the Pr of having double valence (Pr\textsuperscript{3+} and Pr\textsuperscript{4+}). It was observed that the Pr substitution in CeO\textsubscript{2} based oxides improves the electric conductivity, added to the fact that the reduced size of this cation favors the...
formation of oxygen vacancies that improving the ionic conductivity [13-15]. Therefore, it is expected that Pr will play a similar role in LPBC perovskite-type oxides. Samples synthesized at 1000°C exhibit a combination of cubic and tetragonal symmetry for x ≤ 0.1, whereas above this value the cation ordering produces a layering structure with tetragonal symmetry. The Electrochemical Impedance Spectroscopy (EIS) as a function of temperature (T), oxygen partial pressure (pO₂) and time, in combination with 3D focused ion beam-scanning electron microscopy (FIB-SEM) tomography and the inductively coupled plasma-optical emission spectrometry (ICP-OES) studies, were used to analyze the mechanisms of O₂ reduction reaction and electrode degradation with time.

Experimental

Powder samples of nominal composition LaᵦₓPr₀.₂₀Ba₀.₈₀CoO₃-δ (LPBC) were synthesized via a combined EDTA-citrate complexing sol-gel process. Stoichiometric amounts of La(NO₃)₃·6H₂O, Ba(NO₃)₁₂·6H₂O, Co(NO₃)₂·6H₂O and Pr(NO₃)₃·xH₂O were dissolved into a EDTA-NH₃·H₂O solution (pH ≈ 6) under heating and stirring conditions. A proper amount of citric acid-NH₃·H₂O solution (pH = 6) was added at a mole ratio of 1:1:2 for EDTA: total metal ions: citric acid. The mixed solution was firstly evaporated at 80 °C to form a red transparent gel and then heated at 150 °C for several hours to obtain a dark dry foam structure. After decomposition on a hot plate, the powders were calcined at 400 ºC (4 h, in air) and then at 1000 ºC (4 h, in air). Each sample of the LPBC series was labeled according to its corresponding calcined at 400 ºC (4 h, in air) and then at 1000 ºC (4 h, in air). Each sample of the LPBC series was labeled according to its corresponding lanthanum content, i.e., La30 represents the La₀.₃₀ sample of the LPBC series. Life testing was performed at 700ºC in air during 400 hours for La₀₀, La₅₀, La₃₅ and La₅₀ samples.

The crystal structure was studied by X-ray diffraction at the D10B-XPD beamline of the LNLS (Brazilian Synchrotron Light Laboratory, Campinas, Brazil) in static air at room temperature by using the high resolution mode with a Cyberstar detector, a Ge(111) crystal analyzer and a Si(111) monochromator. The wavelength was set at 1.5495(4) Å. Data in the angular region of 2θ=20°–90° were collected at room temperature in a step-scanning mode, with a step length of 0.02° and a step-counting time of 3 s.

Sample nanostructures were also studied by Transmission Electron Microscopy (TEM) with a Philips CM 200 UT (LaB6 gun) and a Tecnai F-20 (FEG) microscopes. HR-TEM images and Selected Area Electron Diffraction (SAED) patterns were obtained and compared to simulated patterns/HR-TEM images. Simulations were performed using the software JEMS (Java versionV3-3526U2008s, CIME-EPFL), using structural parameters obtained from the Rietveld analyses.

Oxygen content (3–6) vs. temperature and isothermal measurements of the equilibrium pO₂ vs. 3–6 were performed using highly sensitive thermogravimetric equipment [16], consisting of a symmetrical thermostable balance based on a Cahn 1000 electrobalance coupled to an electrochemical gas blending system [17]. The oxygen content was determined by in situ reduction in dry H₂ at 1000 °C considering La₂O₃, Pr₂O₃, BaO, and Co as final products (checked by XRD). The sample mass was measured in air with a rate of 5°C/min in the range of 20–800°C. The equilibrium pO₂ isotherms were measured at 600 and 700°C with the pO₂ ranges 1 × 10⁻⁻ atm ≤ pO₂ ≤ 1 atm.

Electrochemical characterization was performed by Electrochemical Impedance Spectroscopy (EIS) in symmetrical cell configuration (LPBC/GDC/LPBC) by using an AUTOLAB PGSTA30 (EcoChemie) potentiostat coupled to a FRA2 analyzer. The symmetrical cells consisted of a dense Ca₀₀₉₀Gd₀₀₁₀O₁⁻₀₅ (GDC, Fuel Cell Materials) electrolyte (area ∼0.8 cm², thickness ∼0.1 cm), where firstly a porous layer of GDC and afterwards a porous layer of the LPBC were deposited consecutively on both sides of the GDC pellets by spin coating. The inks were prepared by mixing the corresponding ceramic powders (GDC or LPBC) with ethanol, α-terpineol (≥96%, Sigma Aldrich), polyvinyl butyral (Sigma Aldrich), and polyvinyl pyrrolidone (Sigma Aldrich) in a 40:40:27:2:1 mass ratio. The porous layer of GDC improves the adherence of LPBC cathode onto the GDC dense electrolyte [18]. After deposition, the porous GDC layer was heat treated at 1400°C during 1 h in air, while the LPBC porous electrode was heat treated at 1000 °C 1 h in air. The EIS measurements for all samples were carried out in synthetic air in a temperature range between 400 and 800 °C. At 600 and 700 °C the EIS spectra were collected varying the oxygen partial pressure (pO₂) between 1 and 5.10⁻⁻ atm by using a home-made device to test symmetrical cells coupled to an electrochemical oxygen pump and sensor. In addition, EIS spectra were also collected at 0.2 and 0.06 atm varying the temperature, with 50 °C step, between 500 and 800 °C. Life testing was performed at 700°C in air during 400 hours for La₀₀, La₃₀, La₃₅ and La₅₀ samples.

Figure 1: a) XRD patterns of La₀₀ and La₅₀ samples. b) XRD pattern fitting for La₃₀ sample (χ² = 2.57, Rp = 16.9 and Rwp = 20.4). The angular range of 45-49° is shown for a better understanding. c) Variation of cubic (a = b = c) and pseudo cubic (a = b, c’ = c/2 for tetragonal) lattice parameters with the lanthanum content (0.5-x) for La₀₀.₅ₓPr₀.₂₀Ba₀.₈₀CoO₃-δ.
The electrode microstructures were characterized by Field Emission Gun Scanning Electron Microscopy (FEG-SEM) with a FEI Nova Nano 230 microscope. The GDC porous layer and the electrode thicknesses are around ∼5-10 µm and ∼12–15 µm, respectively. Samples before (Fresh) and after (Tested) aging test were prepared for FIB-SEM tomographic analysis by fracturing, epoxy infiltration and polishing. Serial sectioning was done on a FEI Helios. Backscattered electron (BSE) detector with an accelerating voltage of 2 kV was used to obtain good contrast between the solid and pore phases. Microstructural parameters including porosity, tortuosity, surface area and particle size distribution were then calculated based on the 3D data.

ICP-OES analysis was also done using a Thermo Scientific iCAP 7600 spectrometer on the fresh and post-tested samples to examine possible changes in the cation surface segregation. The samples were fractured into three fragments and stirred in ultrapure H₂O for 10 min, followed by transferring the samples into a 12 mol·L⁻¹ HCl solution and stirring until the electrodes were completely dissolved. The ultrapure H₂O and the concentrated HCl solutions were mixed with the appropriate amounts of H₂O/HCl/HNO₃ to yield 0.36 mol·L⁻¹ HCl stock solution (10.00 μg/mL from Inorganic Ventures) containing La, Pr, Ba and Co was used to prepare the calibration standards for quantification. The following background corrected emission lines and R₁/₂ parameters obtaining similar goodness of fit, independently of the initial seed (average values for fitting parameters are χ² ≈ 27.7, R_p ~26.7 and R_m ~19.4). The average results indicate that the La00 and La05 samples exhibit tetragonal symmetry, whereas all the other compositions present between 30–50% of cubic phase and 70–50% of tetragonal phase. The evolution of the pseudo cubic lattice parameters (a = b = c for Pm3̅m a = b = c/2 for P4/mmm) with La content is shown in Figure 1.c). As it can be observed from this figure, the samples with high La content (La ≥ 0.20) are a mix of cubic and tetragonal phase with small differences in the lattice parameters. The presence of two phases was confirmed by HR-TEM, where Figure 1.a) shows how La45 sample exhibits zones with the typical layered ordering of tetragonal structure, which become smoothly to the cubic structure with a perfect match between the lattice parameters, in agreement with those observed by XRD (see Figure 2.a - circles amplified areas with typical tetragonal and cubic structures). As the La content decreases, samples tend to be more “tetragonal” with a larger separation of the pseudo cubic lattice parameter between the cubic and tetragonal phases. Figure 2.b) and c) show a HR-TEM images of La15 sample and its electron diffraction pattern, which can be indexed as tetragonal phase with pseudo cubic lattice parameter of a = b = 3.9 ± 0.2 Å and c/2 = 3.9 ± 0.2 Å which are in agreement with those obtained from XRD Rietveld refinements.

Results and Discussion

Structure and microstructure characterization

Figure 1.a) shows the XRD pattern of La50 and La00 samples where the Bragg index of each peak was included in the graphic. At first glance, XRD data of La50 sample could be indexed as a cubic perovskite (space group Pm3̅m), however a peak splitting on La00 indicates the formation of a tetragonal phase (space group P4/mmm). As La content increases, the peaks of the tetragonal phase collapse to a unique broader and distorted peak. The XRD patterns were refined by the Rietveld method with different structural models, including the possibility of a cubic or a tetragonal phase with higher distortion levels, as well as a combination of both cubic and tetragonal phases. The best refinements (see Figure 1.b)) were obtained for a combination of the two phases. Figure 1.b) shows, as an example, the measured data, the calculated and the difference between them for La30 sample. The inset of Figure 1.b) illustrates with more details an example of the peak asymmetries observed in the diffraction patterns due to the overlapping of the Bragg reflections from both phases. The Rietveld refinements considering a mix of phases were also performed from different sets of initial parameters obtaining similar goodness of fit, independently of the initial seed (average values for fitting parameters are χ² ≈ 27.7, R_p ~26.7 and R_m ~19.4). The average results indicate that the La00 and La05 samples exhibit tetragonal symmetry, whereas all the other compositions present between 30–50% of cubic phase and 70–50% of tetragonal phase. The evolution of the pseudo cubic lattice parameters (a = b = c for Pm3̅m a = b = c/2 for P4/mmm) with La content is shown in Figure 1.c). As it can be observed from this figure, the samples with high La content (La ≥ 0.20) are a mix of cubic and tetragonal phase with small differences in the lattice parameters. The presence of two phases was confirmed by HR-TEM, where Figure 2.a) shows how La45 sample exhibits zones with the typical layered ordering of tetragonal structure, which become smoothly to the cubic structure with a perfect match between the lattice parameters, in agreement with those observed by XRD (see Figure 2.a - circles amplified areas with typical tetragonal and cubic structures). As the La content decreases, samples tend to be more “tetragonal” with a larger separation of the pseudo cubic lattice parameter between the cubic and tetragonal phases. Figure 2.b) and c) show a HR-TEM images of La15 sample and its electron diffraction pattern, which can be indexed as tetragonal phase with pseudo cubic lattice parameter of a = b = 3.9 ± 0.2 Å and c/2 = 3.9 ± 0.2 Å which are in agreement with those obtained from XRD Rietveld refinements.

Figure 2: a) and b) HR-TEM image for La45 and La15 sample, respectively. Comparison electron diffraction pattern (c) of the area shown in HR-TEM image b) and kinematical simulation (d) for SAED pattern along the [101]; ZA.
Figure 3.a) and b) are SEM images showing cross sectional and electrode surface views of the symmetrical cell La35/GDC/La35, respectively. Figure 3.c) and d) illustrate 2D FIB-SEM cross-sectional images of the La35-fresh and tested sample, respectively. The bright phase represents the particles and the dark phase are the epoxy-infiltrated pores. The corresponding 3D reconstructed structures of electrode porous layer of the La35-fresh and tested samples are shown in Figure 3.e) and f), note that the GDC porous layer was ignored for the tomography analysis. The structure is typical of SOFC cathode electrodes produced by firing of particle compacts, showing reasonable uniform particle sizes and good necking between particles.

Figure 3: SEM images of La35 symmetrical cell, a) cross and b) top section. Typical 2D FIB-SEM cross-sectional image of c) La35-fresh and d) La35-tested with pore phase infiltrated by epoxy. The corresponding 3D reconstruction of e) La35-fresh and f) La35-tested with LPBC particles shown in green and pores transparent. Note that the 3D view only shows the electrode region. g) Cumulative particle size distribution of LPBC calculated from obtained 3D data sets.

Indicates the microstructural parameters: solid phase fraction (ε), solid phase and pore phase tortuosity (τ_s, τ_p), specific surface area (a) and the mean particle size determined from the analysis of the 3D data and the cumulative particle size distribution (Figure 3.g) of La35 before and after life testing.

Table 1: Microstructural parameters for La35 porous electrode obtained from 3D FIB-SEM reconstruction.

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<th>Sample</th>
<th>solid phase fraction (ε)</th>
<th>solid phase tortuosity (τ_s)</th>
<th>pore phase tortuosity (τ_p)</th>
<th>specific surface area (a)</th>
<th>mean particle size</th>
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<tr>
<td>La35-fresh</td>
<td>52.4 %</td>
<td>1.28</td>
<td>1.22</td>
<td>3.78 μm⁻¹</td>
<td>900 nm</td>
</tr>
<tr>
<td>La35-tested</td>
<td>53.7%</td>
<td>1.28</td>
<td>1.25</td>
<td>3.12 μm⁻¹</td>
<td>1100 nm</td>
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</table>

† the specific surface area is defined as the cathode area per volume unit.

Electrochemical Performance

The total cathode polarization resistances (R_C,P) obtained from the EIS measurements in air at 600 and 700 °C are presented in Figure 4. Regardless the La content, R_C,P takes values between 0.07 and 0.22 Ωcm² at 600 °C and between 0.03 and 0.06 Ωcm² at 700 °C. These values are compared with some typical cubic perovskites (black lines) and double perovskites (red lines) cathodes resistances reported at literature. These figures show that the R_C,P of La0.5-xPr_xBa0.5CoO3-δ are competitive with the best cathodes reported in the literature.

The R_C,P values are the result of different cathode processes that can be separated in frequency by the impedance spectroscopy. As an example, Figure 5.b) and c) show impedance spectra, Nyquist and Bode plots (data points), measured at 600 °C and pO2 = 0.05 atm for the symmetrical cell La30/GDC/La30 and Figure 5.d) and e) show the same information at 700°C. All spectra were normalized to the geometric area of the electrodes in the symmetrical cell configuration and show two arcs denoting the two different processes. Similar results were reported for Pr-free La-Ba cobaltite [10]. The two arcs are observed at temperatures above 600 °C, but
only one EIS arc is observed at lower temperature. All cathode compositions present similar behavior shown in Figure 5.

In order to study the mechanism of the O\textsubscript{2} reduction reaction (ORR), the electrochemical response was analyzed as a function of T and pO\textsubscript{2}. The EIS spectra were fitted using the Electrical Equivalent Circuits (EEC) approximation. This circuit is composed by the inductance of connectors (L) and the electrolyte resistance (R\textsubscript{electrolyte}), whereas the electrode response is fitted by the combination of a Gerischer for high frequency arc (Z\textsubscript{G}) and a resistance (R\textsubscript{LF}) in parallel with a capacitor (C\textsubscript{peLF}) for the low frequency arc (Z\textsubscript{LF}) (see Figure 5.a). The resulting fits show good agreement with the measured spectrum.

**Figure 5:** a) Electrical equivalent circuit (EEC) used for fitting the EIS spectra in the whole frequency range. b,d) Nyquist and c,e) Bode plot obtained for La30 sample in a pO\textsubscript{2} = 0.05 atm at 600 and 700°C, respectively. Data point represents the measured data, solid line represents the arcs resulting of fitting data with the EEC proposed and dashed lines indicating the different contributions.

Figure 6.a) and b) show the log-log plot for the high frequency Gerischer resistance (R\textsubscript{G}) and the low frequency resistance (R\textsubscript{LF}) vs pO\textsubscript{2} for the La30 sample at 600 and 700 °C, respectively. The pO\textsubscript{2} dependences of R\textsubscript{G} and R\textsubscript{LF} fit approximately to R\textsubscript{G} \propto (pO\textsubscript{2})^{-0.25} and R\textsubscript{LF} \propto (pO\textsubscript{2})^{-1}. Note that red lines show the estimation of polarization loss due to O\textsubscript{2} gas diffusion through a porous electrode with a 47.3% of porosity, \( \tau_P = 1.22 \) and length \( l = 15 \mu m \) modeled by considering both normal and Knudsen diffusion as reported in [25,26]. The R\textsubscript{LF} values shows similar values, as well as the same pO\textsubscript{2} and temperature dependence, independently of cathode composition for the series La\textsubscript{0.5-}\textsubscript{x}Pr\textsubscript{x}Ba\textsubscript{0.5}CoO\textsubscript{3-\delta}. This result is in agreement with none significant microstructural differences observed within the series. Figure 6.c) shows the Arrhenius plot of R\textsubscript{G} and R\textsubscript{LF} obtained from the fitting of EIS spectra collected as a function of T in air and pO\textsubscript{2} = 0.05 atm. The pO\textsubscript{2} = 0.05 atm was selected since as it is observed from Figure 5 the two arcs can be easily distinguished. Both process show markedly different activation energies. Whereas the R\textsubscript{G} has an activation energy of \approx 1 eV, the O\textsubscript{2}-gas diffusion is almost independent of T. These results suggest that the electrochemical response is limited by one or two mechanisms, depending on the conditions. At temperatures \leq 600 °C, the target T for low temperature SOFC [1], the high frequency contribution R\textsubscript{G} associated with chemical processes co-limited by O-surface exchange and O-ion diffusion [25,27] is dominant. Whereas at higher temperatures (T > 700°C) R\textsubscript{G} becomes small enough, or at very low pO\textsubscript{2} the low frequency R\textsubscript{LF} response increases being in both cases the O\textsubscript{2}-gas diffusion the main responsible of the cathode polarization losses. However, the chemical process increases its impedance for Pr-rich compositions being comparable to the O\textsubscript{2} gas diffusion.

**Figure 4:** Total polarization resistance as a function of lanthanum content in air. Figures a) and b) compare the R\textsubscript{CP} of La\textsubscript{0.5-}Pr\textsubscript{x}Ba\textsubscript{0.5}CoO\textsubscript{3-\delta} at 600 and 700 °C, respectively, with other porous single phases cathodes with cubic (black lines) and tetragonal (red lines) symmetry [2,10–12,18-24].
Figure 6: a) and b) Log-log plot of the high frequency Gerischer resistance ($R_G$) and the low frequency resistance ($R_{LF}$) with $pO_2$ at 600 and 700 °C for La30 sample. Dotted lines indicate the $pO_2$ dependences $R_G \propto (pO_2)^{-0.25}$ and $R_{LF} \propto (pO_2)^{-1}$. b) Arrhenius plot for the Gerischer resistance ($R_G$) and the low frequency resistance ($R_{LF}$) in air and $pO_2 = 0.05$ atm. The activation energies are indicated on the graphs.

The Gerischer type impedance $Z_G = R_G \frac{1}{\sqrt{1+j\omega \tau_G}}$ can be modeled by the Adler-Lane-Steel (ALS) models [27] mentioned before. In this model the resistance $R_G$ and the time constant $\tau_G$ can be directly related to microstructural, thermodynamic and kinetic parameters by:

$$R_G = \frac{RT}{4F^2} \frac{1}{4\alpha R_0 D_{ef} \delta_{eq}}$$

$$\tau_G = \frac{(1-\varepsilon)^2}{4\alpha R_0 A_0}$$

where $\alpha$ is the oxygen molar equilibrium surface rate and $D_{ef}$ is the effective diffusion coefficient of oxygen vacancies; $c_V$ is the concentration of oxygen lattice sites involved in the diffusion mechanism, $x_V = 0.8$ is the molar fraction of oxygen vacancies at equilibrium and $A_0 = -\frac{\varepsilon}{\tau_G}$ is the thermodynamic factor describing how oxygen non-stoichiometry varies with oxygen chemical potential in the case of O-vacancies defects. The microstructure of the electrode is considered explicitly through the electrode porosity $\varepsilon$ and the electrode specific surface area $a$, whereas the MIEC-phase tortuosity factor $\tau$ is contained within $D_{ef} = \frac{(1-\varepsilon) \tau}{\tau_G}$. The $\alpha$ surface exchange rate can show different $pO_2$ dependences, $\alpha = \frac{k_{chem}}{A_0} c_V pO_2^n$, where $m$ values can takes values between 0 and 1 depending of the mechanism limiting surface reaction rate [28,29]. $c_V$ is molar the concentration of the O-vacancies and $k_{chem}$ is the chemical surface reaction coefficient.

Then, the O-ion chemical diffusion ($D_{chem}$) and chemical surface reaction coefficients ($k_{chem}$) can be obtained by combining $R_G$ and $\tau_G$ from the EIS fitted data as a function of $T$ and $pO_2$, the microstructure parameters $(\varepsilon, a$ and $\tau)$ from 3D-FIB-SEM tomography, and the O-vacancy concentration and $A_0$ from TG data (3-5 vs $T$ and $pO_2$ not show here). Figure 7 shows $D_{chem}$, $\alpha$ and $k_{chem}$ for all samples vs $pO_2$ at 700 °C. Figure 7.a) shows the independence of $D_{chem}$ with $pO_2$, which indicates a O-ion diffusion mechanism dominated by O-vacancies jumps in the bulk [27,30]. The tetragonal $Pr_{0.5}Ba_{0.5}CoO_3$ presents the lower values for $D_{chem}$ (~$10^{-8}$ cm$^2$/s for La00), one and two orders of magnitude lower than samples having a combination of cubic and tetragonal phases. This would indicate that the diffusive process present in these samples is favored with the cationic disorder. Contrary to $D_{chem}$, the $\alpha$ shows a strong dependence with $pO_2$, with $n$ between 0.3 and 0.8 (see Figure 7.b), which can be assigned to a surface process dominated by surface dissociation or surface dissociative adsorption according to Adler’s model [28]. Figure 7.c) shows the $k_{chem}$ obtained from $\alpha$ assuming $m = 0.5$. At difference that is observed for O-ion diffusion there is not an important difference between the $k_{chem}$ obtained for sample with tetragonal phase from those with mixed of phases ($k_{chem} \sim 0.4-2 \times 10^{-4}$ cm/s at 700 °C in air).
The activation energy for $D_{\text{chem}}$ (and $\gamma_0$) obtained from Figure 8.a (and 8.b) suggests a substantial difference between the pure tetragonal Pr$_{0.5}$Ba$_{0.5}$CoO$_{3-\delta}$ and the other samples with mixed phases. Thus, for La00 the activation energy for $D_{\text{chem}}$ is higher (~1.1 eV) than the other samples (~0.7 eV), whereas the contrary is observed for $\gamma_0$ with an activation energy of ~0.9 eV, lower than the value of ~1.3 eV observed for the other compounds.

Table 2 shows $D_{\text{chem}}$ and $k_{\text{chem}}$ at 600 and 700 °C as well as its activation energies.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$D_{\text{chem}}$ [600 °C]</th>
<th>$k_{\text{chem}}$ [600 °C]</th>
<th>$D_{\text{chem}}$ [700 °C]</th>
<th>$k_{\text{chem}}$ [700 °C]</th>
<th>$E_a^D$ [eV]</th>
<th>$E_a^G$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>La00</td>
<td>$1.6 \times 10^{-9}$</td>
<td>$2.8 \times 10^{-5}$</td>
<td>$6.2 \times 10^{-6}$</td>
<td>$1.7 \times 10^{-5}$</td>
<td>$1.1 \pm 0.2$</td>
<td>$0.9 \pm 0.2$</td>
</tr>
<tr>
<td>La10</td>
<td>$1.5 \times 10^{-7}$</td>
<td>$8.7 \times 10^{-6}$</td>
<td>$3.6 \times 10^{-7}$</td>
<td>$7.7 \times 10^{-5}$</td>
<td>$0.8 \pm 0.2$</td>
<td>$1.3 \pm 0.1$</td>
</tr>
<tr>
<td>La20</td>
<td>$6.4 \times 10^{-8}$</td>
<td>$2.1 \times 10^{-5}$</td>
<td>$1.3 \times 10^{-6}$</td>
<td>$9.7 \times 10^{-5}$</td>
<td>$0.7 \pm 0.1$</td>
<td>$1.4 \pm 0.1$</td>
</tr>
<tr>
<td>La30</td>
<td>$3.6 \times 10^{-7}$</td>
<td>$1.6 \times 10^{-6}$</td>
<td>$1.5 \times 10^{-6}$</td>
<td>$1.1 \times 10^{-4}$</td>
<td>$0.72 \pm 0.07$</td>
<td>$1.34 \pm 0.09$</td>
</tr>
<tr>
<td>La40</td>
<td>$5.7 \times 10^{-8}$</td>
<td>$5.1 \times 10^{-5}$</td>
<td>$1.1 \times 10^{-7}$</td>
<td>$9.3 \times 10^{-6}$</td>
<td>$0.65 \pm 0.06$</td>
<td>$1.65 \pm 0.09$</td>
</tr>
<tr>
<td>La50</td>
<td>$2.2 \times 10^{-7}$</td>
<td>$1.6 \times 10^{-5}$</td>
<td>$1.8 \times 10^{-6}$</td>
<td>$7.6 \times 10^{-5}$</td>
<td>$0.89 \pm 0.02$</td>
<td>$1.27 \pm 0.08$</td>
</tr>
</tbody>
</table>
Life Testing

Figure 9: a) Evolution of $R_{CP}$, $R_G$ and $R_L$ values with aging time for La50 sample at 700 °C in air, b) and c) Nyquist and Bode plots obtained for La50 sample at 0, 200 and 400 h, d) and f) show the same information for La30 sample and g), h) and i) for La00. Dashed red lines in figure c, f and i are a guide to the eyes showing the evolution with time of the maximum frequency of $R_G$.

Figures 9.a), d) and g) show the time evolution of $R_0$, $R_{CP}$, and the total polarization resistance $R_{CP}$ measured by EIS at 700 °C in air as a function of time, for the La50, La 30 and La00 electrodes, respectively. The results reveal an increase, after 400 hours, of the total polarization resistance between 45 % and 64 % for samples that have a combination of cubic and tetragonal phases and an increase of ~ 316 % for the sample with tetragonal phase. Error! Reference source not found. contains information about the overall rate of change over the aging, defined as $\frac{1}{R_{CP}^0} \frac{dR_{CP}}{dt}$, and the rate of change for $R_L$ ($\frac{1}{R_L^0} \frac{dR_L}{dt}$) and $R_0$ ($\frac{1}{R_0^0} \frac{dR_0}{dt}$). As can be observed from Figure 9, the low frequency contribution ($R_L$), associated to $O_2$ gas diffusion, is the main contribution to the polarization resistance at 700 °C in air for samples with mixing cubic and tetragonal phases. The change of $R_L$ with time is negligible compared with the evolution of $R_0$ for all samples (see Table 3). The little increase of $R_0$ can be attributed to the particle coarsening reported in Table 1 which reduces the pore fraction ($\varepsilon_P = 1 - \varepsilon$) and increases the pore phase tortuosity ($\tau_p$) - i.e. $R_L \propto \frac{1}{\varepsilon_P}$ [25] supporting an increasing of 5% of $O_2$ gas diffusion polarization resistance. On the contrary, the increases of $R_G$ cannot be totally explained by the reduction of the specific surface area - i.e. $R_G \propto \frac{1}{\sqrt{a}}$ [25]. It can be noted from the Nyquist and Bode plots (Figure 9) and from Error! Reference source not found. that the pure tetragonal phase (La00), at difference of that observed for La30 and La50, not only shows a highest increasing of its $R_L$ resistance but also its time constant $\tau_G$ became slower with time suggesting a different degradation mechanism for the tetragonal phase. The ohmic resistances (not shown here) remains constant with time, indicating thermal compatibility at the electrode/electrolyte interface.

Table 3: Rates of change for $R_{Total}$ ($\frac{1}{R_{CP}^0} \frac{dR_{CP}}{dt}$), $R_L$ ($\frac{1}{R_L^0} \frac{dR_L}{dt}$) and $R_G$ ($\frac{1}{R_G^0} \frac{dR_G}{dt}$) after 400 hours. The percent of change for each contribution is indicated between parentheses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\frac{1}{R_{CP}^0} \frac{dR_{CP}}{dt}$</th>
<th>$\frac{1}{R_L^0} \frac{dR_L}{dt}$</th>
<th>$\frac{1}{R_G^0} \frac{dR_G}{dt}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La00 (tet)</td>
<td>0.008 h$^{-1}$ (~ 316 %)</td>
<td>0.002 h$^{-1}$ (~ 63 %)</td>
<td>0.01 h$^{-1}$ (~ 477 %)</td>
</tr>
<tr>
<td>La30 (cub + tet)</td>
<td>0.001 h$^{-1}$ (~ 46 %)</td>
<td>0.0001 h$^{-1}$ (~ 5 %)</td>
<td>0.005 h$^{-1}$ (~ 86 %)</td>
</tr>
<tr>
<td>La50 (cub + tet)</td>
<td>0.002 h$^{-1}$ (~ 64 %)</td>
<td>0.0007 h$^{-1}$ (~ 28 %)</td>
<td>0.004 h$^{-1}$ (~ 63 %)</td>
</tr>
</tbody>
</table>
Summarizing, La00 with tetragonal phase shows the formation of ~20 nm Ba-rich particles on the perovskite surface. HR-TEM and EDS indicate that Ba segregation consists in sample it amounts increase only ~50%. The study of perovskite increases a 100% after the test for La30 and La50, but for the La00 La50. Also, Figure 10 (a) shows that the amount of Ba in the surface monolayers in the fresh sample is more than twice that for La30 and for the tetragonal phase (La00), where the estimated number of segregation during sample processing in all samples, but especially in comparison with the other cations indicates a Ba surface indicated in Figure 10. The highest value of Ba surface concentration the largest Ba surface concentration, however whereas the R value of R in LPBC series is mainly due to the decrease of $D_{\text{chem}}$ (~100%) and not to $k_{\text{chem}}$ that increases (+66%, La50) or remains approximately constant (-6%, La30) for the samples with mixed cubic and tetragonal phases. While there is a consensus in the literature to associate the degradation of the polarization resistance to the fact that the segregation of SrO species blocks the surface exchange process [32], the effect of Ba segregation is not entirely clear. A few works studying the effect of BaCO$_3$ nanoparticles decorating the surface of LSCF [33] and LSF [34] cathodes demonstrated that Ba ions improve the chemical oxygen surface exchange coefficients may be due to that barium ions on the surface play a key role in the adsorption of oxygen molecules and the formation/decomposition of intermediates [35]. The coexistence of both effects could explain an optimum amount of Ba in the surface to be the reason of different time evolution behavior observed for $k_{\text{chem}}$, being more important the blocking effect in the tetragonal sample as is evident for the reduction of the time constant $\tau_0$ (see Figure 9.i). On other hand, because the $pO_2$ dependence of $D_{\text{chem}}$ suggested a bulk mechanism for ion diffusion, it is reasonable to assume that the decrease of the diffusion coefficient $D_{\text{chem}}$ could be associated to a negative impact of the Ba depletion in the sub-surface region naturally accompanying the Ba-surface segregation which could produce a local lattice distortion affecting the O-ion transport. This Ba segregation could be controlled and reduced as in the case of Sr segregation. Recent work showed that Sr segregation on LSCF slows substantially with decreasing temperature [36], it is possible that our electrodes would be stable enough if operated at 500 – 600 ºC. Tomov demonstrated that composite cathodes decorated with GDC nanoparticles showed stable operation after aging assigned to the suppression of SO degradation by the GDC nano-decoration [37]. This kind of strategy could be also useful to mitigate Ba surface segregation in these materials.

Table 4: Values of $D_{\text{chem}}$ and $k_{\text{chem}}$ at 700 ºC in function of aging time for La50, La30 and La00 samples.

<table>
<thead>
<tr>
<th>Time [h]</th>
<th>$D_{\text{chem}}$ [cm$^2$/s]</th>
<th>$k_{\text{chem}}$ [cm/s]</th>
<th>$D_{\text{chem}}$ [cm$^2$/s]</th>
<th>$k_{\text{chem}}$ [cm/s]</th>
<th>$D_{\text{chem}}$ [cm$^2$/s]</th>
<th>$k_{\text{chem}}$ [cm/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.4 10$^{-6}$</td>
<td>5.5 10$^{-6}$</td>
<td>7.0 10$^{-6}$</td>
<td>1.1 10$^{-4}$</td>
<td>4.7 10$^{-9}$</td>
<td>1.7 10$^{-4}$</td>
</tr>
<tr>
<td>220</td>
<td>2.0 10$^{-4}$</td>
<td>7.9 10$^{-5}$</td>
<td>2.2 10$^{-5}$</td>
<td>9.2 10$^{-5}$</td>
<td>6.3 10$^{-10}$</td>
<td>1.5 10$^{-4}$</td>
</tr>
<tr>
<td>400</td>
<td>7.8 10$^{-6}$</td>
<td>9.1 10$^{-5}$</td>
<td>9.8 10$^{-7}$</td>
<td>1.0 10$^{-4}$</td>
<td>3.0 10$^{-10}$</td>
<td>1.0 10$^{-5}$</td>
</tr>
<tr>
<td>Percent of Change</td>
<td>-94%</td>
<td>66%</td>
<td>-86%</td>
<td>-6%</td>
<td>-94%</td>
<td>-39%</td>
</tr>
</tbody>
</table>
Conclusions

A soft chemical route was used to obtain La_{0.5-x}Pr_xBa_{0.5}CoO_{3-δ} (LPBC) powders. The samples present a mixture of phases: cubic + tetragonal with the exception of those that contain low lanthanum content that have a tetragonal crystalline structure as a single phase. The study of electrode performance by EIS as a function of temperature, pO_2 and time suggested that two processes contribute to R_{c,p}:

1) The low frequency resistance (R_{L}), which is associated to O_2 gas diffusion. This contribution dominates the cathode polarization resistance as T increases or pO_2 decreases in samples with a mixture of phases but it represents the smallest contribution to R_{c,p} in tetragonal samples. The O_2 gas transport resistance shows little changes with time which is in agreement with small change of microstructure.

2) The high frequency Gerischer-resistance (R_o), which can be modeled by using the ALS approximation. This R_o considers that the O_2-reduction reaction is co-limited by O-surface exchange and O-ion diffusion. By the analysis of the dependence of O-ion chemical diffusion (D_{chem}) and the surface exchange rate (κS) with temperature and pO_2 is concluded that the surface process is dominated by surface dissociation or surface dissociative adsorption, according to Adler’s model, and that the O-ion diffusion mechanism is dominated by bulk transport. This mechanism is mostly determined by the crystal structure, microstructure and surface conditions. The R_o is the contribution showing the largest evolution with time and, unlike samples with high lanthanum content, it dominates the cathode polarization resistance for sample with tetragonal phase.

Ageing of LPBC symmetric-electrode cells with GDC electrolytes, carried out at 700 °C for 400 hours in air, resulted in an increase of the electrode polarization resistance by about ~ 50 % for samples with two phases and an increase of ~ 316 % for the sample with tetragonal phase. 3D tomographic analysis indicated no significant changes in the selected microstructural parameters due to ageing. ICP-OES measurements of selectively dissolved surface species shows the amount of surface Ba in the samples was increased on all cases. This increase of Ba concentration at the surface caused a decrease of D_{chem} (-100%) which would be associated with a detriment in the O-ions diffusion, due to local lattice distortion associated to the Ba depleton in the sub-surface region. The variation of R_o due to the Ba surface concentration could be attributed to two opposing phenomena: first, the segregation of Ba ions forms BaO or BaCO species which blocks the surface exchange sites on the LPBC surface but at the same time can contribute to the formation/decomposition of intermediates in the adsorption of oxygen molecules. All samples present a coexistence of this two phenomena being the blocking process more important in tetragonal samples and less significant when the lanthanum content increases.

Finally, the La_{0.5}Pr_{0.5}Ba_{0.5}CoO_{3-δ} cathodes with an unique microstructure intimately mixing cubic and tetragonal phases (La-rich compound), exhibit a low polarization resistance taking values around 0.15 and 0.04 Ωcm^2 at 600 and 700 °C in air, respectively. As T increases the cathode polarization is dominated by the O_2 gas diffusion (~ 50% of the R_o in air), whereas the “true electrode” response associated to a Gerischer-impedance and modeled by the Adler-Lane-Steele model just contributed with R_o values around 0.08 and 0.015 Ωcm^2 at 600 and 700 °C in air, respectively. These La-rich cathodes are also those showing the lower degradation rate, being the more important impact of the Ba surface segregation a decreasing of the O-ion bulk diffusion whereas the O-surface exchange shown a positive effect increasing the surface exchange coefficient with time.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Authors want to acknowledge the support of CONICET-NSF collaborative project, AGNPCyT PICT2016-2965 and CONICET PIP 2015 0565. This work has been supported by the Brazilian Synchrotron Light Laboratory (LNLS, CNPEM, Brazil) under Research Proposal D108-XPD-20150226. The authors also acknowledge the assistance of the Electron Probe Instrumentation Center (EPIC) at the NUANCE Center-Northwestern University, which has received support from the MRSEC program (NSF DMR-1121262) at the Materials Research Center; the International Institute for Nanotechnology (IIN); and the State of Illinois, through the IIN. Metal analysis was performed at the Northwestern University Quantitative Bio-element Imaging Center.

Notes and references

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