Electrochemical impedance spectroscopy of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃- nanofiber cathodes for intermediate temperature – Solid oxide fuel cell applications: A case study for the ‘depressed’ or ‘fractal’ Gerischer element

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Electrochemical impedance spectroscopy of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ nanofiber cathodes for intermediate temperature – solid oxide fuel cell applications:

A case study for the ‘depressed’ or ‘fractal’ Gerischer element

by

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Abstract

Electrospun $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) continuous unbroken nanofiber cathodes are investigated through electrochemical impedance spectroscopy, carried out on symmetrical button cells employing a $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) electrolyte. The Nyquist plot of the EIS experimental data at 550°C shows a single arc displaying typical ‘normal’ or ‘pure’ Gerischer shape. With increasing temperature (600°C to 750°C), this single arc gradually shrinks and deforms, showing a ‘depressed’ or ‘fractal’ Gerischer behavior. Finally, for temperatures higher than 750°C, this arc further shrinks, becoming practically a depressed semicircle at 950°C. These results demonstrate that the depressed Gerischer behavior, whose physical significance has never been demonstrated on theoretical grounds, is not an intrinsic feature of the electrode, since it appears in a clear manner only at certain well defined temperatures, while it disappears at other operating temperatures. Equivalent circuit model fitting is accomplished through the depressed Gerischer element, and also through an alternative circuit based on a pure Gerischer coupled in series to an RQ element. The superior fitting capability of the latter equivalent circuit is demonstrated. The latter circuit allows to assess separately the impedance contribution of the electrode bulk, associated to the pure Gerischer element, and of the electrode/electrolyte interface, associated to the RQ element, providing a powerful tool in view of understanding where the resistances are concentrated, which is the first step for an optimization of the electrode structure. In the LSCF electrospun cathodes investigated here, the higher resistance is associated to the bulk process, and it is proposed to be related to the high void degree (37.5%). Furthermore, with the latter circuit, the EC fitting parameters, having a physical meaning, provide information about the electrochemical process occurring along the LSCF nanofibers, and at the LSCF/CGO interface.

Keywords: Electrochemical Impedance Spectroscopy, Equivalent Circuit Modeling, Gerischer, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, Mixed Ionic-Electronic Conductor

1. Introduction

Electrochemical impedance spectroscopy (EIS) is a useful tool to investigate novel materials, and it is especially used for solid state electrochemical cells such as solid oxide fuel cells (SOFCs) and electrolysis cells. It is well known that, in EIS studies, the limiting step is the analysis of the experimental data, rather than the acquisition of the data themselves [1]. Impedance modeling is therefore an essential step of the EIS methodology. The so-called ‘kinetic approach’ to EIS modeling is based on a set of detailed equations describing the single steps of the electrochemical process, including adsorption and mass transfer, which are then integrated, usually numerically. Finally, fitting of the EIS experimental data is performed, through an error minimization routine (usually, non-linear least squares (NLLS) fitting [2] often implementing the Levenberg-Marquardt (LM) algorithm [3]), allowing to estimate the values of the model parameters. Often, this results in an overdetermined system as the number of free parameters is higher than the number of experimentally varied parameters. An alternative approach to EIS modeling is based on the use of equivalent circuits (ECs). In this case, the analysis of experimental data is carried out through an iterative process based on translating a physical model into an equivalent circuit and fitting the experimental data through NLLS or complex non-linear least squares (CNLLS) algorithms [4]. Knowing the physical meaning of as much as possible of the equivalent circuit parameters is crucial, allowing to draw quantitative information from the fitting parameters and, thus, to assess the appropriateness of the model [1,5]. Several processes are already described and analyzed in terms of their resemblance to equivalent circuits [6,7]. Nevertheless, at present, some aspects of the physical meaning of some widely used circuit elements, namely the constant phase element (CPE) and the ‘depressed’ or ‘fractal’ Gerischer element, are not completely understood. In this situation, the task of identifying the steps in the overall electrochemical process, and the physical nature of each step, becomes a difficult task [8]. An additional complication associated to EC modeling is that various equivalent ECs exist, which display exactly identical impedance for all frequencies. These are named identical circuits, ambiguous circuits, degenerate circuits, or two-terminal non-distinguishable circuits [5,9]. Furthermore, different EC models can be found that fit more or less equally well the experimental data, which makes a critical evaluation of the fitting parameters to be an important part in the model justification.

In a previous paper [10], we have reported the preparation procedure and morphological characterization of non-infiltrated $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) nanofiber cathodes obtained through water-based sol-gel electrospinning. Compared to SOFC cathodes prepared by wet ceramic processing, e.g. screen printing or tape casting, which result in isotropic structures, anisotropic / low

dimensional structures such as fibres offer not only a novel route to more efficient electrode materials, but also novel ways of electrode design. Understanding the structure-performance relation in these directed electrodes is possible by using EIS. Indeed, in a previous work [10], a restricted set of preliminary experimental results of the EIS electrochemical characterization of button cells employing symmetrical electrospun LSCF unbroken nanofiber cathodes and a $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO) electrolyte, has been discussed. In our previous work [10], the ‘depressed’ or ‘fractal’ Gerischer equivalent circuit (EC) element [11] has been employed to perform the fittings. The depressed Gerischer element is widely used for the interpretation of EIS spectra obtained from mixed ionic-electronic conductors (MIECs) currently under investigation for intermediate temperature-SOFC applications [12,13]. Even if this element often provides satisfactory fittings of the EIS arcs obtained from MIEC electrodes, employing only three fitting parameters, nevertheless, as already mentioned, a demonstration of the underlying physical process has never been proved. Boukamp [14] has proposed an interpretation in terms of fractal electrode/electrolyte interface, but, at present, the physical meaning of the depressed Gerischer element is still not unveiled, and as a consequence, the values of the fitting parameters, their behavior with temperature, and the related activation energies do not allow to draw any conclusion about the underlying mechanisms. The terminology ‘electrode/electrolyte interface’ is used here as opposed to ‘electrode bulk’, the previous being defined as the electrolyte surface on which the LSCF fibers are attached, and the latter referring to the inside of the electrode thickness. The terminology ‘fiber bulk’ is used as well, when referring to the inside of the individual fibers, where the oxygen ion transfer takes place (bulk path), and this is opposed to the term ‘fiber surface’, where the oxygen surface exchange phenomenon occurs (surface path).

In the present work, we report a full set of EIS spectra obtained from button cells employing a CGO electrolyte and electrospun LSCF unbroken nanofiber cathodes, tested in a wide range of temperatures (550-950°C) with oxygen partial pressure 0.2 atm, and also in the temperature range 550°C-750°C with oxygen partial pressure varying between 0.05 and 0.2 atm. Similar to what proposed by Monaco et al. [15], and somehow similar to what proposed by Lai et al. [16], who have developed and expanded a previous approach proposed by Jamink et al. [17,18], here, an interpretation of the experimental EIS spectra is proposed in terms of the superimposed effect of two contributions, one associated to the electrode/electrolyte interface, and the other associated to the electrode bulk. The approach is based on EC fitting modeling, which is performed through two different ECs. The first EC embeds the ‘depressed’ or ‘fractal’ Gerischer, while the second is formed by a pure Gerischer element coupled to an RQ element, i.e. a parallel connection of a resistor and a constant phase element (CPE). The pure Gerischer is selected to represent the

physical process of simultaneous charge transport and distributed electrochemical reaction in the electrode bulk, while the RQ element is selected to represent the electrode/electrolyte interface. The second EC employs two additional fitting parameters compared to the depressed Gerischer, but, quoting Orazem and Tribollet [19], ‘The object of modeling is not to provide a good fit with the smallest number of parameters. The object is rather to use the model to learn about the physics and chemistry of the system under study’.

In the ‘Results and discussion’ Section, the fittings performed with the two different ECs are compared, and the values of the fitting parameters of the RQ-G based EC are analyzed in detail; the results obtained point in the direction of validating the physical rationale behind the RQ-G based EC, and allow to formulate some hypotheses about the electrochemical behavior of electrospun LSCF nanofiber cathodes.

2. Experimental

2.1. *Synthesis of LSCF nanofibers and preparation of symmetrical cells*

Details of the preparation procedure are reported in [10,20]. Here, only the main aspects are recalled briefly. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) fibrous electrodes are obtained through a water-based sol-gel electrospinning process. To prepare the electrospinning solution, the LSCF precursors are $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at a molar ratio 0.6:0.4:0.2:0.8. These are dissolved in de-ionized H_2O , which is used as solvent. Polyvinylpyrrolidone (PVP) is used as carrier polymer. The composition of the solution is 0.1 wt% PVP (corresponding to a weight ratio of PVP powder to the overall solutes of about 25wt%), and 62wt% water. The electrospinning laboratory equipment is RT Advanced by Linari Engineering. During electrospinning, the precursor is pumped out of the needle at an injection rate of 0.3 ml/h with an electrical field of 4.4 kV/cm. The chamber relative humidity is controlled at 20%; simultaneously, temperature is kept at 29°C. The dried LSCF nanofiber tissue is cut in circular shape to obtain the electrodes, and then heat treated in a furnace at 800°C. The final area of the nanofiber tissue is 46% of that of the as-spun tissue, with uniform shrinkage in all the directions. Symmetrical button cells are manufactured by applying the LSCF nanofiber electrodes on both sides of a CGO electrolyte disk. The LSCF circular electrodes have a diameter of 0.64 cm (electrode area 0.322 cm²).

2.2. *Morphological characterization*

Morphological characterization of the LSCF fibers is reported and discussed in [10], where it is evidenced that, during the electrospinning process, the nanofiber tissue is formed by laying a single fiber over a flat support surface for multiple times, forming a bundle where the fibers are oriented mainly in-plane. Then, the fibers are attached onto the electrolyte through a process designed to preserve their structure, in order to obtain a continuous unbroken LSCF fiber electrode. Morphological characterization of the symmetrical cells is reported and discussed in [10], demonstrating that the fibers, after application onto the electrolyte, maintain an in-plane orientation with the electrolyte disk itself.

2.3. *Electrochemical tests*

The electrochemical behavior is evaluated experimentally through EIS. For the characterization, the cells are mounted in a four sample set-up in which each cell is fixed between two gold meshes, which also act as current collectors. The set-up is placed in a furnace, sealed and attached to the gas supply system. First of all, the symmetrical cells are fired in situ in the electrochemical testing equipment, at 950°C for 3 h. Then, the EIS spectra are recorded from 950°C down to 550°C in steps of 50°C, while the samples are exposed to a continuous flow of oxygen/argon gas mixture, with $p_{O_2} = 0.2$ atm. Then, after about 60 h, the performance of the symmetrical cells is measured again at 550°C, 650°C and 750°C, at atmospheric pressure, with p_{O_2} varying between 0.05 atm and 0.20 atm in steps of 0.05 atm, with balance Ar. The spectra are recorded in the frequency range $1 \cdot 10^6$ Hz to 0.01 Hz with a 10 mV voltage amplitude using a Gamry Reference 600 potentiostat. Kramers-Kronig analysis, performed by fitting a generalized model (series of connected Voigt elements) to the spectral data through linear equations [21], is accomplished to check that the system is linear, stable and causal [22]. For frequencies lower than $1 \cdot 10^5$ Hz, the error on the impedance experimental measurements is $< 1\%$ [22]. For frequencies between $1 \cdot 10^5$ and $1 \cdot 10^6$ Hz the experimental error is still $< 1\%$, but close to the border of the operating region with error $< 10\%$ [22]. Thus, the data at frequencies up to about $5 \cdot 10^5$ Hz are retained and presented in the figures. The high frequency inductance of the experimental apparatus, evaluated separately through a blank test as $4.9 \cdot 10^{-8}$ H, is subtracted from the raw experimental data.

3. EIS model development

Two different ECs are employed to fit the experimental EIS arcs, the first based on the ‘depressed’ or ‘fractal’ Gerischer, the second formed by a pure Gerischer element coupled to an RQ element, i.e. a parallel connection of a resistor and a constant phase element (CPE). The physical meaning of the two models is discussed below.

3.1. CPE and RQ element

The equation representing the CPE is:

$$Z(\omega) = \frac{1}{Q(j\omega)^\alpha}$$

Eq. 1

When $\alpha = 1$, the equation coincides with that of an ideal capacitor, the system is described by a single time-constant, and the parameter Q has the units of a capacitance (F). On the other hand, for values of $\alpha < 1$ (usually, $0.8 < \alpha < 1$), frequency dispersion appears, i.e. multiple (continuously distributed) time constants for the charge-transfer reaction. In this situation, Q has units ($F s^{\alpha-1}$).

In EC modeling, the CPE is often used in parallel with a resistor R , to form the so-called RQ element, whose impedance is:

$$Z(\omega) = \frac{1}{R^{-1} + Q(j\omega)^\alpha}$$

Eq. 2

When $\alpha = 1$ the representation of the RQ impedance in the Nyquist plot is a semi-circle, while $\alpha < 1$ results in a depressed semi-circle. In these conditions, an equivalent capacitance Q_{equiv} , with units (F), can be evaluated calculated according to the formula below:

$$Q_{equiv} = \frac{(QR)^{1/\alpha}}{R}$$

Eq. 3

At present, the physical meaning of the exponent α remains vague and it is in essence a fitting parameter. Most authors suppose that Eq. 1 is related to the roughness and to the fractal geometry of

the interface [23]. Indeed, it has been demonstrated on theoretical grounds that a fractal geometry of the interface causes frequency dispersion; nevertheless, a correlation between the fractal dimension of the surface and the CPE exponent α has not been found [24]. Recently, Niya et al. [25] have proposed that the anomalous diffusion theory can offer a theoretical demonstration of Eq. 1, and that the CPE power α is equal to the subdiffusion power, being related to the fractal dimension and the pore size distribution of the porous media. In parallel, Córdoba-Torres [26,27] has developed a model of thin film with distributed resistivities arising from inhomogeneous layer composition, causing both ionic and electronic conduction (mixed conduction) across the film, coupled to electrochemical reaction. Based on the model, the Nyquist representation of the impedances obtained in a number of different cases are depressed and distorted impedance arcs, displaying good agreement with typical CPE behavior. A mathematical relationship between the CPE parameters and the physical properties of the film has been demonstrated as well.

3.2. *‘Normal’/‘pure’ Gerischer and ‘depressed’/‘fractal’ Gerischer elements*

The Gerischer impedance element [28] has been demonstrated to provide a suitable representation of the phenomenon of simultaneous charge transport and distributed electrochemical reaction in the electrode bulk. Although originally proposed for a mercury electrode in a liquid electrolyte, it is widely applied to MIECs [29–31] even though some authors have raised criticisms about the lack of fundamental demonstration of the appropriateness of this procedure [16]. The equation is:

$$Z(\omega) = \frac{1}{Y(k + j\omega)^{0.5}}$$

Eq. 4

The representation in the Nyquist diagram displays, in the high frequency region, the so called half tear-drop-shaped feature, which is a straight line with 45° slope with respect to the real axis. Eq. 4 is often referred to as ‘normal’ or ‘pure’ Gerischer, to distinguish it from modified Gerischer arcs frequently encountered experimentally. For MIEC air electrodes in solid oxide cells, the k parameter is related to the oxygen exchange reaction on the MIEC surface, while oxygen mass transport into the porous electrodes via bulk or surface diffusion as well as structural parameters are included in the Y parameter. One deviation reported in the literature is named ‘finite length Gerischer’ [13,32], and it has been demonstrated on theoretical basis to be attributable to the electrode thickness being smaller than the characteristic length of the coupled reaction and charge transport phenomena. Another deviation reported in the literature is associated to an experimental

Nyquist diagram displaying a slope of the high frequency straight line lower than 45°. This behavior has been demonstrated to be well captured by the ‘fractal Gerischer’ or ‘depressed Gerischer’ EC element, represented by the equation [11–13]:

$$Z(\omega) = \frac{1}{Y(k + j\omega)^n}$$

Eq. 5

where $0 < n < 0.5$. Thus, values of n lower than 0.5 account for the depression of the impedance arc in the Nyquist plot, while in the case where $n = 0.5$, the depressed Gerischer coincides with the pure Gerischer element, characterized by the high frequency 45° straight line. Like with the CPE element, the deviation from ideality is associated to the value of the exponent n , and therefore, it is common practice to assume that also the physical rationale is the same in both cases, related to structural inhomogeneities and to the roughness of the interface, i.e. fractal behavior, associated to dispersion of time constants [12–14]. Hence, many theoretical approaches have proposed to evaluate the impedance associated to charge transport coupled to distributed reaction along an electrode with rough surface, either fractal [33] or non-fractal (for example, sinusoidal-shaped [34]). While the effect of surface roughness on the EIS spectrum is demonstrated at low and intermediate frequencies, nevertheless in both cases the high frequency part of the impedance spectrum is found to be of Warburg type, which is essentially the pure Gerischer behavior. In this framework, Nielsen et al. [35] have proposed, for MIEC electrodes, a transmission line model with distributed ionic and electronic conduction, coupled to distributed electrochemical reaction along the electrode thickness. They have demonstrated that, if the double layer capacitor is modelled through a CPE instead of being modelled through an ideal capacitor, then the Nyquist plot obtained for the impedance is a skewed, revealing a ‘depressed’ or ‘fractal’ Gerischer, with a characteristic 22.5 degree high frequency slope. However, according to [35], this behavior has never been observed experimentally.

It needs to be underlined that, as related to structural e.g. fractal properties or to a certain mechanism, the n exponent is usually considered to remain constant for a large range of experimental conditions. Even if this might depend on the distinct underlying processes and might not be universal, nevertheless the general assumption is that a large change in value of the exponent n , with e.g. temperature, is unexpected for a single process.

3.3. *Finite-length-Warburg element*

The finite-length-Warburg element (FLW) has been analytically demonstrated to provide a representation of gas diffusion in the pores or in a stagnant gas layer at the electrode surface [36]. It has been evaluated [32] that for the gases employed in fuel cells, bulk diffusion prevails at pore diameters greater than $\sim 10 \mu\text{m}$, while Knudsen diffusion dominated at pore diameters less than 50-100 nm. Considering the typical pore dimensions of SOFC electrodes, the conclusion [32] is that gas phase diffusion limitations occur not inside the electrode pores, but rather in the limiting gas diffusion layer adjacent to the electrode surface. The mathematical expression for the FLW element is [11]:

$$Z(\omega) = \frac{\tanh(\sqrt{Bj\omega})}{\sqrt{Y_1 j\omega}}$$

Eq. 6

3.4. *EC models applied in this work*

The fittings performed in the present work are based on two different EC models. The first EC is formed by L-Rs-Gd elements in series, with L being the inductance, Rs the serial resistance, and Gd the depressed Gerischer element. As already discussed, this circuit is often employed to fit the EIS arcs obtained from MIEC electrodes [35]. The second EC is based on the consideration that the overall electrode process is highly distributed, both at the electrode/electrolyte interface, mainly due to the highly irregular geometry, and within the electrode bulk, where charge transport coupled to distributed electrochemical reaction occurs. Thus, on the one hand, the RQ element appears suitable to represent to process occurring at the nanoscale (nm) of the electrolyte/electrolyte interface. On the other hand, the pure Gerischer element appears suitable to represent the process occurring in the electrode bulk, at the μm length scale. Thus, the second EC is formed by L-Rs-RQ-G elements, where the RQ element is in series with the pure Gerischer G. In Section 4 - Results and discussion, it is reported that, for operating temperatures equal to or higher than 750°C , an additional low frequency arc appears, related to gas phase diffusion. Then, for temperatures equal to or higher than 750°C , the FLW element is added to both EC models, to fit the low frequency arc.

The software Elchimea [11] is used to implement the two EC models adopted in the present work, and to fit them to the EIS experimental data. When performing the fittings at temperatures equal to or higher than 750°C, care is taken that the FLW element fits only the additional low frequency arc visible in the EIS experimental spectra, and that it does not give contribution in the high frequency range. Concerning the residual inductance L included in the EC models, and evaluated through the fittings, the values obtained for L are in the order of $\sim 3 \cdot 10^{-9}$ H, and thus one order of magnitude lower than the inductance of the experimental apparatus ($4.9 \cdot 10^{-8}$ H). In all the plots reported in the present work, the results (both experimental and fittings) are represented after subtraction of the residual inductance. For this reason, in the remaining of the paper, the two alternative circuits employed will be referred to as Rs-Gd and Rs-RQ-G. Minor differences between the EIS Nyquist plots reported in the present work and those previously reported in [10], are due to the fact that, in [10], the residual inductance L was not subtracted.

In the EIS Nyquist plots, the polarization resistance R_p is evaluated from the fittings as the difference between the low and high frequency intercepts of the Nyquist impedance spectra with the real axis. The fitting process allows to identify a resistance associated to each arc, i.e. R_{HF} (resistance of the high frequency arc) and R_{LF} (resistance of the low frequency arc). In addition, the fittings allow to identify a resistance associated to each EC element, which is named after the element itself. Thus, for example, referring to the Rs-Gd EC, R_{Gd} is the resistance associated to the depressed Gerischer element, and, referring to the Rs-RQ-G EC, R_G is the resistance associated to the pure Gerischer element and R_{RQ} is the resistance associated to the RQ element. The following relationships hold:

$$R_p = R_{HF} + R_{LF}$$

Eq. 7

Referring to the Rs-RQ-G EC:

$$R_{HF} = R_G + R_{RQ}$$

Eq. 8

And, at temperatures lower than 750°C, where no low frequency arc is visible:

$$R_p = R_{HF} = R_G + R_{RQ}$$

Eq. 9

4. Results and discussion

4.1. Analysis of EIS experimental spectra with varying T

Figure 1 and Figure 2 report a complete set of EIS experimental results obtained in the range of temperature 550°C-950°C. The experimental results are plotted in the form of Nyquist plots, together with the fittings performed through the EC models discussed before (Rs-Gd and Rs-RQ-G). In addition to the Nyquist plots, Log-Log plots of the imaginary component of the impedance Z_{Im} as a function of frequency f are presented as well, displaying again both the experimental results and their fittings. This latter type of representation of the EIS results is strongly encouraged [19,37]. On the one hand, on rigorous basis, this latter plot is not exactly a Bode plot (which is a representation of the impedance magnitude and phase angle versus frequency). On the other hand, there is a tendency to name ‘Bode’ plots all the graphs with the frequency on the abscissa. In the light of the considerations above, in the remaining of the paper, Log-Log plots of the imaginary component of the impedance Z_{Im} as a function of frequency will be addressed to as Bode – Z_{Im} plots, in agreement with what previously proposed in [38].

4.1.1. EIS experimental data

Figure 1

Figure 2

In Figure 1, the Nyquist plot of the EIS experimental data at 550°C shows a single arc, which at high frequency turns into a straight line with 45° slope with respect to the real axis. This is usually referred to as Gerischer behavior [29–31]. Figure 1 and Figure 2 show that, with increasing temperature (600°C to 750°C), this single arc gradually shrinks and deforms, with the high frequency straight line becoming remarkably narrower in range and reduced in slope, resulting in an overall arc depression. By increasing temperature above 750°C, the impedance arc shrinks further, and the high frequency straight line typical of the depressed Gerischer behavior tends to bend, so that, at 950°C, the arc has the shape of a depressed semicircle. In addition, by increasing temperature above 750°C, the shrinkage of the high frequency arc reveals a second, low frequency arc. The dimensions and shape of this low frequency arc apparently do not change significantly with temperature, which suggests that this arc is related to the physical process of gas phase diffusion [36].

Correspondingly, in the Bode – Z_{Im} plots, the experimental data display, at low temperature (550°C), a single process with a well-defined sharp maximum, clearly individuating one single time

constant. By increasing temperature, the maximum decreases, and simultaneously it shifts towards higher frequencies, indicating that the process is thermally activated. A further remark about the high frequency maximum is that, at high temperatures (from 800°C to 950°C), this maximum is no more sharp, but rather broad, and simultaneously a curvature appears in the high frequency part of the spectrum, which suggests that more than one process is reflected. Still referring to the Bode – Z_{lm} plots, at temperatures of 750-800°C and above, a second maximum becomes gradually visible in the low-frequency region, corresponding to the diffusive low-frequency arc already individuated in the Nyquist plot. By increasing temperature up to 950°C the frequency of this second maximum, and the impedance, do not change, indicating that this second phenomenon is not thermally activated, which corroborates the hypothesis of an underlying diffusive process.

A direct comparison of the EIS results with previously published experimental data obtained from non-infiltrated $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ electrospun nanofibers [39–41] is not possible, as literature only reports results obtained in the 650°C-750°C temperature range. However, the behavior displayed in the Nyquist plots of Figure 1 and Figure 2 is similar to that reported in the literature by Kournoutis et al. [42] for granular non-infiltrated $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ electrodes at temperatures from 600°C to 850°C, and by Lee et al. [43] for electrospun $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ -CGO electrodes at temperatures from 550°C to 800°C.

4.1.2. Fittings of the EIS spectra through EC models

Figure 1 and Figure 2 show that the fittings obtained with both the Rs-Gd, and the Rs-RQ-G circuits describe well the experimental data. However, better agreement is displayed by the Rs-RQ-G circuit, particularly at the high frequency end. In the Bode – Z_{lm} plots, this is visible practically at all the operating temperatures, while in the Nyquist plots this is clearly visible especially at the highest temperatures of 850°C and 950°C, where the experimental data clearly show a depressed semicircle instead of the half tear-drop-shaped feature typical of the Gerischer and depressed Gerischer behavior. This is well fit through the Rs-RQ-G circuit, while the high frequency linear behavior of the Gd element of the Rs-Gd completely fails the experimental trend.

Figure 3

The fitting error is shown in Figure 3 for both equivalent circuits, and shows a systematic error and higher error values for the depressed Gerischer model, compared to the coupling of pure Gerischer and RQ. This is further confirmed by Table 1, reporting the mean squared error (MSE) of the fits in Figure 1 and Figure 2, demonstrating that the fits performed through the Rs-Gd based circuit are affected by an MSE about one order of magnitude higher than the fits performed through the Rs-RQ-G based circuit.

Table 1

Due to the high number of fitting parameters employed with the Rs-RQ-G equivalent circuit (the G and RQ elements together employ five fitting parameters), the correlation matrix (in the Supporting Materials) displays at all temperatures a high degree of correlation (>0.85) between the k coefficient of the Gerischer element (Eq. 4) and the R coefficient of the RQ element (Eq. 2), as well as between the capacitance Q and the α coefficient of the CPE. The degree of correlation of the other fitting parameters is significantly lower.

Figure 1 and Figure 2 show that the FLW element well captures the low frequency arc. The low fitting error associated to the FLW element fitting is also demonstrated in Figure 3, in the low frequency region where $\text{Log}(f) < 0$, where the error is practically identical with both the Rs-Gd-FLW and the Rs-RQ-G-FLW ECs. The good agreement of the FLW element fitting with the experimental low frequency EIS data, further strengthens the thesis that the low frequency arc is related to gas diffusion. Also in this case, considering the high electrode porosity (37.5% [10]), gas phase diffusion limitations are expected to occur in the limiting gas diffusion layer adjacent to the electrode surface, rather than inside the electrode pores [32].

In Figure 1 and Figure 2, the Bode – Z_{Im} plots display also the individual contributions of the G and RQ components of the Rs-RQ-G circuits. The first remark is that, at all temperatures, both the G and the RQ processes give contribution in the same range of frequencies. Considering that the G element represents the electrochemical reaction coupled to charge transfer occurring along the fibers, within the electrode bulk, while the RQ element represents the electrochemical phenomenon occurring at the electrode/electrolyte interface, this is not surprising since the oxygen reduction reaction (ORR) occurs in proximity of the LSCF nanofiber in both cases, and thus is expected to display some similarities. This might explain also the high degree of correlation between k and R , mentioned above. However, due to the different natures of the processes G and RQ, the fittings display not only similarities but also differences; in this respect, the further analysis is carried out on the basis of the underlying model. At all temperatures, the peak frequency of the G process is lower than that of the RQ process, and this is consistent with the fact that the G process, in addition to the charge transfer reaction, embeds also electron and oxygen ion conduction along the electrode thickness, which is a slow process compared to the electrochemical reaction typically represented by the RQ element. With increasing temperature, both maxima shift towards higher frequencies, and this is a typical behavior due to the fact that both processes are thermally activated.

Still concerning the Bode – Z_{Im} plots, it is well visible that, at low temperature, the G element accounts almost completely for the impedance of the sample, the RQ contribution being practically negligible. Correspondingly, the experimental data show one single maximum, rather sharp in

shape. By increasing temperature, the relative importance of the RQ contribution tends to increase, and at 950°C, the G and RQ contributions are comparable, with the maxima separated by one order of magnitude in frequency. Due to this, the G and RQ contribution merge into one single high frequency impedance maximum, rather broad in shape, as already remarked.

These observations are consistent with a picture of the electrode where the electrochemical reaction, at low temperature, penetrates the electrode in depth, and this is accompanied by charge transport, in particular electrons and oxygen ions, through the electrode thickness. Simultaneously, the electrochemical reaction occurs also at the interface between the electrode and the electrolyte. The features of the electrochemical reaction, and in particular the activation energy, are expected to display some similarities, as already discussed, but also some differences, since the characteristics of the area where the electrochemical reaction takes place are different. In particular, at the interface between the electrode and the electrolyte, the reaction occurs at/close to the boundary between CGO and LSCF, while along the electrode thickness, the electrochemical reaction may occur at/close to the external surface of the LSCF fibers. The fact that the features of the electrochemical reaction occurring on the LSCF surface change noticeably if the LSCF surface is in contact with additional materials is documented in the literature [44], and this further proved by the fact that LSCF doping enhances the electrochemical reaction [45]. By increasing temperature, the phenomenon occurring at the interface between the electrode and the electrolyte gradually becomes more and more important, while the penetration of the electrochemical reaction into the electrode thickness is reduced. The shrinkage of the electrode active thickness by increasing temperature is confirmed by the previous literature on LSCF based electrodes. In particular, in [32] it has been shown that with LSCF/CGO composite cathodes with granule size in the order of 0.5-1 μm , the penetration of the electrochemical reaction into the electrode thickness is in the order of 40 μm at temperature of 550°C, and about 10 μm at a temperature of 850°C. An analogous shrinkage of the electrochemically active electrode thickness has been demonstrated for LSM/YSZ composite cathodes [35].

Figure 4

Regarding the fittings made with the Rs-RQ-G EC, the fact that the contributions of the phenomena associated to the G and RQ processes, i.e. respectively bulk and electrolyte-electrode interface processes, is very different at 550°C, while becoming comparable at 950°C, is further visualized in Figure 4, displaying the polarization resistance R_{HF} associated to the high frequency process, and also the break down into R_G and R_{RQ} . Activation energies are 118 kJ/mol for the overall high frequency process, 126 kJ/mol for the G process and 99 kJ/mol for the RQ process. The temperature dependence of the k and Y fitting parameters of the G element shows Arrhenius behavior as well, as

displayed by Figure 5. It seems consistent that the activation energy of R_G is slightly higher than that of the oxygen surface exchange coefficient k (120 kJ/mol), since the G element accounts also for the oxygen vacancy transport along LSCF, whose activation energy is reported in the literature to be 183 kJ/mol [46]. The fact that the activation energy of the k element (120 kJ/mol) is different from that of the R parameter of the Rs-RQ-G EC (99 kJ/mol), shows that electrochemical reaction on the LSCF fibres has a higher activation barrier than at the LSCF/CGO interface. Figure 5 shows that the Y parameter of the G element has lower activation energy.

Figure 5

Figure 6

Figure 6 reports the fitting values obtained for the exponent α of the CPE element of the Rs-RQ-G EC, and the exponent n of the depressed Gerischer element of the Rs-Gd EC. Figure 6 shows that n decreases continuously by increasing temperature, from a value of 0.52 at 550°C to 0.36 at 950°C. Comparing this result to similar results reported by González-Cuenga et al. [12] for lanthanum based chromite-titanate ($\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.2}\text{Ti}_{0.8}\text{O}_{3-\delta}$) porous electrodes tested in the temperature range 700°C-850°C, where the impedance spectra have been fitted through the ‘depressed’ or ‘fractal’ Gerischer element, some observations arise. Indeed, in [12], it has been reported that $n = 0.35$ and, within the experimental range, is temperature independent. Also in our case the exponent n has rather similar value, and it is practically constant in the same temperature range 700°C-850°C (in our case, $n = 0.44$ at 700°C and $n = 0.39$ at 850°C). However, in our case, enlarging the analysis to the 550°C-950°C range, it is found that $n = 0.52$ at 550°C and $n = 0.36$ at 950°C, and thus it is clear that the variation of n cannot be considered negligible any more. This is an important remark, because it leads to the conclusion that (at least in our case) n cannot be considered as a structural parameter, but rather the change of n with temperature must be explained considering the different temperature dependent behavior of the physical-chemical phenomena occurring in the electrode. In other words, the fact that the n parameter significantly varies with temperature, which corresponds to the change in shape of the high frequency arc in the Nyquist plots reported in Figure 1 and Figure 2, from typical Gerischer shape at 550°C to depressed semicircle at 950°C, demonstrates that the depressed Gerischer behavior is not an intrinsic feature of the electrode, since it appears in a clear manner only at certain well defined temperatures, and then it disappears at other operating temperatures.

Taking now into consideration the α parameter of the CPE appearing in the Rs-RQ-G EC, Figure 6 displays a moderate variation in the temperature range between 600°C and 850°C ($\alpha = 0.60$ -0.67). In this temperature range, the value of α appears rather low (usually $0.8 < \alpha < 1$). The value of the exponent α is associated to the broadness of the distribution of the phenomenon across the interface

thickness, in the sense that $\alpha = 1$ is related to an ideal capacitor (no distribution), and $\alpha < 1$ is associated to a distributed phenomenon (the broader the distribution, the lower the value of α). Therefore, the low value of α identified in our case through the fitting procedure is consistent with a highly distributed process at the nanoscale (nm) of the electrolyte-fiber interface, which, from the geometrical point of view, is obviously highly non-uniform. At the ends of the operating temperature range, $\alpha = 0.76$ at 550°C and $\alpha = 0.80$ at 950°C. This noticeable increase of α at 950°C can be attributed to a dramatic shrinkage of the thickness where the electrochemical reaction occurs at the nm scale, associated to the shrinkage occurring at the μm -scale, which is evidenced by the disappearance of the Gerischer-type behavior in the Nyquist plot. On the other hand, at 550°C, the value of $\alpha = 0.76$ may be explained in terms of poor electrochemical activation of the electrolyte-fiber interface.

Figure 7

Finally, Figure 7 displays the fittings values of the area specific capacitance Q of the RQ element. In the temperature range 600-850°C, the area specific capacitance varies between 64 $\text{mF s}^{\alpha-1} \text{cm}^{-2}$ and 117 $\text{mF s}^{\alpha-1} \text{cm}^{-2}$. The values obtained are in the typical range for pseudo-capacitances, and are in agreement with the results previously reported by Kournoutis et al. for granular non-infiltrated $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ electrodes at temperatures from 600°C to 850°C [42]. Outside the temperature range 600-850°C, rather different values are obtained for Q at 550°C (36 $\text{mF s}^{\alpha-1} \text{cm}^{-2}$) and at 950°C (17 $\text{mF s}^{\alpha-1} \text{cm}^{-2}$). This decrease of capacitance at the ends of the investigated temperature range appears to agree with the increase of the CPE exponent α occurring simultaneously, and may be attributed again to poor activation (at 550°C) or shrinkage (at 950°C) of the electrochemical double layer. Correspondingly, the equivalent capacitance Q_{equiv} displays a different behavior, being practically constant around $Q_{\text{equiv}} = 1.36 \cdot 10^{-2} \text{F cm}^{-2}$ for temperatures from 550°C up to 650°C, followed by a decreasing behavior at increasing temperature, with a minimum value of $2.12 \cdot 10^{-3} \text{F cm}^{-2}$ at the highest investigated temperature of 950°C. Since in this context the equivalent capacitance Q_{equiv} does not seem to offer improved insight, in the remaining of the paper the discussion will focus on the area specific capacitance Q .

4.2. Analysis of degradation effects

After performing the EIS tests reported above, the performance of the symmetrical cell is measured again after about 60 h of continuous operation. EIS spectra are measured at 550°C, 650°C and 750°C, and are analyzed again through the Rs-RQ-G EC.

Figure 8

Figure 9

Comparison of the results obtained after 60h of operation with those obtained at the beginning of the test is reported in Figure 8. The comparison shows that R_{RQ}^{-1} associated to the RQ element does not change at 550°C and 650°C, while an interesting beneficial increase is visible at 750°C (activation energy 116 kJ/mol and 99 kJ/mol respectively at 60 h and at the beginning of the operation), suggesting that the fiber/electrode interface is practically unaffected, or is even improved, after the first 60 h of operation. Instead, R_G^{-1} associated to the G element decreases significantly after 60 h, at both 650°C and 750°C, while the corresponding activation energy decreases (107 kJ/mol and 126 kJ/mol respectively at 60 h and at the beginning of the operation). This suggests that modifications take place in the electrode bulk, i.e. in the nanofiber structure. Associated to these modifications, also the features and mechanism of the electrochemical process occurring along the fibers must change, as indicated by the corresponding change in activation energy. The results in Figure 9 confirm the observations above. In particular, Figure 9 a) shows that the fitting parameters of the RQ element do not vary remarkably within 60 h, which confirms that the features of the electrolyte/fiber interface remain practically unaltered. On the other hand, Figure 9 b) displays the fitting parameters k and Y of the G element of the Rs-RQ-G EC, at the beginning of testing and after 60 h of operation. It is interesting to notice that the fitting parameter Y , including the oxygen vacancy diffusivity along the LSCF nano-fibers together with structural parameters, displays only a minor decrease after the first 60 h of operation, while the oxygen surface exchange coefficient k displays a remarkable drop associated to a remarkable reduction of activation energy, indicating that the electrochemical kinetics along the fibers has degraded during the first 60 h of operation. More in detail, the fitting line for the k parameter, reported in Figure 9 b) and corresponding to 60 h operation, has lower activation energy and higher pre-exponential factor than that at the beginning of operation. This indicates that, considering the surface sites and assuming that not all of them are equally active, after 60 h of operation only the most active ones remain (low E_a), while the number is in general reduced (decrease in pre-exponential factor). Many conjectures can be formulated to explain this phenomenon, including surface poisoning and segregation. However, at present, none of them can be proved definitively on the basis of the available data. Finally, it is interesting to note that the activation energies associated to R_{HF}^{-1} , R_G^{-1} and R_{RQ}^{-1} are noticeably different from each other at the beginning of testing, while they become similar to each other (~109-116 kJ/mol) after 60 h of operation.

4.3. Analysis of experimental EIS spectra with varying p_{O_2}

Figure 10

At 60 h of electrode operation, EIS spectra are measured varying p_{O_2} between 0.05 atm and 0.2 atm. For each value of p_{O_2} , measurements are carried out at 550°C, 650°C and 750°C. The EIS spectra are reported in Figure 10, where both Nyquist and Bode – Z_{Im} plots are displayed. Fittings through the Rs-RQ-G based EC are reported as well.

4.3.1. EIS experimental data

The experimental EIS spectra reported in Figure 10 display that the effect of increasing oxygen partial pressure results in a decrease of the maximum of the imaginary part of the impedance Z_{Im} , and in a simultaneous shift of the maximum towards higher frequencies. A four-fold variation of p_{O_2} from 0.05 to 0.2 atm, causes a shift of the maximum of about one order of magnitude in frequency, and a reduction of the value of Z_{Im} of a factor of about 5. Also in this case, at 750°C, a low frequency additional process, attributed to gas phase diffusion, is slightly visible, particularly at $p_{O_2}=0.05$ atm.

The results in Figure 10 display qualitative agreement with previous findings reported in the literature for granular LSCF-based electrodes [42].

4.3.2. Fittings of the EIS spectra through EC models

Table 2

Fittings of the experimental EIS spectra performed through the Rs-RQ-G are reported in Figure 10. Fittings through the Rs-Gd EC are performed as well (not reported here). Also in this case, the Rs-RQ-G based EC gives more accurate fittings than the Rs-Gd, as demonstrated by the MSE reported in Table 2. In agreement with the fittings reported in Figure 2, the FLW element is included in the EC at 750°C, since, as already observed, at this temperature an additional low frequency process associated to gas phase diffusion starts to appear.

Figure 11

Figure 11 displays the Arrhenius plot of the reciprocal electrode polarization contributions as a function of $1000/T$, by varying p_{O_2} , obtained by fitting the experimental EIS spectra through the Rs-RQ-G based EC. In particular, the results reported in Figure 11 b) display the contributions associated to the G and RQ fitting elements. For each value of p_{O_2} , activation energies are calculated from the slope of the line connecting the data at different temperatures. In this way, for

each value of p_{O_2} , one activation energy is calculated in the range 550°C-650°C and another one in the range 650°C-750°C. The values obtained for the activation energies are reported in Table 3. For $p_{O_2} = 0.2$ atm, the average between the activation energy evaluated at 550-650°C and 650-750°C corresponds to the values previously reported in Figure 8 (~109-116 kJ/mol).

Table 3

Regarding the overall R_{HF}^{-1} , the first remark arising from an analysis of Figure 11 a) and Table 3 is that, while in the range of temperature 550°C-650°C the activation energy is unchanged by varying p_{O_2} (101 kJ/mol), conversely in the range of temperature 650°C-750°C the activation energy tends to increase by decreasing p_{O_2} .

Focusing now the attention on the G and RQ contributions in the 550°C-650°C temperature range, the results in Figure 11 b) show that the G contribution, associated to the electrode bulk, displays very clearly the effect of a variation of p_{O_2} : the slope of the R_G^{-1} lines is the same for all the operating pressures, corresponding to practically identical activation energy (96-97 kJ/mol); the lines just shift down by decreasing p_{O_2} . This suggests that the reaction mechanism is the same for all the values of p_{O_2} , and that R_G^{-1} follows the well-known power law:

$$R_G^{-1} = k_1 p_{O_2}^m$$

Eq. 10

Fittings of R_G^{-1} vs. p_{O_2} , through Eq. 10, are reported in the subsequent Figure 12 b), demonstrating that the value of the m exponent at 550°C and 650°C is $m=0.28$, very close to the well-known value of 0.25 typical of the case where the r.d.s. of the overall phenomenon is an interfacial charge transfer phenomenon involving atomic oxygen. Figure 11 b) shows that, in the same temperature (550-650°C) and pressure range (0.05-0.2 atm), the picture is completely different for the RQ contribution, associated to the electrode/electrolyte interface, which is not influenced by a change of p_{O_2} . This implies that the r.d.s. of the phenomenon occurring at the electrode/electrolyte interface does not involve gaseous oxygen, but only oxygen vacancies, or, in other words, the oxygen incorporated into the electrolyte and LSCF perovskite, whose concentration, under these operating conditions, is not expected to be influenced significantly by the gas phase p_{O_2} [47]. For the temperatures of 550°C and 650°C considered until now, Figure 12 c) displays fittings of R_{RQ}^{-1} vs. p_{O_2} performed through Eq. 10 again, reporting values of $m=0.05$ at 550°C and $m=-0.01$ at 650°C, which confirms that, at 550°C and 650°C, R_{RQ}^{-1} is not influenced by p_{O_2} . As a consequence, the fittings reported in Figure 12 a) for the reciprocal overall high frequency polarization resistance R_{HF}^{-1}

as a function of p_{O_2} display $m=0.24$ at 550°C and 650°C , which is obviously very close to the exponent $m = 0.28$ of R_G^{-1} vs. p_{O_2} at 550°C and 650°C .

Figure 12

Focusing now the attention on the 650°C - 750°C temperature range, Figure 11 a) and Table 3 display a change in activation energy of the overall R_{HF}^{-1} from 119 kJ/mol at $p_{O_2}=0.2$ atm to 127 kJ/mol at $p_{O_2}=0.05$. This may be due to a change in mechanism occurring around 650°C , which has already been observed by Esquirol et al. [47], who have proposed that at temperatures above 650°C oxygen deficiencies in the bulk of LSCF appreciably increase by decreasing p_{O_2} . Arrhenius plots of the G and RQ contributions are reported in Figure 11 b), with the corresponding activation energies reported in Table 3. Focusing the attention on the G contribution, in this range of temperature 650 - 750°C the activation energy of R_G^{-1} continuously increases from 121 kJ/mol at $p_{O_2}=0.2$, up to 133 kJ/mol for $p_{O_2}=0.05$. This is consistent with the hypothesis of an increase of oxygen vacancies in the bulk of the LSCF fibers at 750°C , enhanced at low p_{O_2} , increasing the oxygen ion conductivity. As already remarked, the literature reports values of the activation energy of oxygen self-diffusion in LSCF of 183 kJ/mol [46], and thus an increased contribution of the oxygen ion conductivity to the overall mechanism can explain the increased activation energy of R_G^{-1} , noticeable especially at low p_{O_2} . Coherently, the fittings of R_G^{-1} vs. p_{O_2} , through Eq. 10, reported in Figure 12 b), show that the value of the m exponent at 750°C is small, i.e. $m=0.16$, which is the result of a trade-off between the value 0.28 found at 550°C and 650°C , and related to the interfacial charge transfer phenomenon, and a negative value of m associated to the ionic conductivity being enhanced by decreasing p_{O_2} . In the same temperature (650 - 750°C) and pressure range (0.05-0.2 atm), the picture is completely different for the RQ contribution, associated to the electrode/electrolyte interface. In the lower temperature range (550 - 650°C), we have postulated that the r.d.s. of the phenomenon occurring at the electrode/electrolyte interface does not involve gaseous oxygen, but only oxygen vacancies, or the oxygen incorporated into the electrolyte and LSCF perovskite. In the 650°C - 750°C temperature range, as already discussed, vacancy concentration in LSCF is expected to increase by decreasing p_{O_2} in the gas phase, which means that the oxygen incorporated into the LSCF fibers at the electrode/electrolyte interface is expected to decrease by decreasing the gas phase p_{O_2} . This can offer an explanation for the observable decrease of R_{RQ}^{-1} with decreasing p_{O_2} at 750°C , displayed by Figure 11 b). For the same temperature of 750°C , Figure 12 c) displays the fitting of R_{RQ}^{-1} vs. p_{O_2} , made through Eq. 10, reporting a value of $m=0.21$. As a concluding remark, at 750°C , the fitting reported in Figure 12 a) for R_{HF}^{-1} as a function of p_{O_2} shows $m=0.17$, which again is quite different from the value 0.25 typical of the case where the r.d.s. of the overall phenomenon is an interfacial

charge transfer phenomenon involving atomic oxygen, and is a result of many overlapping effects. The increase of activation energy of the overall R_{HF}^{-1} observed when decreasing p_{O_2} in the 650°C-750°C temperature range can be explained mainly in terms of increased oxygen vacancy concentration along the LSCF fibers.

Figure 13

Finally, Figure 13 displays the fitting values obtained for the capacitance Q of the RQ element, for p_{O_2} varying in the range 0.05-0.2 atm, and temperatures of 550, 650 and 750°C. Again, the values obtained are in the typical range for pseudo-capacitances. An increase of pseudo-capacitance is observed by decreasing p_{O_2} , and this effect is enhanced at higher temperatures, where the pseudo-capacitance increases up to $237 \text{ mF s}^{a-1} \text{ cm}^{-2}$ at $T=750^\circ\text{C}$ and $p_{O_2} = 0.05 \text{ atm}$. It seems reasonable to associate this marked increase of pseudo-capacitance to the increase of oxygen vacancies previously discussed for these operating conditions. A similar increase of pseudo-capacitance by decreasing oxygen partial pressure has been reported for granular LSCF-based electrodes [42].

5. Conclusions

EIS experimental data are reported, obtained from non-infiltrated electrospun LSCF unbroken nanofiber cathodes synthesized through water-based sol-gel electrospinning, tested in the 550°C-950°C temperature range, at $p_{O_2}=0.2 \text{ atm}$. The Nyquist plot of the EIS experimental data at 550°C shows a single arc, which at high frequency turns into a straight line with 45° slope with respect to the real axis, which is usually referred to as ‘normal’ or ‘pure’ Gerischer behavior. With increasing temperature (600°C to 750°C), this single arc gradually shrinks and deforms, with the high frequency straight line becoming remarkably narrower in range and reduced in slope, resulting in an overall arc depression, which is usually referred to as ‘depressed’ or ‘fractal’ Gerischer behavior. This is in line with the typical EIS spectra obtained from MIEC electrodes. Finally, at temperatures higher than 750°C, the arc shrinks further and the shape gradually changes, until it becomes a depressed semicircle at 950°C; furthermore, an additional low frequency arc becomes visible. These results demonstrate that the depressed Gerischer behavior is not an intrinsic feature of the electrode, since it appears in a clear manner only at certain well defined temperatures, and then it disappears at other operating temperatures.

EC model fitting is carried out. The experimental data at 550°C are well captured by the pure Gerischer element, whose physical meaning is associated to the phenomenon of simultaneous charge transport and distributed electrochemical reaction in the electrode bulk. In the 600°C –

750°C, the EIS experimental data are well captured by the depressed Gerischer element, whose physical significance is not demonstrated on theoretical grounds yet. At higher temperatures, fittings through the depressed Gerischer element display a visible deviation from the experimental data. Fitting through an alternative EC is proposed, embedding an RQ element, which is considered to represent the process occurring at the electrode/electrolyte interface, and a pure Gerischer element, which is considered to represent process occurring in the electrode bulk. For temperatures equal to or higher than 750°C the EC includes also an FLW element, aimed at fitting the additional low frequency arc whose physical meaning is associated to gas phase diffusion. It is demonstrated that, at all temperatures, with the alternative EC, the fitting error is one order of magnitude lower than with the EC based on the depressed Gerischer element. The fitting results obtained from the Rs-RQ-G based EC display that the bulk process is responsible for the major part of the polarization resistance, especially in the low temperature range (550°C – 800°C). At higher operating temperatures, the relative importance of the G and RQ contributions changes, with the two contributions being practically equivalent at high operating temperature (950°C). The high resistance associated to the bulk process is proposed to be related to the geometrical features of the bulk of the electrode, in particular the high void degree (37.5% [10]). The low resistance associated to the electrode/electrolyte interface, confirm previous statements expressed in [10] about a long TPB obtained at the electrode/electrolyte interface, where the fibers are attached directly to the electrolyte without crashing.

The Rs-RQ-G based EC used to fit the EIS experimental data obtained at the beginning of the test and after 60 h, allows to infer that the bulk of the electrode, i.e. the fibers themselves, are prone to degradation, while the interface between the CGO electrolyte and the nanofiber LSCF electrode is stable.

Fitting of EIS experimental data obtained after 60 h of testing by varying temperature (550°C, 650°C and 750°C) and oxygen partial pressures (0.05-0.2 atm), allows to deduce that the mechanism of the electrochemical process occurring in the LSCF electrode fibers is different from that occurring at the interface between the CGO electrolyte and the fibers themselves. In both cases, a change in mechanism occurring around 650°C is detected, which is consistent with the results reported by Esquirol et al. [47]. For temperatures in the range 550°C-650°C, the electrochemical process occurring in the bulk of the electrode, along the LSCF fibers, appears to be dominated by an interfacial charge transfer phenomenon involving atomic oxygen. At the same temperatures, the electrochemical process occurring at the electrode/electrolyte interface is not influenced by the oxygen partial pressure in the gas phase. In the temperature range 650°C-750°C the dominating

effect appears to be an increase of oxygen deficiencies in the bulk of LSCF fibers, enhanced by a decrease of p_{O_2} .

In conclusion, the EIS arcs obtained from electrospun LSCF continuous unbroken nanofiber cathodes displaying ‘depressed’ or ‘fractal’ Gerischer shape in the temperature range 650°C-750°C, are well interpreted as a series combination of two simultaneous highly distributed electrochemical processes, one occurring in the bulk of the electrode, which is well represented by a pure Gerischer EC element, and the other occurring at the interface between the electrode and the electrolyte, which is well represented by an RQ EC element. The fitting EC proposed here provides a powerful tool in view of understanding where the resistances are concentrated, whether in the electrode bulk or at the electrode/electrolyte interface, which is the first step for an optimization of the electrode structure.

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List of acronyms

CGO	$\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$
CNLLS	complex non-linear least squares
CPE	constant phase element
EC	equivalent circuit
EIS	electrochemical impedance spectroscopy
FLW	finite length Warburg
HF	high frequency
LF	low frequency
LSCF	$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$
LM	Levenberg-Marquardt
MIEC	mixed ionic-electronic conductor
MSE	mean squared error
NLLS	non-linear least squares
SOFC	solid oxide fuel cell

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Table Captions

Table 1 - MSE of the fittings in Figure 1 and Figure 2.

Table 2 - MSE of the fittings in Figure 10 (through the Rs-RQ-G based EC), and of analogous fittings performed with the Rs-Gd based EC.

Table 3 - Activation energies associated to the Arrhenius plots of R_{HF}^{-1} , R_G^{-1} and R_{RQ}^{-1} given in Figure 11.

Figure Captions

Figure 1 - EIS results at the beginning of testing, at operating temperatures from 550°C to 700°C: experimental data (*) and simulations through the Rs-Gd (○) and Rs-RQ-G (□) equivalent circuits. Left: Nyquist plots. Right: Bode – Z_{lm} plots, displaying also the individual contributions of the Gerischer — and RQ — elements of the Rs-RQ-G EC.

Figure 2 - EIS results at the beginning of testing, at operating temperatures from 750°C to 950°C: experimental data (*) and simulations through the Rs-Gd-FLW (○) and Rs-RQ-G-FLW (□) equivalent circuits. Left: Nyquist plots. Right: Bode – Z_{lm} plots, displaying also the individual contributions of the Gerischer — and RQ — elements of the Rs-RQ-G EC.

Figure 3 - Error of the fittings performed at 950°C through the Rs-RQ-G-FLW and the Rs-Gd-FLW ECs.

Figure 4 - Arrhenius plot of R_{HF}^{-1} , R_G^{-1} and R_{RQ}^{-1} , evaluated at the beginning of testing through the Rs-RQ-G based EC model. Solid lines are linear fittings, reported together with the associated activation energies.

Figure 5 - Arrhenius plots of k and Y fitting parameters of the Rs-RQ-G based EC, at the beginning of the experimental test.

Figure 6 - Exponent n of the depressed Gerischer element in the Rs-Gd based EC, and exponent α of the CPE element in the Rs-RQ-G based EC, as a function of temperature, at the beginning of the experimental test.

Figure 7 - Fitting values of the area-specific capacitance Q and equivalent capacitance Q_{equiv} of the CPE element in the Rs-RQ-G based EC, as a function of temperature, at the beginning of the experimental test.

Figure 8 - Arrhenius plot of R_{HF}^{-1} , R_G^{-1} and R_{RQ}^{-1} , evaluated through the Rs-RQ-G based EC, after 60 h of testing. Results at the beginning of testing are reported for reference (same data as in Figure 4). Linear fittings are represented together with the associated activation energies.

Figure 9 - Fitting parameters of the Rs-RQ-G based EC after 60 h of testing. Values at the beginning of testing (same data as in Figure 5, Figure 6 and Figure 7) are reported for comparison.

Figure 10 - EIS experimental spectra (black symbols) and fittings made through the Rs-RQ-G based EC (in color) at 550°C, 650°C and 750°C. Left: Nyquist plots; right: Bode – Z_{Im} plots. p_{O_2} : ($\blacktriangle, -\triangle-$) 0.05 atm, ($\bullet, -\circ-$) 0.1 atm, ($\blacklozenge, -\lozenge-$) 0.15 atm, ($\blacksquare, -\square-$) 0.2 atm.

Figure 11 - Arrhenius plots of: a) R_{HF}^{-1} (the dashed straight line is reported to guide the eye); and b) R_G^{-1} (circles) and R_{RQ}^{-1} (triangles), obtained from the fittings of the EIS experimental data carried out through the Rs-RQ-G based EC. EIS data obtained after 60 hours of testing, with p_{O_2} varying between 0.05 atm and 0.2 atm.

Figure 12 - a) R_{HF}^{-1} ; b) R_G^{-1} ; and c) R_{RQ}^{-1} after 60 hours of testing, for p_{O_2} varying between 0.05 atm and 0.2 atm and temperature 550°C, 650°C and 750°C. Results obtained from the fittings of the EIS experimental data carried out through the Rs-RQ-G based EC. In all figures, fittings through the equation $R_p^{-1} = k p_{O_2}^m$ (Eq. 10) are reported as well, together with the values of the fitting exponent m .

Figure 13 - Fitting values of the capacitance Q of the RQ element in the Rs-RQ-G based EC, as a function of temperature and p_{O_2} .

Temperature (°C)	MSE	
	Rs-RQ-G	Rs-Gd
550	$1.69 \cdot 10^{-06}$	$4.17 \cdot 10^{-05}$
600	$3.15 \cdot 10^{-06}$	$3.21 \cdot 10^{-05}$
650	$4.71 \cdot 10^{-06}$	$2.45 \cdot 10^{-05}$
700	$9.69 \cdot 10^{-07}$	$1.71 \cdot 10^{-05}$
	Rs-RQ-G-FLW	Rs-Gd-FLW
750	$4.91 \cdot 10^{-07}$	$5.53 \cdot 10^{-06}$
800	$3.99 \cdot 10^{-07}$	$4.17 \cdot 10^{-06}$
850	$2.65 \cdot 10^{-07}$	$2.63 \cdot 10^{-06}$
950	$1.83 \cdot 10^{-07}$	$9.99 \cdot 10^{-07}$

Table 1

MSE of the fittings in Figure 1 and Figure 2.

Temperature (°C)	p_{O_2} (atm)	MSE	
		Rs-RQ-G	Rs-Gd
550	0.2	$1.65 \cdot 10^{-06}$	$4.57 \cdot 10^{-05}$
	0.15	$1.82 \cdot 10^{-06}$	$5.06 \cdot 10^{-05}$
	0.1	$2.23 \cdot 10^{-06}$	$5.06 \cdot 10^{-05}$
	0.05	$3.09 \cdot 10^{-06}$	$4.71 \cdot 10^{-05}$
650	0.2	$1.54 \cdot 10^{-06}$	$1.94 \cdot 10^{-05}$
	0.15	$1.46 \cdot 10^{-06}$	$1.65 \cdot 10^{-05}$
	0.1	$1.41 \cdot 10^{-06}$	$1.38 \cdot 10^{-05}$
	0.05	$1.34 \cdot 10^{-06}$	$1.03 \cdot 10^{-05}$
		Rs-RQ-G-FLW	Rs-Gd-FLW
750	0.2	$4.28 \cdot 10^{-07}$	$1.54 \cdot 10^{-06}$
	0.15	$4.32 \cdot 10^{-07}$	$1.64 \cdot 10^{-06}$
	0.1	$4.24 \cdot 10^{-07}$	$1.58 \cdot 10^{-06}$
	0.05	$5.17 \cdot 10^{-07}$	$1.59 \cdot 10^{-06}$

Table 2

MSE of the fittings in Figure 10 (through the Rs-RQ-G based EC), and of analogous fittings performed with the Rs-Gd based EC.

p_{O_2} (atm)	Temperature range (°C)	E_a (kJ/mol)		
		R_{HF}^{-1}	R_G^{-1}	R_{RQ}^{-1}
0.2	550-650	101	97	118
	650-750	119	121	114
0.15	550-650	101	96	124
	650-750	123	126	105
0.1	550-650	101	96	126
	650-750	125	130	95
0.05	550-650	101	97	125
	650-750	127	133	90

Table 3

Activation energies associated to the Arrhenius plots of R_{HF}^{-1} , R_G^{-1} and R_{RQ}^{-1} given in Figure 11.