Performance of $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4_{\pm \delta}$ Ruddlesden-Popper manganite as electrode material for symmetrical solid oxide fuel cells. Part A. The oxygen reduction reaction

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**ABSTRACT**

The electrochemical performance of $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_4_{\pm \delta}$ (LS515M) as SOFC cathode was studied using Electrochemical Impedance Spectroscopy (EIS) measurements. The influence of the sintering temperature on the electrochemical performance was examined in air for $\text{Au/LS515 M/GDC/YSZ/GDC/LS515 M/Au}$ symmetrical cell. For the oxygen reduction reaction, the electron transfer between the electrode and oxygen, and the incorporation of oxygen ions into the electrode are the main controlling processes of oxygen reduction reaction for electrodes sintered at 1150 and 1200 °C. Increasing the sintering temperature up to 1250 °C increases the Sr diffusion through GDC interlayer, which leads to Sr accumulation at the GDC/YSZ interface with SrZrO3 formation and subsequent cell performance degradation. The lowest area specific resistance (ASR) values was obtained for the LS515 M electrode sintered at 1150 °C.

**Keywords:**
Symmetrical SOFC
Ruddlesden-Popper
Manganite
Electrochemical impedance spectroscopy
Oxygen reduction reaction

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**1. Introduction**

The generation of energy through Solid Oxide Fuel Cells (SOFC), an electrochemical device that operates at high temperature, is an option of energy solution since this highly efficient technology is based on the direct conversion of fuels into electricity with efficiency values that are theoretically higher than those of thermal machines (such as motors, turbines, etc.). However, one of the main critical issues to solve for viable SOFCs is their high prices mainly related to the difficulty in finding and producing efficient, reliable, durable and cheap cell materials for the three main components of the device, i.e. the anode, the electrolyte and the cathode [1,2].

In recent years, researchers have focused on finding better electrocatalysts for electrode reactions by studying new structural arrangements exhibiting some anisotropy (two-dimensional structure) in order to find mixed ionic and electronic conducting materials (MIEC). The mixed conductivity can potentially extend the triple phase boundary (TPB) active region over the entire electrode, thus greatly reducing the electrode polarization at low operating temperature. The replacement of a pure electronic conductor such as LSM ($\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$) state-of-the-art material by a Mixed Ionic Electronic Conducting (MIEC) perovskite such as LSCF ($\text{La}_{0.8}\text{Sr}_{0.2}\text{CoFeO}_3$) is expected to significantly decrease the polarization resistance, which is seen as a consequence of the fast surface oxygen exchange kinetics and the high diffusivity for oxygen of the LSCF perovskites [3]. At 800 °C, under the same operating conditions, the polarization resistance of LSM cathode (YSZ electrolyte) is $3.8 \Omega \cdot \text{cm}^2$ while for LSCF cathode (SDC electrolyte) it is $0.05 \Omega \cdot \text{cm}^2$, with activation energies of 2.2 eV and 1.3 eV, respectively [4,5]. The Mixed Ionic Electronic Conductors based on the Ruddlesden-Popper phases have also attracted significant attention as alternative cathodes in place of the conventional perovskites. For $\text{La}_3\text{NiO}_4_{\pm \delta}$ cathode deposited by screen-printing on GDC electrolyte, the polarization resistance reported at 700 °C is $0.42 \Omega \cdot \text{cm}^2$ [6].

The different members of the $\text{La}_3\text{Sr}_{2-x}\text{MnO}_{4-x}$ ($x = 0.4, 0.5, 0.6$) [7,8] series and the recently published $\text{La}_{0.5}\text{Sr}_{1.5}\text{MnO}_{4-x}$ series [9] have become very interesting due to their good redox stability, electrical conductivity and acceptable electrochemical behavior in both oxidizing...
and reducing atmosphere. Particularly, the area specific resistance (ASR) at 800 °C reported for La0.5Sr1.5MnO4±δ as cathode material was 0.39 Ω cm² with an activation energy of 1.39 eV [7]. The impedance measurements carried out at different oxygen partial pressures (pO₂) provided some knowledge of the oxygen reduction mechanism occurring at the electrode. The resistance variation as a function of oxygen partial pressure (pO₂) allowed to associate with certainty the response at high frequency to the charge transfer reaction at the triple-phase boundary. However, the process related to the low frequency contribution was not clearly identified, the authors suggesting that it may be related either to surface diffusion of the dissociative adsorbed oxygen or the gas diffusion phenomenon [7,10]. It is clear that the impedance strongly depends on the nature of the electrode. Various processes may be limiting depending on electrode composition, processing parameters, and the measurement conditions, although there are discrepancies about the nature of the elementary processes that contributes to polarization resistance in the case of the oxygen reaction mechanism [11].

Electrochemical impedance spectroscopy (EIS) has proven itself as a powerful technique for breaking down the losses within a SOFC, but also to provide insight into which component and/or process primarily degrade during operation [12,13]. This work describes and thoroughly analyzes the influence of electrode sintering temperature for the symmetric cells with LSS15 M electrode, based on the determination by EIS of the electrochemical behavior. The detailed EIS study is divided into two parts and thus published as a series of two articles. The first part concerns the oxygen reduction reaction (cathode) and the second part the hydrogen oxidation reaction (anode). The results are discussed in order to correlate the different contributions that constitute the cathode and anode polarization resistances with the nature of the elementary processes of the corresponding electrode reactions and the characteristic parameters of the electrode elaboration process.

2. Experimental

2.1. Material synthesis and characterization

La0.5Sr1.5MnO4±δ (LSS15 M) powder was prepared by the citric acid sol gel method (also referred to as the citrate-nitrate sol-gel method), using La2O3 (Alfa Aesar 99.99%), SrCO3 (Alfa Aesar 99.9%) and MnCO3 (Sigma Aldrich 99.9%). The La2O3 and SrCO3 powders were pre-calcined at 1000 °C and 500 °C for 1 h, respectively. These precursors were dissolved in an excess (two times the amounts corresponding to the stoichiometric conversion of oxides/carbonate into nitrates) of nitric acid HNO3 (Merck ≥95%) and citric acid (CA, Merck ≥99.5%) added in a molar ratio of CA:nitric = 3:1. The solution was stirred and heated at 90 °C, and, subsequently, polyethylene glycol (≥99%, Panreac) was added as polymerization agent, in a proportion of 1.5 mL per gram of targeted product. The heating was kept over several hours until all water has been evaporated and the polymerized complex started to form. The resulting mixture was heated at 180 °C and a viscous gel was obtained which was subsequently calcined at ~300 °C in air for about 3 h, then brought to ~500 °C to ensure total organic matter decomposition. Finally, the sample was pressed into pellets, and then sintered in air at 1100 °C during 6 h using two successive heating cycles, with intermediate grinding and pelletizing steps. The sample was characterized by powder X-ray diffraction (XRD) using a Bruker D8 ADVANCE powder diffractometer working in Bragg Brentano geometry with Cu-Kα1,2 radiation and Lineal LynxEye detector.

2.2. Chemical reactivity

Possible chemical reactivity between La0.5Sr1.5MnO4±δ (LSS15 M) and YSZ, LSGM and GDC was studied in air at high temperature. Preliminary, LSS15 M powder was mixed with a powder of YSZ ((ZrO2)/82(Y2O3)/18, Tosoh-Zirconia TZ-8Y), LSGM (La0.8Sr0.2Ga0.8Mg0.2O3-d, Nextech Materials, USA, # 121501) and GDC (Ce0.8Gd0.2O1.95 Nextech Materials, USA, # 112010) in 50:50 wt ratio, pressed into pellets and heat treated at 1200 °C for 10 h in the case of YSZ and GDC and at 900 °C for 10 h for LSGM. When no reactivity was observed for these first conditions, higher temperatures were considered, in agreement with the studied range of temperature for electrode sintering. The resulting samples were analyzed by X-ray diffraction (XRD) using a Bruker D8 ADVANCE powder diffractometer working in Bragg Brentano geometry with Cu-Kα1,2 radiation equipped with 1D Bruker LynxEye detector.

2.3. Elaboration of symmetrical cells

Dense YSZ electrolytes (15 mm in diameter and 1.8 mm in thickness after sintering) were prepared with YSZ commercial powder (Tosoh-Zirconia TZ-8Y). Initially, YSZ powder was placed in a circular holder, applying pressure at 1 Ton for 2 min, using a manual die-casted. Subsequently, the YSZ pellets were isostatically pressed at 1700 bar for 15 min and sintered at 1400 °C for 12 h. The last step was the polishing of the as-obtained pellets. The polishing was necessary to ensure the parallelism between both faces and adjust the thickness. The relativity density of the electrolytes was, in general, of 96%. Theinks were prepared by mixing the powder with a dispersant and an organic binder. The material (usually 3 g) was mixed with 2% w/w of organic dispersant (T01 Cerlase). The mixture was submitted to planetary milling for 5 h using zirconia jar filled with zirconia balls (1 cm) and covered with ethanol (2/3 vol). Later, the mixture (powder + ethanol) was dried overnight. The resulting powder was mixed with 65% w/w of a terpenoid binder (Mixton EC3, Ferro Couleurs, France), and homogenized with a three-roll mill. A GDC buffer layer was deposited by screen printing. The GDC ink was prepared according to the procedure described above, using GDC (HSA Rhodia, Paris, France) pre-sintered at 1100 °C. The GDC layer was heat treated in air at 1250 °C for 3 h.

LSS15 M ink was screen-printed on each side of the GDC/YSZ/GDC sandwich. The range of sintering temperature for the electrode active layer was chosen based on the dilatometric curve for LSS15 M. The dilatometric measurements were carried out in air from 50 °C to 1600 °C, using a Netzsch DIL 402C system in horizontal geometry. The obtained curve (Fig. S1 in Supplementary Information) can be divided into three parts as the temperature increases: the first section (for T < 1100 °C) is linear and corresponds to the simple thermal expansion of the powder grains, the second corresponds to the beginning of the sintering process with neck formation between grains (for 1100 °C < T < 1300 °C) and the third represents the elimination of porosity in part due to grain growth, i.e. the section in which the sintering rate is the highest. The best range of temperature for the elaboration of the conducting but porous electrode layer is the second one, which corresponds generally to the best compromise. Consequently, in this case, the LSS15 M electrode active layers were sintered in air for 10 h using a temperature of T = 1150, 1200 or 1250 °C. In order to improve the current collection with the collecting grid of the EIS setup, a thin gold layer was deposited by sputtering on the top of each electrode. The cross-sectional studies of cells before EIS test were performed using scanning electron microscopy (SEM, JSM-7800F, JEOL, Japan) and energy dispersive X-ray spectroscopy (EDS SDD, X-Max 80 mm² Oxford Instruments AztecEnergy, England) analysis. A
Camra SX100 electronic probe microanalyzer (EPMA) was also used to complete the elemental analysis with Wavelength-Dispersive Spectrometry (WDS). Back scattered electron images were carried out at 15 kV, 15 nA and X-ray mappings were carried out at 15 kV, 40 nA. For mapping, the crystals used were a TAP to detect Sr-, Zr- and Y-Lz, a LiF to detect Ce-Lz and Mn-Kz and a PET to detect Gd- and La-Lz.

2.4. Electrochemical measurements

The symmetrical cells were evaluated performing electrochemical impedance spectroscopy (EIS) in a single atmosphere. The experiments were carried out with a Solaron SI 1260 frequency response analyzer in the 10 mHz and MHz frequency range, using an AC signal of 50 mV amplitude under OCV conditions. Such device allows the simultaneous measurement of three symmetric cells, ensuring identical experimental conditions. The electrochemical measurements were carried out in air with a flow rate of 150 mL/min. Before starting each measurement, the samples were stabilized at high temperature (~850 °C) until there is no variation in the impedance spectra (~24 h). Data were collected every 25 °C, from 850 °C to 600 °C, with a temperature accuracy of ±1 °C and a stabilization time of 1 h at each temperature. The raw data were used to fit the spectra to equivalent circuits using the ZView software (version 3.4 c) [14]. All impedance data were normalized with the electrode area (1.02 cm²). For better clarity and in view of our objective to focus our study on the limitations due to electrode polarization, the reported impedance spectra were plotted in the first (positive) quadrant of the -Z’ vs Z’ space and set to zero to not represent the effects of inductance L due to electric leads and series resistance Rₚ, respectively.

3. Results and discussion

3.1. Chemical reactivity

Fig. 1 shows the XRD patterns for each electrode/electrolyte mixture before and after heat treatments in air. In the case of YSZ (Fig. 1a), L5515 M reacts to form the insulating phase SrZrO₃ with lanthanum strontium manganite (LaₓSr₂−ₓMnO₃) by-product. Apparently, an LaxSr₂−ₓMnO₄₋ₓ-type phase remains after heating but in a very low proportion. The formation of SrZrO₃ as secondary phase has been previously reported between LSCF cathode and YSZ electrolyte. This high reactivity begins around 800°C after 200 h of heating, and is more evident above 1100 °C when La₂Zr₂O₇ begins to form concomitantly [4,15]. Even if the first probed sintering temperature in air was lower with respect to other electrolytes, the chemical reactivity of La₄-0.5Sr₁.5MnO₄₋₄₃ with LSGM electrolyte is also high, resulting in the formation of additional phases such as LaSrGaO₄ and La₂O₃ with partial decomposition of the initial RP manganite (Fig. 1b). Such result is in disagreement with what was recently described by J. Zhou et al. [16], who reported that La₄-0.5Sr₁.5MnO₄₋₄₃ is chemically compatible with LSGM (La₀ₙSr₀.₉Gd₀.₃Mg₀.₇O₃₋₃), the difference being possibly due to the higher Sr content of both phases in our case. The chemical compatibility between L5515 M and GDC in air shows that, after a heat treatment up to 1250 °C, both materials remain unchanged and no major modification of XRD patterns or additional peaks are evidenced (Fig. 1c). This stability with GDC electrolyte has also been proven for LSM [17] and La₂Sr₂₋ₓMnO₄₋ₓ (x = 0.4, 0.5, 0.6) synthesized in different conditions, but tested at lower temperature (1000 °C) [7,8]. Nevertheless, after heating at 1300 °C, an additional (La₂Sr)₃Mn₂O₇ phase is formed, possibly due to the fact that the high temperature begins to destabilize the n = 1 RP structure in favor of higher terms of the RP series. In this precise case, it is worth mentioning that during the synthesis of LaSr₂Mn₂O₇, such phase only begins to form at 1200 °C in coexistence with a Sr₂MnO₄ phase, and becomes single phase at 1400 °C [18]. As a collateral effect of this reactivity, the GDC and LSM diffraction peaks are slightly shifted (in 20), meaning a possible change in the phases’ composition, i.e. a cationic cross-diffusion. For example, for cubic GDC, the XRD peaks are shifted to low angles, corresponding to an increase of the corresponding a lattice parameter, in agreement with the possible substitution of Ce⁴⁺ (ionic radius in nine-fold coordination R⁴⁺₆ = 1.02 Å) and/or Gd³⁺ (R³⁺₆ = 1.107 Å) by La³⁺ (R³⁺₆ = 1.216 Å) and/or Sr²⁺ (R²⁺₆ = 1.31 Å) [19].

3.2. Influence of sintering temperature

The EIS measurements in air were carried out from 835 to 600 °C in the frequency range between 1 MHz and 10 mHz. For all impedance spectra presented below, the numbers at the top indicate the frequency logarithms. The impedance spectra of Au/L5515 M/GDC/YSZ/GDC/L5515 M/Au cells sintered at 1150, 1200 and 1250 °C are shown in Fig. 2 as a function of the temperature of measurement.

Globally, and as a first approach to those results, the sintering temperature affects noticeably the electrode polarization resistance (Rₚ). Such phenomenon is quite common and is generally associate to the following effects of the temperature on the electrode microstructure: a too low temperature allows to keep a large surface area within the porous electrode but causes a poor adherence between electrode and GDC buffer layer. Increasing the temperature of elaboration of the electrode improves the contact between electrode and electrolyte, but generates an increase in the grain size decreasing the specific surface area of the electrode [20]. Even if such explanation seems reasonable, we decided to embark on a deeper examination of the EIS data in order to try to correlate them to the exact effect of the sintering temperature.

Fig. 3 shows the spectrum obtained at 800 °C for the electrodes sintered at 1150, 1200 and 1250 °C and the corresponding equivalent circuits used to fit the spectra.

3.3. Electrode sintered at 1150°C

As seen in Fig. 3a, the obtained impedance spectrum is asymmetric in shape, indicating more than one processes contribute to electrode polarization resistance. The circuit LRₛ(RₛCPE1)(RₛCPE2) that describes the spectra obtained between 835 and 600 °C consists of an inductance (L) due to electrical leads, an ohmic resistance (Rₛ) and two (R-CPE) components that refer to the limiting electrode processes. The Constant Phase Element (CPE) is defined by two values CPE-T and CPE-p. The capacitance values (C) were calculated using the following equation [21]:

\[
C = \frac{R^\frac{1}{p}}{\pi R^p Q^p} \tag{1}
\]

where R is the resistance, Q (T) is the pseudo-capacitance and p is an exponent. The relaxation frequency f of each electrode process corresponding to a specific (R-CPE) component was calculated from:

\[
f_{max} = \frac{1}{2\pi RC} \tag{2}
\]
Fig. 1. XRD patterns after reactivity test of LS15 M in air with (a) YSZ at 1200 °C, (b) LSGM at 900 °C, (c) GDC at 1200, 1250 and 1300 °C.
where $S$ is the electrode surface area (cm$^2$) and the factor 2 accounts for the fact that the cell is symmetrical.

According to Fig. 4 and Table 1, two processes contribute to the polarization resistance. A first arc in the high frequency region ($10^5$ and $10^6$ Hz) and a second one in the ultra-medium frequency region ($10^3$ and $10^4$ Hz), labeled as HF and MF, respectively. The activation energies of the whole electrode process and of each elementary contribution were obtained from the Arrhenius plots of the ASR and each elementary component resistance as a function of temperature (Fig. 4a and b). As depicted in Fig. 4a, the overall activation energy obtained from the ASR is 1.35(4) eV. This activation energy value is similar to that reported for other mixed ionic-electronic conductors such as LSCF (1.5–1.65 eV) [22,23], La$_2$NiO$_4$ (1.07–1.3 eV) [6,24] and La$_{0.6}$Sr$_{1.4}$MnO$_4$ (1.39–1.86 eV) [7,25]. In a similar way, the two identified controlling processes of oxygen reduction reaction are thermally activated; however, the resistive component of the medium frequency arc (MF$^c$) presents the highest contribution to the polarization resistance (Fig. 4b). For example, at 800 °C, the ASR value is equal to 1.32 Ω cm$^2$, for which $RMF^c$ corresponds to ~88% of the total resistance. This ASR is larger than that reported in air at the same temperature for La$_{0.6}$Sr$_{1.4}$MnO$_4$ cathode (0.39 Ω cm$^2$ [25]) or for LSCM (0.43 Ω cm$^2$ [26]) symmetrical electrode.

In the same way, the equivalent capacitance and relaxation frequency (Schouler methodology [27]) are characteristic parameters very useful to identify the electrode processes (Fig. 4c and d). The capacitances of each process do not vary significantly with the temperature and, in both cases, have similar values ($10^{-5}$ F cm$^{-2}$), while the relaxation frequencies are decreased by almost two orders of magnitude with decreasing temperature, signifying a thermally activated mechanism. According to the literature, the electrode process corresponding to (HM$^c$) can be tentatively attributed to the charge transfer of oxygen ions (O$_2^–$) at the interface between the electrode and electrolyte [28,29]. This limiting process with equivalent capacitances of $10^{-6}$–$10^{-5}$ F cm$^{-2}$ has been identified in LSCF cathode calcined at 800 °C [30], La$_2$NiO$_4$, calcined at 950 °C [31] and La$_{0.6}$Sr$_{1.4}$MnO$_4$, calcined at 1000 °C [7]. The simulations carried out by Sunde suggest that this contribution may be related to the lack of connectivity between electrode and electrolyte particles, which is consistent with the low sintering temperature [32]. Nevertheless, the activation energy obtained for this process (1.64(5) eV) is much higher than the value reported for the same process in La$_2$NiO$_4$, for example (0.61 eV [31]). The main contribution to ASR is the medium frequency element (MF$^d$) with capacitance values around $10^{-5}$–$10^{-4}$ F cm$^{-2}$. It can be assigned to electron transfer between the electrode and oxygen, referring to ionization of oxygen species on the surface and subsequent incorporation into the electrode [33]. A contribution of this type was identified in the electrochemical study of La$_{1.2}$Sr$_{0.8}$NiO$_{4.8}$ cathode sintered at 950 °C, with an activation energy of 1.11(3) eV [34], similar to that obtained in our case (1.29(6) eV).

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDXS) analyses were performed on the cross-section of the Au/L5S15 M/GDC/YSZ/GDC/L5S15 M/Au cell prepared at 1150 °C, before EIS test (Fig. 5a). This analysis was focused on the evaluation of the efficiency of the GDC layer as a diffusion barrier for hindering the interaction between the cathode and YSZ electrolyte, preventing the formation of insulating phases at the electrode/electrolyte interface. The SEM image with the corresponding atomic concentration mapping for La (Lx, 4.65 keV), Sr (Lx, 1.81 keV), Mn(Kz, 5.89 keV), Ce (Lx, 4.84 keV), Gd (Lx, 6.06 keV),
Y (Lx, 1.92 keV) and Zr (Lx, 2.04 keV) is shown in Fig. 5a.

A good interface between the electrode-GDC interlayer and the YSZ-electrolyte is observed, confirming the chemical and thermal compatibility of the materials. EDXS mapping of the elements indicates that, globally, all the elements are located in the phase where they are expected; nevertheless, it seems to be a very slight diffusion of Sr through the GDC interlayer, indicated by a very thin green line at GDC/YSZ interface (indicated by white arrows in Fig. 5a). In order to avoid misinterpretation due to some peaks overlap (e.g. Y and Sr) using EDXS-based atomic mapping, we performed complementary analysis using WDS-EPMA technique. In Fig. 5b, we now clearly evidence that Sr atoms diffused through the GDC interlayer to segregate at the interface between ceria and YSZ electrolyte. According to the literature the Sr diffusion may occur during the sintering heat treatment of the cell layers [35,36], promoting the formation of SrZrO3 at the GDC/YSZ interface, which somehow leads to a reduction of electrolyte ionic conductivity [37–39]. On the other hand, it has been demonstrated that the SrZrO3 formation depends on the electrode sintering temperature; for example, SrZrO3 phase is formed when the LSCF electrode is fired at 1000 °C, but not at 1100 °C [36,40,41]. Even if the techniques we used were not sufficient to confirm the presence of a perovskite phase at the interface between GDC and YSZ, it is clear that, at such high temperature, the presence of Sr in the vicinity of YSZ grains induces the direct formation of SrZrO3 insulating phase, as it has been clearly evidenced in similar treatment conditions by Chou et al. using Electron Diffraction [42]. Hence, in our case, the formation of SrZrO3 at the GDC/YSZ interface seems possible but remains limited at a sintering temperature of 1150 °C.

Table 1

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Fig. 3. Impedance spectra at 800 °C for L5S15 M electrodes sintered at (a) 1150 °C, (b) 1200 °C and (c) 1250 °C. The serial resistance has been removed for better comparison. The numbers indicate the frequency logarithms.

3.4. Electrode sintered at 1200 °C

The impedance spectrum obtained at 800 °C under air for Au/L5S15 M/GDC/YSZ/GDC/L5S15 M/Au cell prepared at 1200 °C is displayed in Fig. 3b. Globally (see Fig. 3b and Table S1), the increase of the electrode sintering temperature yields an increase of ASR; for example, at 800 °C values of 1.32 Ω cm² and 1.89 Ω cm² are obtained for the electrodes sintered at 1150 and 1200 °C, respectively. This behavior has also been reported for the well-known LSCF cathode, for which the ASR cathode was increased with sintering at 1000 °C (0.04 Ω cm²) rather than 850 °C (0.03 Ω cm²). In that case, the authors suggested that the high temperature led to the densification of the electrode, making it more prone to gaseous diffusion limitations [23]. The spectra obtained in the whole range of temperature were deconvoluted into two arcs: a large arc at the ultra-medium frequency (10⁴ and 10² Hz) and a small one at medium frequency (10²-10¹), labeled as MF¹ and MF², respectively. Table S1 lists the electrical parameters for each element derived from spectra fitting. Fig. 6 shows the Arrhenius plots of the resistances, relaxation frequencies and equivalent capacitances. According to those results, the (RMed) resistance values are very close to those obtained for the electrode sintered at 1150 °C, representing in both cases the greatest contribution to the total resistance. As previously discussed, with an activation energy of 1.52(8) eV similar to that obtained for the electrode sintered at 1150 °C (1.29(6) eV), the MF² response is assigned to the electron transfer between the electrode and oxygen with incorporation of the adsorbed oxygen ion into the electrode. At 1200 °C, there is no apparent high frequency contribution (HF¹), what seems in agreement with a better sintering
process of the electrode layer that allows an improved transport of oxygen ions at the electrode/electrolyte interface. However, a new contribution of lower activation energy (0.91(9) eV) appears in the spectra (MF/C0). As seen in Fig. 6, the new contribution at medium frequency (MF/C0) with a capacitance of 10^-3 F cm^-2 refers to processes occurring on the electrode surface: dissociation of the adsorbed molecular oxygen and/or surface diffusion [43]. This contribution identified at medium frequency (10^2-10^1 Hz) in La2NiO4,d and Sr3FeMO6,d (Fe, Co, Ni) cathodes was described as a rate-limiting step due to oxygen dissociative adsorption on the electrode surface [34,44]. Specifically, for the Sr3FeMO6,d (Fe, Co, Ni) cathode, the impedance study realized as a function of oxygen partial pressure allowed to identify that such process occurs at 700 °C (measured temperature) when pO2 was less to 10^-2 atm, varying according to the relation RMF = pO2^-0.2 [44]. On the other hand, the impedance spectra obtained for La0.35Sr1.5MnO4 cathode also present a contribution in the range of 10^1-10^2 Hz, but in this case, it was related to surface diffusion of adsorbed oxygen (Oad); a study as a function of pO2 at 750 °C confirming that above 0.03 atm the process presents a relation RMF = pO2^-0.51 [8]. Accordingly, we suggest that the contribution observed in our case is due to one or both processes of dissociative adsorption/desorption and/or surface diffusion of adsorbed oxygen. The appearance of this phenomenon by increasing the sintering temperature may be related to the increase in grain size, i.e. to the decrease of specific surface area, which does not favor the dissociative adsorption process that is intimately linked to the surface area of the electrode.

In order to evaluate the influence of the sintering temperature on the elemental diffusion across the GDC interlayer and the quality of adhesion between layers, and also possibly identify another origin to the limiting phenomena that are observed, SEM/EDXS and WDS-EPMA have been performed on the cross-sectional of Au/L5S15 M/GDC/YSZ/GDC/L5S15 M/Au cell prepared at 1200 °C before EIS measurements, in a similar manner as for the lower sintering temperature T = 1150 °C. At the difference of the latter sample, both EDXS and WDS-EPMA techniques reveal clearly that, at the GDC/YSZ interface, an abnormally high Sr concentration is detected (Fig. S2 in Supplementary Information). The Sr diffusion across the GDC “diffusion” barrier is a phenomenon that has been unequivocally confirmed in the literature, showing that SrZrO3 is formed during sintering of the electrode [36,39]. Such SrZrO3 presence is redhibitory as such compound presents a very low oxygen ion conductivity [45], leading generally to a decrease of the ionic conductivity at the GDC/YSZ interface [4]; nevertheless, such phenomenon seems not to be preponderant in our case as the series
resistance of the cell elaborated at 1200 °C are approximately the same as for a sintering temperature of 1150 °C (see below). However, the increase of Sr diffusion from L5S15 M to GDC/YSZ interface by increasing the sintering temperature can also generate a Sr depletion from the manganite, and be an indirect source of performance degradation, as it has been described for LSCF cathodes [46,47]. In our case, such phenomenon, and the related modification of the materials chemistry, can have negatively affected, on the one hand, the $R_{\text{MF}}$, contribution, which is related to the oxygen exchange and diffusion properties of the material, i.e. its oxygen exchange ($k^*$) and/or oxygen diffusion ($D^*$) coefficients [28,48]. On the other hand, a chemical modification of the material surface associated to Sr depletion could also be one of the source of the $R_{\text{MF}}$ contribution that has been associated to oxygen dissociative adsorption and/or surface diffusion of adsorbed oxygen.

3.5. Electrode sintered at 1250 °C

The spectra of electrode sintered at 1250 °C and obtained between 835 and 785 °C were described by two arcs (Fig. 3c), however, with decreasing the temperature further, a third concentration is observed at ultra-high frequency. In this latter case, the spectra can be simulated using three ($R$-CPE) elements connected in series, as follows $LR_1(R_2\text{CPE}_1)(R_3\text{CPE}_2)(R_3\text{CPE}_3)$ (see Fig. S3).

Fig. 7a shows the Arrhenius plot of ASR and the elementary phenomena resistances (Table S2), from which the activation energies can be calculated. Clearly, the high sintering temperature (1250 °C) has a negative effect on the area specific resistance (ASR), which increased from 1.32 $\Omega$ cm² to 73.44 $\Omega$ cm² at 800 °C for the electrode sintered at 1150 °C and 1250 °C, respectively. For an electrode sintering temperature of 1250 °C, around 75% of the ASR is due to the low frequency contribution ($10^{-1}$-$10^{-2}$ Hz), which is accompanied by a contribution at medium frequency ($10^{2}$-$10^{4}$ Hz) present in the whole temperature range (Fig. 7b). Below 750 °C a small additional contribution appears at ultra-high frequency ($10^{6}$-$10^{7}$ Hz), labeled as $HF^{+}$ (probably masked by the other contributions at higher temperature). Fig. 7c and d depict the evolution of relaxation frequencies and equivalent capacitances as a function of temperature, helping to deduce the origin of each limiting phenomenon. The arc located at low frequency (LF) side dominates the impedance response and is the most important feature with respect to lower sintering temperatures, with capacitances of the order of $10^{-1}$-$10^{-2}$ F cm$^{-2}$. Typically, such low frequency contribution has been associated to gas phase diffusion; however, in this case, the dominant arc cannot be assigned to such process for two reasons: (i) the gas diffusion resistance is temperature-independent, with a very low activation energy ($E_a \approx 0$ eV) [49,50], while in our case the process at LF is thermally activated $E_a^{(LF)} = 1.23(6)$ eV and (ii) the capacitance values reported to O$_2$ gas diffusion into the porous electrode (e.g. PrBaCoO$_{2.5}$ or Sr$_3$FeMO$_{6.8}$ (M = Fe, Co, Ni)) are between $10^{-1}$-$10^0$ F cm$^{-2}$ [44,51], higher than what we obtained here. According to the literature, such phenomenon has been associated to the formation of secondary phases at electrode/electrolyte interfaces; for example, a contribution of this type ($10^{-2}$-$10^{-1}$ Hz) has been identified in the spectra of
LSM:YSZ/GDC and LSM:YSZ/YSZ cells when the electrodes are sintered at 1180 °C; by contrast, such phenomenon is not present in an LSM:GDC/GDC cell prepared and measured under the same conditions [12]. The formation of a resistive layer could be a consequence of the high reactivity already reported between LSM (or LSCF) and YSZ electrolyte [52,53]. For example, some studies carried out on LSM electrodes report a marked increase in polarization resistance after electrode sintering above 1100 °C, which is interpreted as an effect of the formation of La2Zr2O7 and/or SrZrO3 (depending on Sr content) at the LSM/YSZ interface [54,55]. In order to overcome this problem, a thin buffer layer based on gadolinia doped ceria (GDC) has been deposited between the electrolyte (YSZ) and the cathode [56,57]. However, other parallel studies performed on cells consisting of LSCF cathode and YSZ electrolyte protected by a GDC buffer layer show the formation of an insulating SrZrO3 barrier between GDC and YSZ, due to Sr and Zr diffusion through the interlayer when the electrode is sintered above 1100 °C [40,46].

The element distribution on polished cross sections of the Au/L5S15 M/GDC/YSZ/GDC/L5S15 M/Au cell sintered at 1250 °C was examined by EDXS and WDS-EPMA before EIS measurements (Fig. S4 and Fig. 8, respectively). As shown in both figures, a gap due to partial delamination at the GDC/YSZ interface is observed in the cell. This delamination is probably caused by the Sr diffusion from L5S15 M cathode through the GDC interlayer, since high Sr accumulation is observed at the GDC/YSZ interface. Strontium can subsequently react with zirconium forming SrZrO3 in the vicinity of the GDC/YSZ interface and leads to performance degradation [40,58,59]. To confirm the cation diffusion along the L5S15 M electrode - GDC interlayer - YSZ electrolyte, a linear EDXS analysis was carried out, that is shown in Fig. S4b. The intensity of Sr begins to increase within the GDC layer (35 μm) and becomes more intense at the GDC/YSZ interface (around 43 μm), where a strong Zr peak is also visible. In addition, this analysis confirms that Sr is also detected after the gap (56 μm), suggesting that this is the reason for the delamination. Some studies have demonstrated that Sr segregation is mainly produced during the sintering process, where the formation of insulating phases or cracks increase with increasing the sintering temperature [36].

Based on those results, the greatest contribution to polarization resistance (LF arc) could be related to the formation of a resistive phase rich in strontium at the GDC/YSZ interface. Apparently, at 1250 °C, the formation of such insulating phase during sintering is such that it causes a delamination at the interface, which might also

Fig. 6. Arrhenius plot of the (a) area specific resistance (ASR), (b) individual resistances (elementary processes), (c) relaxation frequencies and (d) equivalent capacitances for L5S15 M electrode prepared at 1200 °C.
explain the higher resistance values. The contribution at medium frequency (MF) has the same characteristics as that observed in the electrode sintered at 1200 °C; however, the rise of temperature up to 1250 °C results in the increment of the $R_{MF}$ resistance by
almost two orders of magnitude. As observed in the sample sintered at 1200 °C, the high sintering temperature may have caused an excessive grains growth, which is unfavorable for the processes occurring on the surface such as dissociative adsorption of molecular oxygen and/or surface diffusion (Oad), as a first source of explanation. Additionally, and in a similar way as for the cell sintered at 1200 °C, but in a much higher extent, a consequence of Sr diffusion from L5S15 M to the GDC/YSZ interface is the strontium depletion of the manganite and in particular of the surface of the L5S15 M grains. Such Sr depletion may have modified in an unfavorable way the surface properties of the material creating stronger limitation to the oxygen dissociative adsorption and/or adsorbed oxygen surface diffusion. Indeed, extrapolating the direct reactivity tests between L5S15 M and YSZ presented in section 2.5 to the reactivity between both materials throughout the GDC barrier layer, the loss of strontium at the A-site can locally destabilize the RP n = 1 structure and induce the formation of secondary phases like La1−xSr3MnO3 (LSM) perovskite that can be considered, in comparison to the RP phase, as a poor cathode material. Under this assumption, the poor ionic conductivity of LSM formed in the electrode would be blocking oxygen surface diffusion paths, which is reflected in a drastic increase in polarization resistance [54,60]. Such hypothesis would require the use of high resolution electron microscopy techniques to confirm the existence of such LSM perovskite phase within the electrode material, in particular on the surface of its grains.

According to the literature, the high frequency arc (HFa) can be related to the grain boundary resistance of the electrolyte. The capacitance values for this contribution are around 10−7. 10−6 6 F cm−2 for YSZ electrolyte [61] and around 10−8–10−7 F cm−2 for GDC electrolyte [62]. In the present case, the capacitances obtained are in the order of 10−8–10−7 F cm−2, which are similar to those reported for the same phenomenon observed in cells based on LSCF (or LSM) cathodes on a GDC electrolyte [12,30]. The appearance of such grain boundary resistance is probably due to the presence of Sr within YSZ electrolyte, that segregated at the grain boundaries [35,63].

Finally, many authors have suggested that cell degradation can be related to a simultaneous increase of serial as well as polarization resistance [64,65]. The evolution of the serial resistance can also be examined as a consequence of the reactivity between the electrode and oxygen, and incorporation of oxygen ions are the dominant contribution to the overall polarization when the electrodes are sintered at 1150 and 1200 °C. However, sintering the electrode at 1200 °C generated microstructural modifications affecting the oxygen dissociative adsorption/desorption or surface diffusion processes occurring on the electrode surface. As this is generally the case in several electrolyte-electrode systems, the increasing temperature promotes the chemical reactivity between both materials, reflected in an increase of polarization resistance. The use of a sintering temperature of 1250 °C promotes the Sr diffusion from the electrode to the GDC/YSZ interface and the Sr accumulation (and SrZrO3 formation) at the GDC/YSZ interface leads to the partial delamination of the electrode and Sr depletion within the manganite, resulting in cell performance degradation. The increase of sintering temperature was probably responsible for modifications in the electrode microstructure, e.g. grain growth, and clearly induced the Sr diffusion to the GDC/YSZ interface, which generated a depletion of strontium from the manganite. The combined effects generate strong limitations mainly related to the oxygen dissociative adsorption and/or adsorbed oxygen surface diffusion. These observations suggest that the electrode performance could be improved with the surface modification, for example, using an infiltration process [67,68].

4. Conclusions

In this first part of our work concerning the Ruddlesden-Popper manganite La0.5Sr1.5MnO4±δ (L5S15 M), we studied the electrochemical behavior as SOFC cathode material considering, in particular, the influence of the sintering temperature. Concerning the electrode process taking place in air, the electron transfer between the electrode and oxygen, and incorporation of oxygen ions are the dominant contribution to the overall polarization when the electrodes are sintered at 1150 and 1200 °C. However, sintering the electrode at 1200 °C generated microstructural modifications affecting the oxygen dissociative adsorption/desorption or surface diffusion processes occurring on the electrode surface. As this is generally the case in several electrolyte-electrode systems, the increasing temperature promotes the chemical reactivity between both materials, reflected in an increase of polarization resistance. The use of a sintering temperature of 1250 °C promotes the Sr diffusion from the electrode to the GDC/YSZ interface and the Sr accumulation (and SrZrO3 formation) at the GDC/YSZ interface leads to the partial delamination of the electrode and Sr depletion within the manganite, resulting in cell performance degradation. The increase of sintering temperature was probably responsible for modifications in the electrode microstructure, e.g. grain growth, and clearly induced the Sr diffusion to the GDC/YSZ interface, which generated a depletion of strontium from the manganite. The combined effects generate strong limitations mainly related to the oxygen dissociative adsorption and/or adsorbed oxygen surface diffusion. These observations suggest that the electrode performance could be improved with the surface modification, for example, using an infiltration process [67,68].

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[60] A. Endo, H. Fukunaga, C. Wen, K. Yamada, Cathodic reaction mechanism of dense La0.5Sr0.5CoO3–δ and La0.8Sr0.2MnO3 electrodes for solid oxide fuel cells, Solid State Ionics 135 (2000) 353–358, https://doi.org/10.1016/S0167-2738(00)00466-5.


