



More accurate macro-models of solid oxide fuel cells through electrochemical and microstructural parameter estimation – Part I: Experimentation



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H I G H L I G H T S

- The effects of the electrical artifacts must be eliminated during EIS measurements.
- DRT is a powerful method to deconvolute EIS spectra.
- Gas diffusion-related DRT spectrum is composed of numerous peaks.
- Association of peaks to physicochemical processes must be done experimentally.
- ECM generated from the DRT spectra is robust.

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The distributed relaxation times (DRT) method has been employed in order to deconvolute the electrochemical impedance spectroscopy (EIS) measurements carried out on a Ni-YSZ|YSZ|Pr₂NiO_{4+δ} – GDC solid oxide fuel cell (SOFC). This has enabled to shed light on the diverse physicochemical processes occurring within the aforementioned cell by individuating the characteristic relaxation times of these by means of a specifically designed experimental campaign where temperature and gas compositions in anode and cathode were varied one at a time. A comprehensive equivalent circuit model (ECM) has thus been generated based on the processes observed in the DRT spectra. This ECM has proved to be instrumental for the obtainment of parameters which describe the microstructural and electrochemical properties of the SOFC when used contemporaneously with experimental results and modelling theory (described in Part II of this work).

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1. Introduction

The fact that near future energy scenarios foresee a gradual penetration of solid oxide fuel cells (SOFCs) in the power generation market denotes that this technology is closer than ever in

competing face-to-face with traditional powering technologies. However, the existing generation of cells presents a number of drawbacks regarding performance and robustness which could hinder mass commercialization if these still persist in the next generation of SOFCs. Attending to these considerations, the scientific and industrial communities should work hand-in-hand developing improved analysis tools and techniques so to fully understand the degradation phenomena affecting the cells (and ancillaries) enhancing the production of a high-performing, robust and cost-effective product.

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Regardless of the fact that significant performance information can be obtained from traditional analysis techniques such as polarization curves and current interruption method, these lack in providing relevant information of the diverse physicochemical processes occurring in the cell (e.g. reaction kinetics, charge transfer, mass transport, Ohmic losses, etc ...), hence making it hard to pinpoint its criticalities. Electrochemical impedance spectroscopy (EIS) represents a step further to what high quality information it refers as it has the potentiality to shed light on the abovementioned different-nature processes, being each one of them associated to a unique time constant (known as relaxation time) and therefore exhibiting at different characteristic frequencies. However, being such a responsive technique, external instruments and processes – so called electrical artifacts – alter the EIS measurements of the SOFC cell by adding parasitic inductances, therefore an emendation of the measured data must be undertaken so as to minimize their effects. This can be done by carrying out an EIS measurement on a specimen with a prominent electrical conductivity (i.e. gold) in the same test station used to characterise the fuel cells and under the same operating conditions and subtracting its spectra to that of the electrochemical cell by means of Eqs. (1) and (2). Fig. 1 illustrates a Nyquist plot with the EIS results as measured and the corrected results being evident how the electrical artifacts affect the spectrum in the high frequency region.

$$Z'_{corrected}(\omega) = Z'_{measured}(\omega) - Z'_{gold}(\omega) \tag{1}$$

$$Z''_{corrected}(\omega) = Z''_{measured}(\omega) - Z''_{gold}(\omega) \tag{2}$$

Unfortunately this is not the only drawback associated to impedance measurements: due to the high complexity of fuel cells, the responses of the individual physicochemical processes to the EIS excitation signal are often convoluted, hindering in this way their individualization and monitoring. In order to overcome this issue an alternative approach for analyzing impedance spectra has been employed in the present work with a method that allows the calculation of a distribution function of relaxation times and relaxation amplitudes of impedance-related processes from experimental data (DRT method) [1,2].

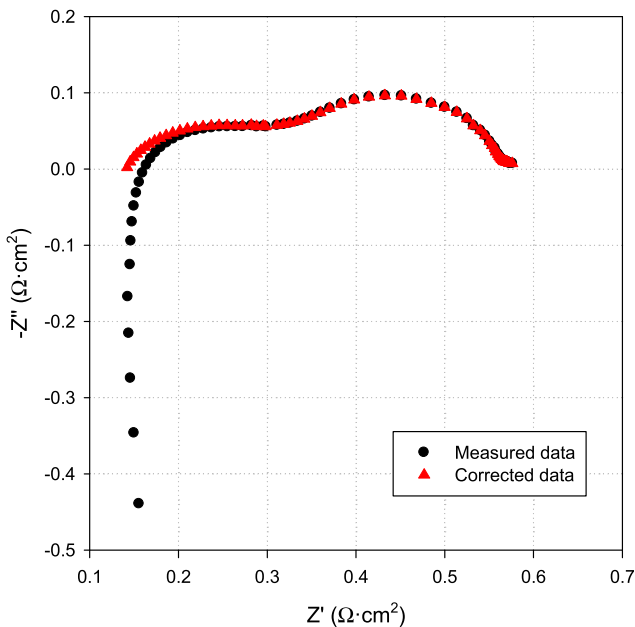


Fig. 1. Nyquist plot of the measured EIS and the corrected EIS.

2. Distributed relaxation times (DRT) method

In the frequency domain and in the discrete form, the SOFC cell's real and imaginary impedances (sum of relaxator terms) can be expressed by means of Eqs. (3) and (4) respectively, both of them linked by means of the Kramers–Kronig relations.

$$Z'(\omega) = R_0 + R_{pol} \sum_m \frac{1}{1 + (\omega\tau_m)^2} a_m \tag{3}$$

$$Z''(\omega) = R_{pol} \sum_m \frac{-\omega\tau_m}{1 + (\omega\tau_m)^2} a_m \tag{4}$$

where R_0 is the cell's electrical resistance, R_{pol} the polarization resistance, $\omega = 2\pi f$ the angular frequency of the input signal, τ_m the relaxation time of process m and a_m is the contribution of process m to the total polarization loss.

It is this contribution function which is the cornerstone of the DRT method and it can be obtained either from Eq. (3) or Eq. (4); still, being examples of Fredholm integral equations of the first kind, the inversion of the equation is an ill-posed problem and cannot be solved directly. Even if there are numerous methods which can solve this kind of problems, the most renowned and reliable one is the Tikhonov regularization algorithm which uses a self-consistent regularization parameter [3,4]. In this work the imaginary part of the data has been employed, hence rewriting Eq. (4) in matrix form and introducing the constant value of the polarization resistance into the distribution vector (i.e. $b_m = R_{pol}a_m$) gives:

$$\begin{pmatrix} Z'_1 \\ \vdots \\ Z'_m \end{pmatrix} = \begin{pmatrix} \frac{-\omega_1\tau_1}{1 + (\omega_1\tau_1)^2} & \dots & \frac{-\omega_1\tau_m}{1 + (\omega_1\tau_m)^2} \\ \vdots & \ddots & \vdots \\ \frac{-\omega_m\tau_1}{1 + (\omega_m\tau_1)^2} & \dots & \frac{-\omega_m\tau_m}{1 + (\omega_m\tau_m)^2} \end{pmatrix} \begin{pmatrix} b_1 \\ \vdots \\ b_m \end{pmatrix} \tag{5}$$

which for simplicity can be expressed as: $Z' = Kb$.

The Tikhonov regularization foresees the solution of the following minimization problem:

$$\min_b \left\{ \|Kb - Z'\|_2^2 + \lambda^2 \|b\|_2^2 \right\} \tag{6}$$

where λ is the self-consistent regularization parameter that constrains the smoothness of b .

The solution to the previous minimization problem (expressed by means of Eq. (7)) is governed by λ ; too small values result in artificial, meaningless peaks while too large values tend to over-smooth the shape of b , hence suppressing valuable information.

$$b = (K^T K + \lambda^2 I)^{-1} K^T Z' \tag{7}$$

where I is the identity matrix.

Various methods have been developed for the optimal selection of regularization parameters (e.g. Discrepancy principle, L-curve, Generalized cross validation method) the L-curve being the most extended one in applied mathematics due to its robustness and ability to treat perturbations consisting of correlated noise [5–7]. The L-curve is basically a trade-off curve between two quantities that ought to be controlled contemporaneously: data fitting and contribution from data errors. On the one hand too large values of lambda tend to over-smooth the shape of the solution curve not fitting well with the given data and hiking the value of the following residual: $\|Kb - Z'\|_2$. On the other hand too small values

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