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Parameter functional dependence in an electrochemical model: theoretical and computational issues

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Abstract. In this article we study the simplest parameter dependent ODE model that allows to describe the electrochemical impedance as a curve $Z(\omega) = X(\omega) + iY(\omega)$, $\omega \in [\omega_0, \omega_f]$ in the complex plane. The parameters of the original ODE having a straightforward physical meaning appear in $Z(\omega)$ combined in a highly nonlinear form. Usually, a nonlinear least squares procedure is applied to identify these parameters by fitting experimental impedance data and, as shown in [2], this can yield an ill-posed and ill-conditioned problem. In fact, several sets of different parameters, called Numerical Global Minima (NGM) can be identified that produce undistinguishable fitting curves. In this paper, we show that: 1) ill-posedness can be avoided by working in a different parameter space, where the new parameters have a physical meaning that is different from the traditional one but nevertheless exhibit a clear relationship with them, and a unique optimal set can be identified; 2) there exist curves of NGMs in the original space.

Keywords: Ordinary differential equation, nonlinear least squares, electrochemical impedance, parameter identification

MSC 2000 classification: 65L05, 65D10, 65H10

Introduction

The electrochemical model considered in this paper is derived from an ordinary differential equation (ODE) describing an electrochemical reaction with an adsorbed electroactive intermediate. For the sake of simplicity in the exposition, we consider the simplest case with only one linear ODE whose coefficients are nonlinear parameter-dependent functions. The following analysis can be generalised to a system where $n > 1$ coverage degrees $\theta_i, i = 1, \ldots, n$ are involved.

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Therefore, let us consider the following ODE

$$\beta\dot{\theta} = A_1(1-\theta) - A_2\theta, \qquad t > 0, \qquad \theta(0) = 0, \tag{1}$$

where β is the constant linking the surface concentration (mol cm^{-2}) to the fractional coverage θ. If

$$a = \frac{A_1 + A_2}{\beta} > 0, \quad b = \frac{A_1}{\beta} > 0, \tag{2}$$

the steady state solution is $\theta^* = b/a$ and the analytical solution is

$$\bar{\theta}(t) = \theta^*(1 - e^{-a\,t}), \qquad \forall t > 0. \tag{3}$$

The coefficients are parameter-dependent functions given by

$$A_i := A_i(\bar{\eta}) = a_i e^{b_i\bar{\eta}}, \quad i = 1, 2, \tag{4}$$

where $\bar{\eta}$ is the baseline potential, which can be interpreted physically as reaction rates. This is the widespread model considered, for example, in [5, 9].

The actual observable quantity is an electric current density, given by

$$\bar{I}(t) = \alpha_0 + \alpha_1\bar{\theta}(t), \tag{5}$$

where $\bar{\theta}(t)$ is given by (3), $\alpha_0 = FA_1$, $\alpha_1 = F(A_2 - A_1)$ and F is the Faraday constant.

The *Faradaic Electrochemical Impedance* (FEI) is defined as the first order variation of the current $I(t)$ obtained when a sinusoidal perturbation of the potential $\bar{\eta}$ is applied to the system for angular frequencies ω in a given range $\Omega = [\omega_0, \omega_f]$. If the potential variation is expressed by

$$\eta(t) = \bar{\eta} + \delta\eta(t), \qquad \delta\eta(t) = \Delta\eta\, e^{j\omega t}, \omega \in \Omega \tag{6}$$

where $\Delta\eta > 0$ is the amplitude of the perturbation and j is the imaginary unit, then the FEI is defined as $Z_F^{-1} := \dfrac{\delta I}{\delta\eta}$.

If we consider the *linearisation* around $\bar{\eta}$ of the resulting perturbed rates $\widetilde{A}_i(\eta)$, for $i = 1, 2$, then we have $\widetilde{A}_i(\eta(t)) \simeq A_i(1 + b_i\delta\eta(t))$. Consequently, if we indicate the coefficients of the ODE (1) evaluated in the perturbed rates as

$$\widetilde{a} := a(\widetilde{A}_i(\eta(t))), \qquad \widetilde{b} := b(\widetilde{A}_i(\eta(t))), \quad i = 1, 2,$$

their linearisation yields

$$\widetilde{a} \simeq a + c\delta\eta, \qquad c = \frac{b_1 A_1 + b_2 A_2}{\beta}, \tag{7}$$

$$\widetilde{b} \simeq b(1 + b_1 \delta\eta).$$

Similarly, the current coefficients $\widetilde{\alpha}_0$ and $\widetilde{\alpha}_1$ obtained after the perturbation can be linearized.

Hence, after some well known analytical and algebraic manipulations (see e.g. [3]), for each $\omega \in \Omega$, the FEI can be identified with the following complex number:

$$(Z_F^{-1})(\omega) = \frac{1}{R_t} + f(\omega)e^{j\phi(\omega)} = X_F(\omega) + j\ Y_F(\omega). \tag{8}$$

The angle $\phi(\omega)$ is such that $atan(\phi(\omega)) = -\omega/a$ (see [3]) and then

$$X_F(\omega) = \frac{1}{R_t} + af(\omega); \quad Y_F(\omega) = -\omega\ f(\omega). \tag{9}$$

The real part is shifted by the quantity

$$\frac{1}{R_t} = \alpha_0 b_1 + F(A_2 b_2 - A_1 b_1)\theta^* = F\frac{(b_1 + b_2)A_1 A_2}{A_1 + A_2}. \tag{10}$$

The modulus $f(\omega)$ is given by

$$f(\omega) = \frac{\alpha_1(b\ b_1 - c\theta^*)}{\omega^2 + a^2} = \frac{\xi}{\omega^2 + a^2}; \tag{11}$$

where ξ is given by

$$\xi = FA_1A_2\frac{(A_2 - A_1)(b_1 - b_2)}{\beta(A_1 + A_2)}. \tag{12}$$

Note that using the parameters ξ and a in (11) is the simplest way to express the rational function $f(\omega)$. By the way, it easy to see from (10), (12) and (2) that these parameters and $1/R_t$ are highly correlated in the space of the physical parameters $P = \{p \in \Re^4 | p = [a_1, a_2, b_1, b_2]\}$, in fact in P each of them can be expressed as a function of the other, namely $\xi = a \cdot (1/R_t)\,\frac{(A_2 - A_1)(b_1 - b_2)}{(b_1 + b_2)(A_1 + A_2)}$.

The resulting expression of $Z_F^{-1}(\omega)$ in (8) coincides with that commonly found in the literature (see e.g. [5, p. 3612]) and derived in a different way, whose drawbacks have been highlighted in [3].

It should be noticed that an experimental electrochemical set-up cannot measure FEI directly, but it yields a different related quantity called *Total Electrochemical Impedance* (TEI), whose mathematical expression is:

$$Z_{TOT}(\omega) = R_0 + \frac{1}{Z_F^{-1}(\omega) + j\omega C}, \quad \omega \in \Omega. \tag{13}$$

All the quantities F, β and C can be regarded as known constants; the following typical values can be assigned: $F = 96500\ C/eq$, $\beta = 2.7\text{e-}9\ mol\,cm^{-2}$ and $C = 25\text{e-}6\ mF/cm^2$. Here for simplicity, R_0 is set equal to zero.

Of course, by using the previously reported relationships, also TEI for each frequency ω identifies a point in the complex plane, such that

$$Z_{TOT}(\omega) = X(\omega) + jY(\omega), \quad \omega \in \Omega.$$

A typical range for the frequencies is $\Omega = [10^{-r_0},\ 10^{r_f}]$, where $r_0, r_f \in N$ specify the frequency range variation measured in Hertz. Analysis and experimental study of the corresponding curves in the complex plane are the basis of the so called Electrochemical Impedance Spectroscopy (EIS). Impedance spectra exhibit distinct patterns for different types of electrochemical reaction. Typical experimental spectra have the following features: i) one capacitive loop ($Y < 0, \forall\omega$) spanning the whole frequency range from 0 to infinity; ii) two capacitive loops at high and low frequencies; iii) one capacitive loop at high frequencies and one inductive loop ($Y > 0$) at low frequencies.

Generally a qualitative comparison of different impedance loci is not sufficient to understand the phenomenon involved and a quantitative analysis is needed. Usually, for this aim, an estimate of numerical values of the reaction rates is required. At this point, the importance of studying the phenomenon by a mathematical model reveals its importance. In fact, as formulae (8)-(13) indicate, reaction rates A_i appear as parameters both of FEI and TEI mathematical expression. Usually, an explicit approximation is sought of the physically relevant parameters a_i, the exchange current densities and b_i the Tafel slopes (see [1]).

Given as EIS spectrum as a set of experimental data (X_i, Y_i), $, i = 1, \ldots, m$ obtained for a discrete set of frequencies $\omega_i \in \Omega$, $i = 1, \ldots, m$ the most famous tool for parameter identification is the well know Least Squares approximation.

Hence, if $p = [a_1, a_2, b_1, b_2]$ is the vector of the positive parameters to be identified, we have $Z_{TOT} \equiv Z_{TOT}(\omega, p)$ and $X \equiv X(\omega, p)$, $Y \equiv Y(\omega, p)$. Physical reasons imply that $p \in P = P_a \times P_b \subset \Re^2 \times \Re^2$, where P_a and P_b indicate the feasible ranges for the values of a_i and b_i, respectively. Hence, the Least Square method to fit the TEI model on the EIS data is the following minimization problem:

$$\begin{gathered} \min_{p \in P} F_Z(p), \\ F_Z(p) = \sum_{i=1}^{m} \left(w_i^x (X(\omega_i, p) - X_i)^2 + w_i^y (Y(\omega_i, p) - Y_i)^2 \right). \end{gathered} \tag{14}$$

The objective function $F_Z(p)$ is the squared 2-norm of the residuals, weighted if $w_i^x, w_i^y \neq 1$ or unweighted if $w_i^x, w_i^y = 1$. Since, Z_{TOT} is nonlinear in the parameters p, then a nonlinear optimization problem has to be solved and, in general, the uniqueness of a global minimum cannot be assured theoretically.

In many electrochemical papers the identification problem is faced by a software well known in this field, called Zplot [6] and based on the Levenberg-Marquardt method. But, as shown in [2], also for the simple model analysed in this paper, the application of different Nonlinear Least Squares (NLS) techniques suffers from ill-posedness and ill-conditioning.

In fact, for a given set of EIS data, several distant local minima of (14) with very low residuals and therefore equally good fittings can be identified. According to the following definition, these particular local minima have been denominated in our previous paper [2] Numerical Global Minima (NGM).

Definition (NGM)
Let be p^* the known theoretical global minimum, that is $\mathrm{grad}(F_Z(p^*)) = 0$ *and* $F_Z(p^*) = 0$*. If, for all* $\epsilon > 0$ *there exist* k *parameter vectors* $p^{(1)}, \ldots, p^{(k)}$, $k = k(\epsilon)$ *and there exist* $\delta_1, \delta_2 > 0$ *such that the following properties hold*

(1) $\| \mathrm{grad}(F_Z(p^{(i)}))\| < \epsilon, \quad F_Z(p^{(i)}) < \epsilon,$ *for all* $i = 1, \ldots, k$*;*

(2) $\|p^{(i)} - p^*\| > \delta_1$, *for all* $i = 1, \ldots, k$*;*

(3) $\|p^{(i)} - p^{(j)}\| > \delta_2$, *for all* $i, \ j$*;*

then $p^{(1)}, \ldots, p^{(k)}$ *are called Numerical Global Minima.*

The presence of NGMs have been highlighted in [2] for simulated EIS data, such that the theoretically global minimum is a priori known, and in [4] for true experimental EIS data of copper electrodeposition, a system relevant to semiconductor fabrication. In the latter case, of course, the above property (2) is not available.

In [3] we have proposed a method of regularization for the above ill-posedness. The main idea is to include in the TEI model information deriving from the nonlinear behavior of the process, since the usual definition of TEI (13) considers only linear effects. In fact, we have shown for the same simulated EIS data considered in [2] that, by using information related to the higher harmonics of the TEI, it is possible to filter off the NGMs and identify the one nearest to the global one. Moreover, the new regularization technique has been successfully applied to experimental data in [4], identifying among the NGM sets the one with lowest relative error obtained by the linear model of TEI.

In this paper, for the simple model described above and for the classical (linear) TEI (13), we show that a different kind of regularization can be obtained by considering the optimization in a low dimensional space with the choice of a new set of parameters that are suitable functions of a_i, b_i. Ill-conditioning will be removed if it can be proved that the new NLS problem has a unique minimum in the new admissible domain. The new parameters are defined in Section 1. For a set of simulated EIS data in Section 2 we show that the LS problem admits a unique minimum in the new space. In the last section we prove that this unique minimum correspond to a continuum of NGMs and those found by the NLS procedure in [2] belong to the NGM curves identified.

1 New variables

By using the relationships (10) and (2), we define

$$\alpha := \frac{1}{R_t}, \quad \tau := \frac{1}{a}. \tag{15}$$

Hence

$$\alpha = F\frac{(b_1+b_2)A_1A_2}{A_1+A_2}. \tag{16}$$

$$\tau = \frac{\beta}{A_1+A_2} \tag{17}$$

and we can rewrite ξ in (12) as $\xi = \dfrac{\alpha}{\tau}\dfrac{(A_2-A_1)(b_1-b_2)}{(b_1+b_2)(A_1+A_2)}$. If we define the new further variable

$$\gamma := \frac{(A_2-A_1)(b_1-b_2)}{(b_1+b_2)(A_1+A_2)} \tag{18}$$

then (11) becomes:

$$g(\omega) := f(\omega) = \frac{\alpha\tau\gamma}{(\tau^2\omega^2+1)}.$$

Let us define $q := [\alpha, \tau, \gamma] \in Q \subset \Re^3$ and Q the new parameter space. Consequently, we can define FEI in this parameter space as

$$X_F(\omega) = \alpha(1+\frac{\gamma}{\tau^2\omega^2+1}), \quad Y_F(\omega) = -\omega\frac{\alpha\tau\gamma}{\tau^2\omega^2+1}. \tag{19}$$

Note that the expression of the FEI given by (19) in the Q space has the simplest mathematical form, since these expressions are rational polynomial functions of lowest possible order.

The TEI in the parameter space Q is then given by

$$Z_{TOT}(\omega, q) = \frac{1}{(\alpha+\frac{g(\omega)}{\tau}) + j\omega(C-g(\omega))} = X_g(\omega) + j\,Y_g(\omega)$$

$$\begin{aligned} X_g(\omega) &= \frac{\alpha}{M^2}\left(1+\frac{\gamma}{(\tau^2\omega^2+1)}\right), && (20)\\ Y_g(\omega) &= -\frac{\omega}{M^2}(C-g(\omega)), && (21)\end{aligned}$$

$$M^2 = \left(\alpha + \frac{g(\omega)}{\tau}\right)^2 + \omega^2(C - g(\omega))^2$$

We note that, by definition $\alpha > 0$ and $\tau > 0$, but γ could be positive or negative. Moreover, from (18) it is easy to see that $A_i > 0$, $b_i > 0$, for $i = 1, 2$, imply that $|\gamma| < 1$.

The parameters α, τ and γ belonging to the Q-space have a straightforward physical interpretation. In the case that one of the two reactions is rate-determining, we have that: α^{-1} is the Tafel constant of the fast reaction multiplied by the exchanged current density of the slow one; τ is the time constant of the rate-determining reaction at the potential of interest and γ is the relative difference between the Tafel slopes of the two reactions, i.e. a measure of the difference between the potential-sensitivities of the two electrochemical reaction rates.

2 Global minimum in the parameter space *Q*

By fixing the global minimum in the P-space equal to $p^* = [a_1^*, a_2^*, b_1^*, b_2^*] =$ [1e-6, 1e-5, 1.7, 0.05] and the baseline potential $\bar{\eta} = 0.5$, in [2] a set of simulated EIS data were generated to show that for different weighting choices of objective function in (14) the minimization algorithm converges to several NGMs. It is worth to note that the same mathematical expression of TEI is obtained if both the parameters a_1 is exchanged with a_2 and b_1 with b_2. Then for these data there exists in the P-space the *symmetric* global minimum $p^{**} = [a_1^{**}, a_2^{**}, b_1^{**}, b_2^{**}] = [a_2^*, a_1^*, b_2^*, b_1^*] =$ [1e-5,1e-6, 0.05, 1.7].

The parameter set $q^* \in Q$ corresponding to the p^* and p^{**} is the same since the mathematical expressions of α, τ, γ are symmetric w.r.t. a_i and b_i and it is given by:

$$q^*_{NGM} = [\alpha^*, \tau^*, \gamma^*] = [0.3217,\ 0.00021441,\ 0.59251] \tag{22}$$

Let us consider the NGMs identified in [2] for this data set by means of the proportional weighting NLS strategy both with respect to p^* and p^{**}. The threshold value $\epsilon = 5e\text{-}2$ was been used to apply the NGM's definition. In the following Table 1 we report the numerical values of the physical parameters a_i, $b_i, i = 1, 2$ and also:
the residual in the NLS technique, that is $res^2 = F(\mathbf{p}^{(i)})$;
the relative error $E_p^*(\mathbf{p}^{(i)}) = \dfrac{\|\mathbf{p}^{(i)} - \mathbf{p}^*\|_2}{\|\mathbf{p}^*\|_2}$ (similarly E_p^{**}) that measures the distance from the optimum set of parameters (see NGM's Definition, point (2)).

Note that an estimate for δ_2 in the NGM's Definition, point (3), can be obtained by evaluating the maximum distance among the NGMs.

Table 1. *NGM sets with residuals and relative errors*

NGM	a_1	a_2	b_1	b_2	res^2	$E_p^*\%$
$\mathbf{p}^{(1)}$	1.0547e-6	1.0023e-5	1.6693	0.029397	3.9354e-5	2.1761
$\mathbf{p}^{(2)}$	1.0803e-6	1.0028e-5	1.6563	0.019915	3.9410e-5	3.1209
$\mathbf{p}^{(3)}$	1.1314e-6	1.0037e-5	1.6325	0.001	4.0642e-5	4.9028
$\mathbf{p}^{(4)}$	8.4882e-7	9.9612e-6	1.803	0.1073	3.9902e-5	6.9323
$\mathbf{p}^{(5)}$	8.2116e-7	9.9487e-6	1.8257	0.11835	3.8822e-5	8.4151
$\mathbf{p}^{(6)}$	7.9075e-7	9.9336e-6	1.8523	0.13072	3.8741e-5	10.133

	a_1	a_2	b_1	b_2	res^2	$E_p^{**}\%$
$\mathbf{p}^{(7)}$	1.0002e-5	9.6752e-7	0.06177	1.719	3.9689e-5	1.3156
$\mathbf{p}^{(8)}$	1.0037e-5	1.1314e-6	0.001	1.6325	3.9752e-5	4.9023
$\mathbf{p}^{(9)}$	9.9448e-6	8.1337e-7	0.1215	1.8324	3.7425e-5	8.8467
$\mathbf{p}^{(10)}$	9.9140e-6	7.5622e-7	0.14518	1.8845	3.5757e-5	12.207
$\mathbf{p}^{(11)}$	9.9085e-6	7.4675e-7	0.1492	1.8938	3.6343e-5	12.799

For p^* we have $\max_{i,j} \|p^{(i)} - p^{(j)}\| = 0.25522 \equiv \delta_2$ (the minimum distance is $\min_{i,j} \|p^{(i)} - p^{(j)}\| = 0.016091$). Similarly for p^{**} we have $\max_{i,j} \|p^{(i)} - p^{(j)}\| = 0.3004 \equiv \delta_2$ ($\min_{i,j} \|p^{(i)} - p^{(j)}\|^2 = 0.010132$).

We show that all the NGMs found correspond to the same point in the parameter space Q defined above.

First of all, we note that, the relationships (16), (17) and (18) give $q = [\alpha, \tau, \gamma]$ and then imply that $q = \mathcal{F}(p)$, where $p = [a_1, a_2, b_1, b_2] \in P$. Hence for each NGM in Table 1 the new parameter values $q^{(k)} = \mathcal{F}(p^{(k)}), k = 1, \ldots, 11$ - reported in Table 2 - are obtained. It is easy to see that all NGMs collapse on an approximation of q^* with an error up to the first four digits. These parameter sets in the Q-space are shown in Table 2 together with the corresponding errors. In particular, we have that the maximum error is $\max_k \|q^{(k)} - q^*\|_2 = 9.1762e\text{-}4$, $k = 1, \ldots, 11$ (the corresponding maximum relative error is about 0.09%).

This result shows that if p is a solution of the minimization problem (14) in the P-space, then $q = \mathcal{F}(p)$ is a solution of the minimization problem

$$\min_{q \in Q} \widetilde{F}_Z(q),$$

$$\widetilde{F}_Z(q) = \sum_{i=1}^{m} \left(w_i^x (X_g(\omega_i, q) - X_i)^2 + w_i^y (Y_g(\omega_i, q) - Y_i)^2 \right). \tag{23}$$

in the Q-space, where X_g and Y_g are given by (20)-(21) (the weights depend only on the data).

On the other hand, if $(X_i, Y_i), i = 1, \ldots m$ are the simulated data and we solve (23) starting from one thousand of random guesses in the feasible space $Q = [10^{-4}, 10^4] \times [10^{-4}, 10^4] \times [-1, -10^{-3}]$, by using the Matlab routine *lsqcurve-*

Table 2. *New parameters* $q^{(k)} = \mathcal{F}(p^{(k)})$, *evaluated for each NGM* $p^{(k)}, k = 1, \ldots, 11$ *in Table 1*

	α	τ	γ	$\lVert q^{(k)} - q^* \rVert_2$
$\mathbf{q}^{(1)}$	0.32153	0.00021426	0.59306	5.8239e-4
$\mathbf{q}^{(2)}$	0.3215	0.00021426	0.59308	6.0683e-4
$\mathbf{q}^{(3)}$	0.32149	0.00021426	0.59309	6.1867e-4
$\mathbf{q}^{(4)}$	0.32149	0.00021427	0.59308	6.1551e-4
$\mathbf{q}^{(5)}$	0.32149	0.00021427	0.59307	6.0022e-4
$\mathbf{q}^{(6)}$	0.32152	0.00021427	0.59306	5.8763e-4
$\mathbf{q}^{(7)}$	0.32149	0.00021427	0.59308	6.0891e-4
$\mathbf{q}^{(8)}$	0.32149	0.00021426	0.59309	6.1867e-4
$\mathbf{q}^{(9)}$	0.32151	0.00021427	0.59305	5.8086e-4
$\mathbf{q}^{(10)}$	0.32151	0.00021427	0.59304	5.6332e-4
$\mathbf{q}^{(11)}$	0.32152	0.00021427	0.59304	5.6770e-4

fit.m of the Optimization Toolbox, we found about 40% of local minima with high residual, and the remaining 60% of local mimima always correspond to the same minimum under the threshold of ϵ = 2e-7. In this case, if $q_{num}^{(i)}$ are the numerical solutions, we have $\max_i \lVert q_{num}^{(i)} - q^* \rVert_2 = 4.6752e\text{-}6$ (the corresponding maximum relative error is 0.00069343%).

It is worth to noting that the above results on simulated data suggest to perform the parameter identification for real experimental data sets by applying the NLS optimization (23) in the $Q-$space instead than (14) in the P-space. For example, let us consider a set of experimental data obtained in [4], whose spectrum is given in Figure 1.

Starting from one thousand of random initial guesses in the domain $Q = [10^{-4}, 10^2] \times [10^{-4}, 10^2] \times [10^{-3}, 1]$, by using the above Matlab routine for the unweighted NLS (23), we found several local minima with high residuals and few local minima under the threshold of $\epsilon = 1.2e3$. These q-parameter sets with the lowest residual $res^2 = 1661.2$ all converge to

$$q^* = [\alpha^*, \tau^*, \gamma^*] = [0.043552,\ 0.059821,\ -0.77764]. \tag{24}$$

In Figure 1 we report the data and the fitting results corresponding to these values of parameters. In Figure 2, the real and imaginary parts of the data with their fitting and also the corresponding relative errors on the data are reported.

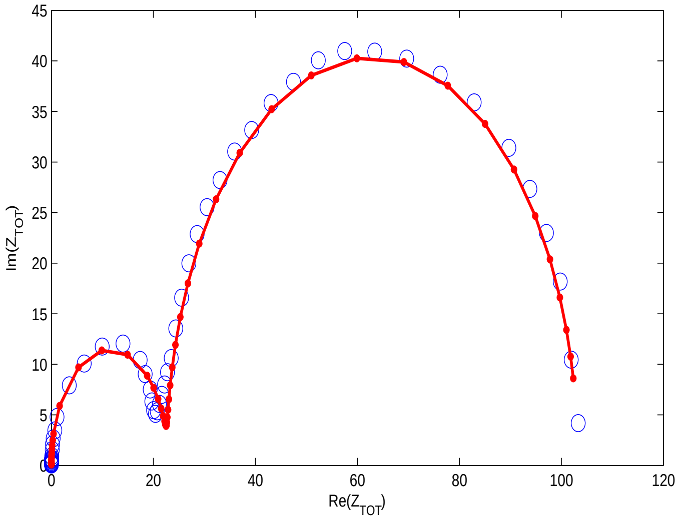

Figure 1. Electro-chemical Impedance spectrum Z_{TOT}: *experimental data (o) and fitting results (.) corresponding to the parameter values in* (24)

3 Proof of NGM existence

In the previous section we set $q = \mathcal{F}(p)$. The relationships (16), (17) and (18) imply that for each fixed value of the vector q, say $q = q^* = [\alpha^*, \tau^*, \gamma^*]$, the following equations hold:

$$\begin{cases} a_1 a_2 e^{\bar{\eta}(b_1+b_2)} \dfrac{b_1+b_2}{a_1 e^{\bar{\eta} b_1} + a_2 e^{\bar{\eta} b_2}} = \bar{\alpha} \\ \\ a_1 e^{\bar{\eta} b_1} + a_2 e^{\bar{\eta} b_2} = \bar{\tau} \\ \\ \dfrac{a_2 e^{\bar{\eta} b_2} - a_1 e^{\bar{\eta} b_1}}{(a_1 e^{\bar{\eta} b_1} + a_2 e^{\bar{\eta} b_2})} \dfrac{(b_1 - b_2)}{(b_1 + b_2)} = \gamma^* \bar{\tau}, \end{cases} \tag{25}$$

where $\bar{\alpha} = \alpha^*/F$, $\bar{\tau} = \beta/\tau^*$.

That is, an over-determined nonlinear system has to be solved to recover the unknown physical parameters a_1, a_2, b_1, b_2 in the P space.

We prove that (25) can admit a continuum of (real) solutions and we find the analytic expressions for it. This will justify the NGM existence in the P space.

Let us consider $d_1 = e^{\bar{\eta} b_1}$, $\bar{\eta}$ given and let us rewrite the above system in the

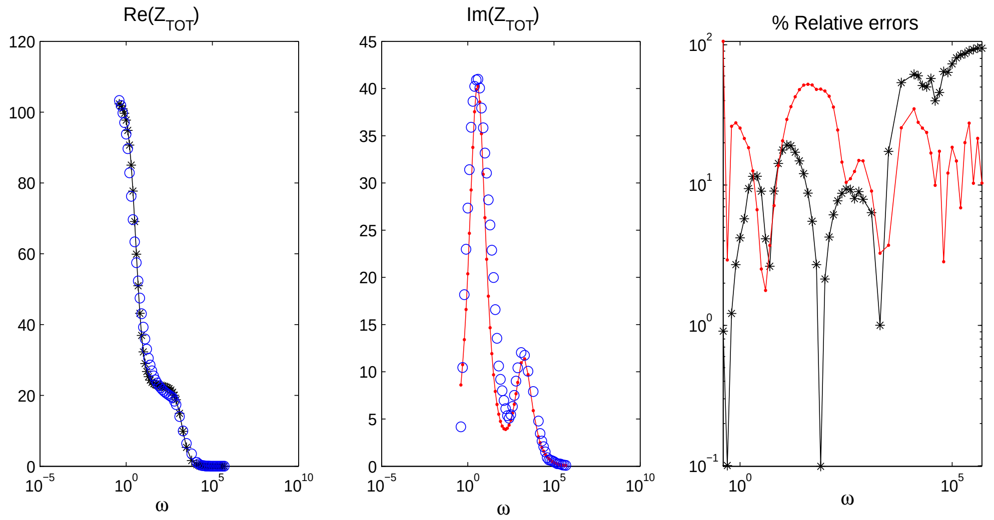

Figure 2. *Real and imaginary part of the Total Impedance Z_{TOT}: experimental data (o) and fitting (left, middle plot) and relative errors (right plot)*

three unknowns $x = a_1, y = a_2, z = b_2$, that is:

$$\begin{cases} d_1 x\, y e^{\bar{\eta} z}(b_1 + z) = \bar{c}, \\ \\ d_1 x + y e^{\bar{\eta} z} = \bar{\tau}, \\ \\ (y e^{\bar{\eta} z} - d_1 x) \dfrac{b_1 - z}{b_1 + z} = \bar{g}, \end{cases} \tag{26}$$

where $\bar{c} = \bar{\alpha}\bar{\tau}$, $\bar{g} = \gamma^* \bar{\tau}$.

By solving the equation $(26)_2$ for x, the substitution in the third equation $(26)_3$ yields y according to the following formulae:

$$\begin{cases} x = (\bar{\tau} - y e^{\bar{\eta} z})/d_1, \\ \\ y = \dfrac{1}{2} e^{-\bar{\eta} z} \left(\bar{\tau} + \bar{g}\, \dfrac{b_1 + z}{b_1 - z} \right) \end{cases} \tag{27}$$

Then plugging x and y in the first equation $(26)_1$ yields

$$\left(\bar{\tau}^2 \, (b_1 - z)^2 - \bar{g}^2 \, (b_1 + z)^2 \right) (b_1 + z) - 4\, \bar{c}\, (b_1 - z)^2 = 0, \tag{28}$$

thus a third order polynomial for z is obtained. If this equation has at least a unique real positive root z^*, then by (27) y^* and x^* can be easily recovered. By a symbolic software (e.g. Maple), the form of the third order polynomial roots can be found exactly as functions of b_1. Hence, for b_1 in a given range I_1 of physical parameter values such that $z^* \in \Re$ and positive, we can calculate: $x^* = x^*(b_1; q^*), y^* = y^*(b_1; q^*)$ and $z^* = z^*(b_1; q^*)$.

This result holds true for any value of $q \in Q$. Therefore, the existence of a unique minimum q^* in the Q-space implies that there exists a continuum (infinity) of minima in the P-space given by

$$[b_1, x^*(b_1; q^*), y^*(b_1; q^*), z^*(b_1; q^*)] \quad \Leftrightarrow \quad p \equiv p(b_1) = [a_1(b_1),\ a_2(b_1), b_1, b_2(b_1)]. \tag{29}$$

Therefore, for $b_1 \in I_1$ the functions in (29) give the "NGM curves" corresponding to q^*.

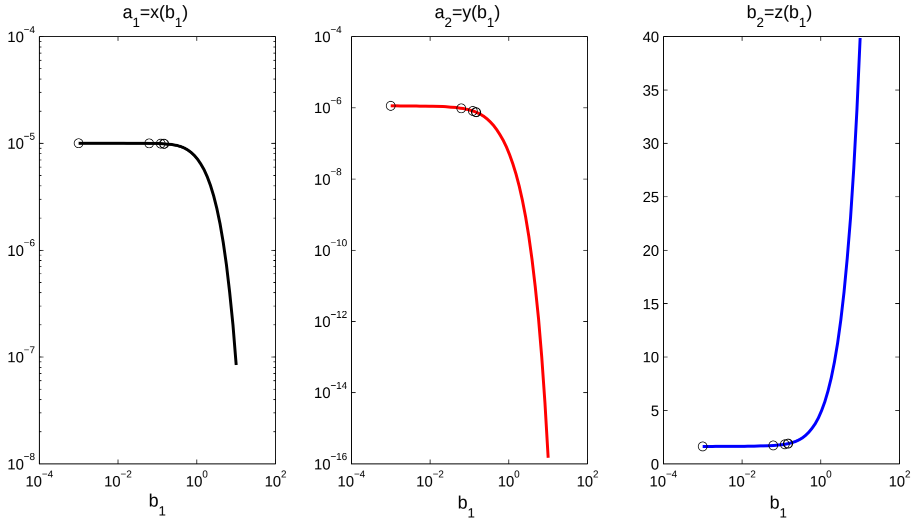

Figure 3. *NGM curves described by* (29) *with* q^* *given by* (22)*. The symbols (o) indicate the NGM parameter sets* $p^{(k)}, k = 7, \ldots, 11$ *in the P-space reported in Table 1 and related to the global minimum* p^{**}*.*

It is worth to note that the above discussion for the starting system (26) can be done similarly by the *symmetric* choice of variables $\hat{x} = a_2, \hat{y} = a_1, \hat{z} = b_1$ such that in this case b_2 is free. It is easy to show that $\hat{x}, \hat{y}, \hat{z}$ satisfy equations similar to (27) and (28) where b_1 is replaced by b_2 and d_1 by $d_2 = e^{\bar{\eta} b_2}$. Hence the "symmetric" continuum of solutions is obtained where

$$[b_2, \hat{x}(b_2; q^*), \hat{y}(b_2; q^*), \hat{z}(b_2; q^*)] \quad \Leftrightarrow \quad p \equiv p(b_2) = [a_1(b_2),\ a_2(b_2), b_1(b_2), b_2]. \tag{30}$$

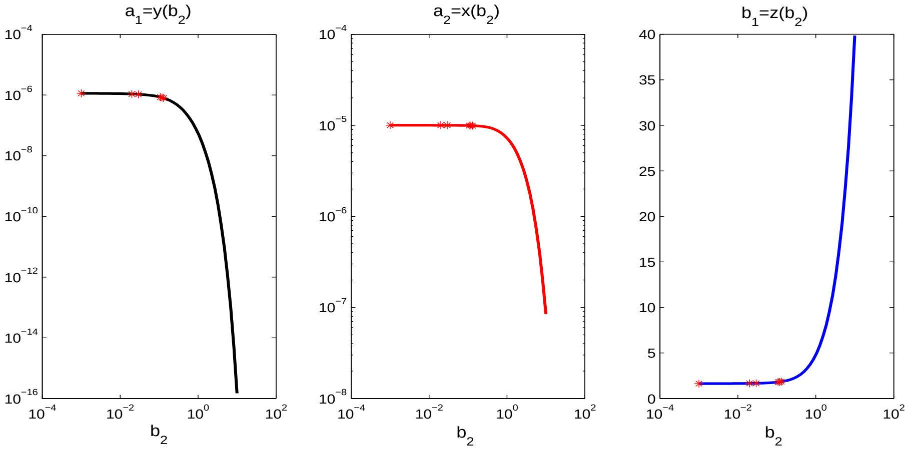

Figure 4. *NGM curves described by* (30) *with* q^* *given by* (22)*. The symbols (*) indicate the NGM parameter sets* $p^{(k)}, k = 1, \ldots, 6$ *in the P-space reported in Table 1 and related to the global minimum* p^**.*

By considering the optimal solution q^* in the Q-space given by (22), the corresponding NGM curves in (29) are reported in Figure 3 for $I_1 = [1\text{e-}3{,}15]$. We note that (28) has always a unique real root. The symbols "o" indicate the NGM set of parameters $p^{(k)}, k = 7, \ldots, 11$ related to the global minimum p^{**} reported in Table 1 and identified by the NLS procedure solving (14). The values belong to the NGM curves given by (29).

Similarly for the same values of q^* in (22), in Figure 4 we report the NGM curves described by (30). Here the symbols "*" indicate the NGM sets of parameters $p^{(k)}, k = 1, \ldots, 6$ in Table 1, related to the global minimum p^* ad corresponding to the NGM curves given by (30).

4 Conclusions

In this paper, we have proved that the choice of the space of the governing parameters for an electro-chemical impedance model is critical in avoiding ill-conditioning and ill-posedness of the related NLS fitting procedure. In fact, we have shown that it is possible to find a unique minimum for the nonlinear least squares problem, both for simulated and real experimental data, if the optimization is performed in a space of parameters different from the traditional space of electrochemical kinetic quantities (Tafel slopes and exchange current densities), but with a related physical meaning.

Moreover, we have shown that several sets of different parameters, called Numerical Global Minima (NGM) giving rise to undistinguishable fitting curves in the original space are indeed some “points” - sampled upon repeating NLS fitting runs - belonging to NGM curves. The mathematical forms of the NGM curves have been found analytically by simple mathematical arguments and are given by (29) and (30).

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