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Additional Information

Tailoring $\text{La}_{2-x}\text{A}_x\text{Ni}_{1-y}\text{B}_y\text{O}_{4+\delta}$ cathode performance by simultaneous A and B doping for IT-SOFC

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Abstract

The present work focuses on the study of different Ruddlesden-Popper based cathode materials for Solid Oxide Fuel Cells at Intermediate Temperature (IT-SOFC). The partial substitution of La and Ni by Pr and Co, respectively, were studied in the $\text{La}_{2-x}\text{Pr}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_{4+\delta}$ system, with the purpose of enhancing their mixed ionic-electronic conductivity and the electrocatalytic activity for the O_2 -reduction while the crystal structure was preserved. All synthesized compounds were characterized by electrochemical impedance spectroscopy (EIS), DC conductivity measurements, X-Ray diffraction (XRD), iodometric titration and scanning electron microscopy (SEM). XRD analyses by Rietveld refinement revealed the influence of the ionic radius on the crystalline phase for the different dopants, i.e., variation of the cell parameters and M-O bond lengths. The substitution in both La and Ni sites improves $\text{La}_2\text{NiO}_{4+\delta}$ electrochemical properties as IT-SOFC cathode, since higher conductivity and lower polarization resistance were obtained. Finally, $\text{La}_{1.5}\text{Pr}_{0.5}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_{4+\delta}$ cathode exhibited the lowest electrode polarization resistance and activation energy values in the temperature range of 450-900 °C. $\text{La}_{1.5}\text{Pr}_{0.5}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_{4+\delta}$ was applied on an anode supported cell and a maximum power density of $\sim 400 \text{ mW}\cdot\text{cm}^{-2}$ was obtained at 700 °C using pure hydrogen and air.

1. Introduction

One of the major societal challenges is the production of energy in a green and efficient way. Due to the limited fossil fuels sources and their associated greenhouse gases emissions, makes it necessary to look for new and clean energy sources. Fuel cells have grown interest in the market, due to their high efficiency, noiseless operation and the fuel flexibility. One of the principal challenges in Solid Oxide Fuel Cells (SOFC) technology is the reduction of the operation temperature. During last decades, $\text{La}(\text{Sr})\text{MnO}_3$ (LSM) has been set as the state-of-the-art cathode for SOFC; as a single phase or composite electrode [1-5] due to its adequate properties at high temperatures. Due to its negligible oxide-ion conductivity and modest electronic conductivity at low temperatures (below 600 °C), other type of materials has been investigated as alternative cathodes for IT-SOFC [6-8]. Materials which exhibit mixed ion-electron conductivity (MIECs) can enlarge the triple phase boundary (TPB) to the whole electrode surface. Consequently, the Oxygen Reduction Reaction (ORR) is not exclusively restricted to the mere cathode-electrolyte interface. Additionally, the enhancement of the electrocatalytic properties of the cathode would further improve the cell performance and hence would allow the reduction of the operation temperature.

Ruddlesden-Popper series oxides, with the general formula $\text{La}_{n+1}\text{Ni}_n\text{O}_{3n+1}$, have attracted great interest due to its excellent electrochemical properties as SOFC cathodes [9, 10]. Those properties are related to its anisotropic structure, consisting of rock-salt and perovskite layers interspersed [11-13]. The value of n in the general formula indicates the number of perovskite layers between two rock-salt layers. Due to its layered structure, these compounds are able to accommodate hyperstoichiometric oxygen in the interstitial sites of the rock-salt layer [14], exhibiting good oxygen ion conductivity at intermediate temperatures [11, 15-17]. The highly anisotropic oxygen diffusion is produced *via* interstitial oxygen defects in the lattice [18] and the cooperative diffusion of the oxygen vacancies in the perovskite layer [15], but the oxygen migration is mainly dominated by the oxygen transport through *ab*-plane [19, 20].

It has been reported that the substitution of La in the parent $\text{La}_2\text{NiO}_{4+\delta}$ structure by other elements with smaller ionic radius leads to the variation of the cell parameters and the increase of the oxygen hyperstoichiometry [21]. Pr was introduced in the La site, in order to improve the cathode electrocatalytic activity [22, 23] and due to the similar ionic radius (La= 1.216 Å and Pr= 1.179 Å). As reported previously [24, 25], if the Pr amount substituted in the La site is low, the orthorhombic *Fmmm* space group of $\text{La}_2\text{NiO}_{4+\delta}$ is preserved, however, higher amounts of Pr will shift the structure to *Bmab* space group. Furthermore, this aforementioned change in the structure agrees with the chemical instability observed for nickelates compounds with higher Pr content [25]. In the present work, the crystal symmetry changes were precluded by restraining the Pr content to 25 % and 50 % molar.

Regarding Ni position, Co was selected due to its similar ionic radius and the enhanced oxide-ion diffusion coefficient ascribed to the high redox activity [26]. Only 20 % of Co was substituted in the structure in order to maintain the orthorhombic structure and not to alter the Thermal Expansion Coefficient (TEC) of the parent material. It has been reported that higher contents of Co (> 60%) lead to a *Bmab* symmetry, and have a detrimental influence on thermal expansion behavior [27, 28]. Finally, a double substitution was carried out to assess the synergetic influence of both cations on the nickelate electrochemical behavior.

2. Experimental

$\text{La}_{2-x}\text{Pr}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_{4+\delta}$ materials were prepared following the Pechini method. First, stoichiometric amounts of the different metal nitrates were mixed and dissolved into distilled water. Then, citric acid was added as a chelator and heated at 80 °C. Ethylene glycol was incorporated into the solution, and the resulting mixture was heated up to 120 °C to start the polymerization reaction. After that, the gel obtained was dried at 210 °C, followed by a calcination step in air at 750 °C. Finally, the powder was grinded, pressed and sintered in air at 1350 °C for 4 h to get the crystalline phase. In order to obtain a homogenous particle size distribution and low particle size, powders after calcination steps were ball milled with ZrO_2 balls in acetone for 48 hours.

Powder after synthesis were characterized by X-ray diffraction (XRD) analysis, measurements were carried out in a PANalytical Cubix fast diffractometer by using $\text{CuK}\alpha_{1,2}$ radiation, and an X'Celerator detector and Bruker D8 in Bragg-Brentano geometry. XRD patterns were recorded in the 2θ range from 20 to 90 ° and analyzed using the X'Pert HighScore Plus and Fullprof software. Structure refinements were performed by the Rietveld method with pseudo-Voigt peak shape and manual backgrounds selection. The occupancy of the metal and oxygen site

were fixed according to the compound composition, while the overall atomic displacement parameter was used for all sites. In the final run, zero shift, peak shape, scale factor, lattice parameters, atomic positions and overall atomic displacement parameter were refined.

Electrical conductivity measurements were conducted by standard four-point DC technique on sintered rectangular bars. Powders of the different cathode materials were uniaxially pressed in rectangular bars and fired at 1430 °C for 5 h. Silver paste and wires were used to obtain the electric contact. Measurements were carried out in air and the current was supplied by a Keithley 2601 programmable current source. Voltage drop through the sample was detected by a Keithley 3706 multimeter.

The oxygen hyperstoichiometry (δ) for all samples was obtained by Iodometric titration method at room temperature. For that purpose, $\text{Na}_2\text{S}_2\text{O}_3$ solution was used as reagent for the iodine titration and N_2 was flowed into the solution to avoid the reoxidation of the solution.

With the premise of operate at intermediate temperatures (400-600 °C), 20 mol% gadolinia doped ceria oxide ($\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$, GDC) was selected as electrolyte material. GDC exhibits higher ionic conductivity and faster oxygen surface exchange kinetics than the zirconia-based electrolytes at intermediate temperatures [29]. Dense GDC electrolytes were prepared by pressing uniaxially commercial powder (Treibacher) impregnated with 5% of Co (with a solution of $\text{CoN}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$). A final firing temperature of 1480 °C was selected to reach fully densified electrolyte disks.

Screen-printable inks made of $\text{La}_{2-x}\text{Pr}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_{4+\delta}$ and $\text{Nd}_2\text{NiO}_{4+\delta}$ cathode compounds were prepared by mixing in a three-roll mill; the powders and a 6% wt. ethylcellulose-terpineol solution in a 1:1 weight ratio. The resulting pastes were screen printed on both sides of a ≈ 1 mm dense electrolyte (15 mm OD). Porous electrodes were obtained after calcining the resulting screen-printed layers at 1050 °C for 2 h. A top screen-printed gold mesh was applied on the electrodes to ensure proper current collection.

Symmetrical cells were tested by Electrochemical Impedance Spectroscopy (EIS), using a Solartron 1470E/1455 FRA with an AC potential of 20 mV and a frequency sweep from 0.03 Hz to 1MHz. The EIS measurements were performed at different operation temperatures (between 450 °C and 900 °C) and with different oxygen containing atmospheres. Post mortem analysis of the symmetrical cells was done by Scanning Electron Microscopy (SEM) using a JEOL JSM6300 electron microscope.

The best electrode material, $\text{La}_{1.5}\text{Pr}_{0.5}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_{4+\delta}$, was screenprinted on Ni-YSZ/YSZ/GDC anode supported fuel cell, provided from Forschungszentrum Jülich, and it was tested in fuel cell mode. For that purpose, H_2 -reduced cell was measured in the SOFC mode: Ni-Yttria stabilized Zirconia anode chamber was fed with moist pure hydrogen, whereas synthetic air was introduced in the cathode chamber. The humidity level of hydrogen was assumed to be 2.5 % vol. and the total flow on each chamber was $200 \text{ mL} \cdot \text{min}^{-1}$.

3. Results and discussion

3.1. Characterization of $\text{La}_{2-x}\text{A}_x\text{Ni}_{1-y}\text{B}_y\text{O}_{4+\delta}$ compounds

3.1.1. Cell parameters and δ determination

XRD patterns of the different compositions (see labeling in Table 1) are presented in the Figure 1. The diffraction peaks of all samples can be assigned to the $\text{La}_2\text{NiO}_{4+\delta}$ phase [11, 30] with an orthorhombic structure [30-32]. In order to investigate the influence on the crystal structure of La partial substitution, different Pr ratios were studied. Firstly, 25 % molar of Pr (LPNO) was substituted in La site obtaining a single phase (Figure 1), i.e. no traces of other oxides were detected to the limit of X-ray diffraction measurement. However, the 50% molar substitution of La by Pr (LPNO11) produces the apparition of a second phase. It seems that the increase in the Pr amount [24, 25] leads to the space group transition from *Fmmm* to *Bmab*, and the apparition of an impurity which could be assigned to $\text{La}_3\text{Ni}_2\text{O}_7$ phase.

Regarding Ni position, only 20 % molar was substituted by Co, permitting to preserve the orthorhombic structure of the parent $\text{La}_2\text{NiO}_{4+\delta}$. Finally, a double substitution of Pr and Co (LPNCO) in La and Ni position, respectively, was carried out. As can be inferred from Figure 1 both cations are well incorporated in the parent $\text{La}_2\text{NiO}_{4+\delta}$ structure. The stability of these synthesized materials was checked previously [33] and it was confirmed that after annealing for two weeks in air at 750 °C the powders do not showed secondary phases.

In order to shed further light on the influence of the cations on the structure, the lattice parameters were obtained by Rietveld refinement [34]. This method allows elucidating the structural changes induced by the introduction of the different cations. For the cell refinement, the position and occupancies were assumed from Skinner *et al.*[35]. The structural parameters values obtained and presented in the Table 2 are in agreement with the values calculated by Rabenau *et al.* [36] and Jorgensen *et al.*[37]. All materials prepared in this study exhibit an orthorhombic *Fmmm* [25, 26, 37-39] space group at room temperature with La occupying the *8i* site position, Ni occupying the *4a* and oxygen occupying four sites (*8e*, *16j*, *8i*, and *32p*) with fractional occupancies using the values that appear in literature (Table 2).

The size and nature of the La and Ni site affect the structure and properties of this K_2NiF_4 type compounds. For instance, the size of La-site ions in 9-fold coordination affects predominantly *c* distances [40]. Thus, partial substitution in La-site by smaller cations should decrease the *c* distance. The *c* cell parameter contraction [41] obtained by the introduction of the Pr^{+3} with a smaller ionic radius cation (Table 2) validates the aforementioned statement. Furthermore, Pr increases the Ni-O bond covalency and the La/Pr-O distance, as can be ascribed from Figure 2. On the other hand, a negligible reduction in the *a* and *b* cell parameters are induced when partial substitution of La with Pr is done. The concomitant effect of the Ni-O bond strength and Pr radius produces a huge reduction in the cell volume (Table 2).

Regarding the Ni position, the partial substitution by Co produces a small change in the cell volume. It has been suggested, that the variation of the covalency/ionicity nature of the Co-O bonds in this type of materials [42] is associated with the transition of the metal spin state (HS –High Spin or LS- Low Spin) [39]. For instance, Co can be found with oxidation +2 and +3 states at room temperature and these Co atoms can adopt an intermediate spin state, producing an intermediate Co-O bond distance [43]. However, when temperature is increased, the excitation of Co atoms is produced, achieving high spin states and higher Co-O distances. Thus, it makes difficult to estimate the real ionic radius of Co atoms. In order to have an orientation, Co ionic radius values according to the spin state are written in the Table 2. Figure 2 shows that the

introduction of Co increases the covalency of the Ni/Co-O bond and also the La-O bond distance, indicating a LS state of Co atoms at room temperature. The reduction in the c cell parameter and the slightly increase of a and b length are produced due to the bond distance variation, and the values obtained in the current work match with the results previously reported [44].

Finally, the synergetic effect of both Pr and Co is reflected in the cell volume reduction of the doubly-substituted compound. It should be highlighted the significant contraction in the c distance and in the Ni/Co-O bond distance. Amow *et al.* [44] suggested that the reduction of the c cell parameter can be related with higher bond covalency of Ni-sites induced by electronic state of Co ions and the smaller La-site ions radius. The c distance reduction was also observed for the aforementioned LNCO. On the other hand, La/Pr-O bond distance increases but the contraction in c parameter and Ni/Co-O bond length is significant enough to produce the cell volume reduction.

In summary, the strength of the Ni/Co-O bond is enhanced while the La/Pr-O bond distance is enlarged, improving the anisotropic diffusion of oxygen and presumably the electrochemical properties as will be discussed below. Furthermore, there is a bigger influence of Pr and Co on c than on a and b cell parameters, which remain almost constant.

The oxygen hyperstoichiometry (δ) for LNO, LPNO, LNCO and LPNCO was determined by iodometric titration method at room temperature. Pr with an oxidation state of +4/+3, smaller radii and also higher La/Pr-O distance allows to accommodate higher content of oxygen ($\delta=0.16$) [25] in LPNO than the pristine $\text{La}_2\text{NiO}_{4+\delta}$. In addition, the Ni/Co-O bond energy, the oxidation state of Co (+2/+3) and the relatively bigger La-O distance permits to accommodate higher content of interstitial oxygen (O^{2-}) in the rock-salt layer reaching values up to $\delta=0.2$ for LNCO. Finally, LPNCO has the highest oxygen hyperstoichiometry ($\delta=0.21$) originated from the combined contribution of both cations in the structure (Table 2 and Figure 2). The variation of the oxygen hyperstoichiometry was measured by thermal gravimetric analysis (Supporting information, S1), results prove that the trend obtained at room temperature prevails for all measured temperatures. In addition, a small reduction of the oxygen hyperstoichiometry is observed due to the oxygen release and material reduction.

3.1.2. DC total conductivity measurement

Some authors have reported predominant p-type conductivity (electron holes) [45-48] of $\text{La}_2\text{NiO}_{4+\delta}$ based phases. Furthermore, the ionic conductivity in oxides with K_2NiF_4 structure consists of two independent contributions; (i) the interstitial sites in the rock-salt-type layer, due to the sufficient space to accommodate an excess of oxygen at expense of the oxidation of the Ni sites cations, and (ii) oxygen vacancies in the perovskite-like layer. The preferential oxide-ion conduction mechanism for these K_2NiF_4 -based materials has been widely studied, being higher in the a - b plane (perovskite-like layer or rock-salt-layer) than in the c plane (through the different layers) [26, 47].

The total electrical conductivity of sintered bar-shaped samples was measured in air using the four-probe DC technique in the 450-800 °C temperature range. The conductivity of each composition is represented as a function of temperature in Figure 3.

The partial substitution of La and Ni sites resulted always in higher conductivity with respect to the parent $\text{La}_2\text{NiO}_{4+\delta}$, although, two distinct behaviors can be distinguished in the Figure 3 depending on the Co presence in the structure. The Co-containing compounds exhibit a continuous increase in total conductivity with increasing temperatures (Figure 3). Compounds with Co undergo a change in the Ni/Co-O bond distance with temperature [43, 44], which can be related with the variation of the coordination environment. The higher redox activity of Co with regard to Ni induces a change in the Ni/Co-O covalency and its transport properties [39]. Furthermore, at high temperatures there is a transition from low-spin to high-spin, and it can be ascribed to a thermal expansion of the lattice and the subsequent Co-O bond enlargement. Thus, the high-spin state becomes stable affecting the electronic behavior [42]. Both variations; the spin state and Co/Ni-O bond distance in the structure, produce higher conductivities at higher temperatures for the Co-substituted materials (Figure 3). The smaller activation energy observed above 600 °C for both LNCO and LPNCO in Figure 3 can be ascribed to the reduction of the Co^{+3} ions, the subsequent oxygen release (oxygen vacancy generation and slightly diminish of the oxygen hyperstoichiometry) and the concomitant electron hole reduction. On the other hand, Co-free compounds undergo a cation reduction when the temperature is increased, which results in the concomitant release of molecular oxygen, leading to the formation of oxygen vacancies at the expense of p-type electronic carriers (electrons holes) reduction [48]. Consequently, at high temperatures the total conductivity decreases for these Co-free compounds (LNO, NNO and LPNO), since the effect of the reduction of electron hole concentration prevails over the thermal activation on p-type conduction and the oxygen vacancies generation, as can be inferred from Figure 3.

In addition, the replacement of Ni by Pr reduces the cell parameters but increases the total conductivity as has been described before [41]. Since the electronic conductivity prevails over the oxygen conductivity [49] in the measured temperature range, the total conductivity enhancement would be associated with the electronic conductivity promotion connected with the shrinkage of the Ni-O bond distances.

3.1.3. Electrochemical impedance spectroscopy measurements

3.1.3.1. Temperature influence on EIS results

In order to study the performance of the different materials as SOFC cathodes, symmetrical cells were tested by means of Electrochemical Impedance Spectroscopy (EIS). Inks of different compounds were screen printed on both sides of a dense GDC. SEM cross-section images of each compound after electrochemical measurements (Supporting information, S2) revealed electrodes thickness around 22-30 μm and adequate electrodes porosity for gas diffusion.

The enhancement of the electrocatalytic properties with the co-doping is shown in Figure 4 in terms of the electrode polarization resistance (R_p), obtained upon equivalent-circuit modelling. Dissociation of molecular oxygen into atomic oxygen ions [50], oxygen diffusion and surface oxygen coefficients [26, 38, 51] are thermally-activated and thus R_p decreases with temperature. La and Ni substitution by Pr and Co, respectively, enhances significantly the electrode performance, i.e. R_p is reduced for each synthesized compound with respect to the parent $\text{La}_2\text{NiO}_{4+\delta}$. At higher temperatures the lowest values are obtained by NNO, whereas LPNCO exhibits better performance at low temperatures (< 650°C).

On the other hand, LNCO, which shows the highest total conductivity (Figure 3), has the highest polarization resistance when it is compared with the other co-doped compounds. This suggests that there is not a direct relationship between the total conductivity and the Rp behavior, other factors can affect the polarization resistance; as the interface electrode-electrolyte, the electrode microstructure or the electrocatalytic activity of the compound for the oxygen reduction reaction (ORR).

The polarization resistance of the parent electrode material (LNO) exhibits higher value ($10.3 \Omega\cdot\text{cm}^2$) than the values obtained in literature by Philippeau et al. [52] ($2.2 \Omega\cdot\text{cm}^2$) or Sharma et al. [53] at $600 \text{ }^\circ\text{C}$ ($3.32 \Omega\cdot\text{cm}^2$), indicating that the electrode microstructure can be improved and smaller electrode particle size would reduce the Rp. Likewise, the incorporation of Pr and Co in the structure leads to a huge reduction of the polarization resistance, achieving values of $1.95 \Omega\cdot\text{cm}^2$ at $600 \text{ }^\circ\text{C}$, i.e., Rp of LPNCO cathode is five times smaller with respect to LNO electrode. If these results are compared with previous reports[52] on $\text{Pr}_2\text{NiO}_{4-\delta}$ electrode (Rp at $600 \text{ }^\circ\text{C}$; $0.83 \Omega\cdot\text{cm}^2$ [53] and $0.28 \Omega\cdot\text{cm}^2$ [52]), the present LPNCO electrode exhibits lower performance, indicating that further improvement in the electrode microstructure should be done. Despite presenting a good performance, the stability of $\text{Pr}_2\text{NiO}_{4-\delta}$ has been questioned [24, 25, 54] under realistic operating conditions. Therefore, LPNCO electrode ,exhibiting higher stability[33], seems to be a better cathode candidate for IT-SOFC. Furthermore, the double substitution of Pr and Co in the structure (LPNCO) leads to better electrocatalytic promotion at low temperatures with respect to other Co-containing compounds belonging to the Ruddlesden-Popper series ($\text{LaSrCoO}_{4-\delta}$, $9 \Omega\cdot\text{cm}^2$ at $600 \text{ }^\circ\text{C}$ [55]).

Concerning the activation energy, there is not a big difference between all compounds studied in the current work. As it has been previously reported [22, 23, 41, 56], the introduction of Pr with double oxidation state (+2, +3) improves the electrocatalytic activity of the electrode for the ORR, hence, the activation energy is reduced. Indeed, LPNCO electrode shows the best electrochemical results at low temperatures, whereas at the highest tested temperatures LPNCO has similar behavior than the well-studied NNO. The doubly-substituted compound combines both; (i) electrocatalytic improvement thanks to Pr [22, 23, 41, 56, 57] incorporation and (ii) the induced reduction of Co(Ni)-o-Co(Ni) bond by the Co partial substitution, which improves the electronic conductivity of the compound.

3.1.3.2. Co-doped influence on EIS results

The materials synthesized and partially substituted in A and B positions by Pr and Co could improve the performance of the parent LNO. In order to understand this enhancement, EIS spectra recorded at $750 \text{ }^\circ\text{C}$ (Figure 5) and $600 \text{ }^\circ\text{C}$ (Figure 6) were fitted to an equivalent circuit and the data obtained were compared. All compounds were fitted by $\text{LR}_\Omega(\text{R}_{\text{LF}}\text{CPE}_{\text{LF}})-(\text{R}_{\text{MF}}\text{CPE}_{\text{MF}})$ circuit at $750 \text{ }^\circ\text{C}$ and $600 \text{ }^\circ\text{C}$, where L is the inductance related to platinum wires and equipment connections; R_Ω is a real resistance associated with the electrolyte resistance (dependent on the operation temperature), and CPE is a Constant Phase Element.

Two different contributions can be distinguished in the Nyquist plot for all compounds at $750 \text{ }^\circ\text{C}$ and $600 \text{ }^\circ\text{C}$ (Figure 5a and Figure 6a), one related to low frequency (LF) processes (3-70 Hz) and the other associated with medium frequencies (MF) processes (2-8 kHz). The capacitances related with LF processes are in the range of $4\cdot 10^{-4} \text{ F/cm}^2$ and $1\cdot 10^{-2} \text{ F/cm}^2$, whereas at MF the

capacitances are in the range of $6 \cdot 10^{-5}$ F/cm² and $5 \cdot 10^{-3}$ F/cm² and are in accordance with the values obtained by Mauvy et al. [50]. According to these capacitances determined from the equivalent electrical circuit fitting, and the results reported from other authors [50, 58-60], the arc at low resistance (LF) can be related with the charge-transfer reaction occurring on the electrode/gas interface[61]. However, the resistance at MF should be attributed to the electrode/electrolyte charge-transfer reaction [58]. As can be inferred from the graphs (Figure 5c and Figure 6c), the incorporation of a dopant in La site or Ni site improves the performance of the electrode, obtaining lower polarization resistance values and enhancing LF and MF processes[61].

As the operation temperature decreases, the oxygen ions transport in the GDC electrolyte is reduced and it could be ascribed to the scarce transport in the GDC grain boundary [62]. Therefore, the transport of oxygen ions from the electrode to the electrolyte is reduced, producing an increase in resistance at medium frequencies. It can conclude that MF contribution is originated from the O₂- transfer in the electrode/electrolyte interface, since the results obtained in the present work match with the frequency and associated capacitances shown by Dusastre et al. [58].

The reduction of the R_{LF} due to Pr incorporation can be ascribed to the enhancement of the catalytic properties [22, 23] and the electronic conductivity promotion at the surface [63, 64], both, associated with the mixed valence of Pr (+3/+4). Furthermore, Bassat et al. reported the reduction of the activation energy for the oxygen surface exchange coefficient (k*) and the oxygen diffusion coefficient (D*) [65] with the Pr incorporation. This, coupled with the higher hyperstoichiometry ($\delta=0.16$) [66] improve the oxygen reduction reaction on the cathode surface, i.e., the resistance at low frequency is reduced.

On the other hand, the introduction of Co in the Ni-site can slightly improve the polarization resistance related with LF and MF at 750 °C. It has been suggested that, as a rule of thumb, the addition of Co in the La₂NiO_{4+ δ} structure produces an enhancement in the oxygen surface exchange coefficient (k*) and the reduction of the activation enthalpy for this process [67-69]. Then, Co-containing materials may have higher electrocatalytic activity than non-substituted compounds[70], and low frequency processes (molecular oxygen dissociation) are improved. However, at lower temperatures (below 600 °C) it seems that the presence of Co in the structure has no impact in the polarization resistance, since both resistances are very similar to LNO cathode.

Moreover, the presence of both Co and Pr (LPNCO) in the structure improves the performance of the cathode, due to the combination of features from both dopants, and leads to the lowest polarization resistance obtained in the current work at low temperature (< 600 °C). The beneficial influence of Pr and Co in the structure is reflected in the low polarization resistance and it can be mainly linked with the LF processes enhancement (Figure 6).

Finally, a short stability test of LPNCO electrode was performed at 900 °C by means of EIS recorded with time (Figure 7), obtaining a degradation slope as low as $1 \cdot 10^{-6}$ $\Omega \cdot \text{cm}^2/\text{min}$. This value is only mostly related with analytical error. According to this results and the stability performed in air at 750 °C for two weeks[33], the LPNCO exhibits good stability and performance at intermediate temperatures.

3.1.4. Fuel cell mode performance

The fuel cell performance of the LPNCO/CGD/YSZ/Ni-YSZ (Figure 8 (a) and (b)) fully assembled cell is shown in Figure 8 (c) at different temperatures. Maximum power densities achieved with these operating conditions are 385, 258 and 126 $\text{mW}\cdot\text{cm}^{-2}$ at 700, 650 and 600 °C, respectively. The high OCV value is maintained at all tested temperatures, indicating the goodness of the sample sealing.

These results confirm that LPNCO electrode seems a suitable cathode for IT-SOFC applications. An et al.[71] obtained power densities of 76 $\text{mW}\cdot\text{cm}^{-2}$ at 600 °C using a pure electronic conductor cathode (LSM) on Ni-YSZ/YSZ tape casted anodes, without any active layer. Leng et al.[72] tested a fully-assembled fuel cell composed of LSM-YSZ/YSZ/Ni-YSZ, and they obtained at 700 °C a maximum power density of 267 $\text{mW}\cdot\text{cm}^{-2}$. Moreover, Tsai et al.[73] studied a LSM/YSZ composite cathode on a YSZ/Ni-YSZ anode cell with a $(\text{CeO}_2)_{0.84}(\text{Y}_2\text{O}_3)_{0.16}$ as interfacial layer, with a cell performance of $\sim 250 \text{ W}\cdot\text{cm}^{-2}$ at 0.7 V and 700 °C, whereas the LPNCO-based SOFC, tested in the present work, shows a power density of 308 $\text{W}\cdot\text{cm}^{-2}$ at the same voltage. On the other hand a Ni-YSZ/YSZ/GDC anode supported fuel cell has been measured by Serra et al. [74], using a $\text{La}_{0.58}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ (LSFC) cathode. The power density obtained at 0.7 V was 293 $\text{mW}\cdot\text{cm}^{-2}$ showing a similar performance than the LPNCO-based cell tested in this work. However, authors were aware that further improvement had to be done in the SOFC cathode microstructure in order to improve the overall cell performance [74]. Finally, Zhang et al. measured $\text{La}_2\text{Ni}_{0.98}\text{Mg}_{0.02}\text{O}_{4+\delta}$ and $\text{La}_2\text{NiO}_{4+\delta}$ as cathodes on a $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-d}$ /NiO-Samarium Doped Ceria system obtaining a power density of 277 $\text{mW}\cdot\text{cm}^{-2}$ and 236 $\text{mW}\cdot\text{cm}^{-2}$, respectively[75].

4. Conclusions

The present study summarizes the influence of different dopants on the $\text{La}_{2-x}\text{A}_x\text{Ni}_{1-y}\text{B}_y\text{O}_{4+\delta}$ structure for the IT-SOFC cathode performance. The incorporation of Pr in the La site and Co in Ni site induces the reduction of the *c* cell parameter length, even though the orthorhombic *Fmmm* structure is preserved. Additionally, Ni/Co-O bond distance is reduced, leading to an electronic conductivity improvement, while the enlargement of La/Pr-O bond and the higher hyperstoichiometry promote the ionic conductivity. On the other hand, even all Ruddlesden-Popper materials studied in the current work show a p-type conductivity, the conductivity behavior depends on the dopant incorporated in the structure. For instance, Co confers higher total conductivity over the full range of temperature measured, whereas the Co-free compounds conserve the metal-like behavior of the parent $\text{La}_2\text{NiO}_{4+\delta}$.

The structural changes promoted by the Co and Pr incorporation and the electrocatalytic properties of the selected dopants play an important role in the oxygen reduction reaction enhancement, since the *R_p* is reduced for all compounds tested. The best cathode performance was obtained for $\text{La}_{1.5}\text{Pr}_{0.5}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_{4+\delta}$ compound at the tested temperatures, with similar recorded values than the well-studied $\text{Nd}_2\text{NiO}_{4+\delta}$ SOFC cathode. However, the lower activation energy of $\text{La}_{1.5}\text{Pr}_{0.5}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_{4+\delta}$ best the electrode performance at operation temperatures below 650 °C. The electrochemical performance and stability tests obtained for the $\text{La}_{2-x}\text{Pr}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_{4+\delta}$ compounds yield promising results for the selection of these synthesized compounds as IT-SOFC cathodes.

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Captions

Table 1: List of the different synthesized compositions and its abbreviation name used in the text.

Table 2: Refined structural parameters for $\text{La}_{2-x}\text{A}_x\text{Ni}_{1-y}\text{B}_y\text{O}_{4+\delta}$ and oxygen hyperstoichiometry (δ) at room temperature. Data are refined in *Fmmm* orthorhombic space group. Numbers in parentheses are the standard deviations of the significant digits.

Figure 1: XRD patterns of $\text{La}_{2-x}\text{A}_x\text{Ni}_{1-y}\text{B}_y\text{O}_{4+\delta}$ and $\text{Nd}_2\text{NiO}_{4+\delta}$ after sintering recorded at room temperature. Impurities are marked on the graph (*).

Figure 2: From top to bottom: oxygen hyperstoichiometry (δ), cell parameters and bond distances obtained by iodometric titration and Rietveld refinement for the different $\text{La}_{2-x}\text{A}_x\text{Ni}_{1-y}\text{B}_y\text{O}_{4+\delta}$ compositions.

Figure 3: Total conductivity results in air for the different $\text{La}_{2-x}\text{A}_x\text{Ni}_{1-y}\text{B}_y\text{O}_{4+\delta}$ synthesized compounds.

Figure 4: Polarization resistance values in an Arrhenius plot of the different MIEC electrodes in a temperature range from 900 °C to 550 °C. The numbers in brackets are the activation energies (E_a) of each compound.

Figure 5: (a) Nyquist and (b) Bode plots at 750 °C for the different electrodes in air. Results of the equivalent circuit fitting at 750 °C; (c) resistance, (d) capacitance and (e) frequency of the associated processes.

Figure 6: (a) Nyquist and (b) Bode plots at 600 °C for the different electrodes in air. Results of the equivalent circuit fitting at 600 °C; (c) resistance, (d) capacitance and (e) frequency of the associated processes.

Figure 7: LPNCO electrode polarization resistance values time stability in air at 900 °C.

Figure 8: SEM images of (a) cross section of fully-assembled fuel cell of LPNCO on anode supported fuel cell with an GDC interlayer; and (b) SEM magnification of particles for both electrodes. (c) Full fuel cell performance plots for LNPCO/GDC/YSZ/Ni-YSZ at different temperatures.

Figure S1: Rietveld refinements (lines) of $\text{La}_2\text{NiO}_{4+\delta}$ data (circles), shown above the corresponding difference patterns. Vertical bars indicate the Bragg positions.

Figure S2: SEM micrographs of the different electrodes measured as symmetrical cells.

Figure S3: Oxygen hyperstoichiometry as function of temperature in air. Results obtained by TGA.

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