

On Benefits of the Zero-Pole Representation of Electrochemical Impedance Spectroscopy Data Close to Discontinuity Point*

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Unusual electrochemical impedance spectroscopy (eis) data obtained for dissolution and passivation of a copper rotating disc electrode in copper sulphate solution and analogous to data reported recently by other authors was represented as a rational function of frequency in terms of zeros and poles. The conditions of stability under potential control (pc) and galvanostatic control (gc) were formulated based on values of zeros and poles and were illustrated with calculated responses to potential and current steps. The loss of stability under pc due to resistance added in series was interpreted as change of the sign of the impedance zero.

Key words: electrochemical impedance spectroscopy, eis, fitting, stability

Electrochemical Impedance Spectroscopy (eis) is certainly the most in-depth method of characterizing the linear response of electrochemical systems [1–4]. While originally developed mainly as complementary method of electroanalysis [5], known also as the AC impedance [6–8], AC polarography [9] or method of Faradaic impedance [10], it is now the full-fledged method of experimental electrochemistry with numerous applications in basic research of electrode processes [1,2,4], transport properties of electrolytes [11] and ionic and mixed solid conductors [12] and also in testing of corrosion resistance, passivity, protective layers *etc* [13].

It is a long tradition to represent and to analyse experimental eis data invoking various kinds of electrical equivalent circuits (eqc). This practice is well rooted in the old (and still the most precise!) methods of measuring impedance with AC bridges [8,14,15] in which the eqc in the “comparison branch” of the bridge, the vis-à-vis of the tested electrode in the opposite branch of the bridge, was impedance model of the electrode under test. For ideal polarizable electrodes [16] this eqc consists simply of the series resistor R_s representing electrolyte resistance and the capacitor C_d representing double layer capacitance. In the presence of the charge transfer (faradaic) reaction additional resistance R_f representing its kinetics has to be connected in parallel to the “double layer capacitance” C_d and this simple R_s -($C_d||R_f$) configuration appeared suitable in surprisingly many instances.

* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

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With the advent of frequency response analysers (FRAs) [15,17] and Fast Fourier Transform (FFT) methods of eis measurements [18–20] there is no more necessity to model the electrode impedance with eqc. It is the more so, that it became obvious that for complex electrode reactions there is no way to establish a one-to-one correspondence between components of the eqc and thermodynamic or kinetic parameters [21] as can be done for ideally polarizable electrodes [16] or electrodes with simple faradaic reaction modelled with $R_s-(C_d||R_f)$ [2] in which C_d and its dependence on electrode potential, charge and electrolyte composition represents thermodynamic properties of the double layer, R_f is easily related to the kinetics of the charge transfer reaction and R_s to the transport properties of the electrolyte.

The situation became even more cumbersome when it appeared [22,23] that for complex electrode reactions there is no unique solution in terms of unique eqc representing eis data. Consequently, the single set of eis data can be modelled with more than one electrical eqc with no simple way to choose between them considering the thermodynamics and kinetics of electrode processes. Even so, most of the procedures available at present to validate and to analyse eis data [1,24–27] are still based on electrical circuits with addition of several “distributed elements” to account for effects of diffusion (Warburg impedance [28]) and non-uniformity of the electrochemical interface (constant phase element, cpe [2,29,30]).

It became also apparent that to account for passivity and inhibition effects and for strong interactions of adsorbed intermediate particles, the electrical model of the electrode has to involve negative capacitances and/or negative differential resistances which in some cases represent unstable circuits [3,31]. This can be easily contested in case when the electrode is stable in real experiment and its postulated eqc suggests instability. In these problematic situations the better choice may be representation of the electrode impedance by the mathematical function of complex frequency [32–34] with no direct recourse to electrical circuit as a model. This is especially so in case of some uncommon eis data reported all the more often recently [35–41] for electrodes at states close to the point of instability representing saddle-node (bistability) or Hopf bifurcation [42–44]. Without going too much into details of interesting by itself and intensively investigated electrochemical non-linear phenomena manifested as instabilities, bifurcations, sustained oscillations [3,31,45,46] and pattern formation [47,48] one may point at least three main sources of these phenomena: a) double layer (Frumkin) inhibiting effect [49–51], b) inhibition and passivation by adsorbed intermediates resulting in negative electrode resistance as a source of instability at certain values of potential [31,52,53], and finally, c) nonlinear coupling between fast charge transfer reaction and slow transport of substrates and/or products [46,51]. The case of products accumulation may be also ranked in group a) above as special kind of passivation by the, so called, “salt layer”. The common feature of all electrochemical instabilities is appearance of negative electrode resistance, either seen directly on steady-state current-potential plots as descending part of the plot ($dI/dE < 0$) or, more intriguing case, “hidden negative resistance” [31,54] manifested as negative real part of the impedance $\text{Re}(Z) < 0$ at intermediate frequency

range, with high and low frequency limits of real impedance both positive: $\text{Re}(Z_{\omega \rightarrow \infty}) > 0$, $\text{Re}(Z_{\omega \rightarrow 0}) > 0$. Reviews of electrochemical non-linear phenomena may be recommended for further reading [3,31,45–48,51].

EXPERIMENTAL

As a basis for the analysis we used eis data recorded for Cu rotating disc electrode (5 mm diam., 994 rpm) in 0.15 M $\text{CuSO}_4 + 5\text{M H}_2\text{SO}_4$ solution at ambient temperature [41] simulating to some extent the conditions of industrial copper electrorefining [55]. Experimental conditions corresponded to those of earlier experiments, in which instabilities, periodic and chaotic oscillations of copper under potential control (pc) and galvanostatic control (gc) were reported [56–58]. Analysis of our data revealed uncommon properties similar to those reported recently [35–40] and our conclusions should be therefore applicable also to those data.

The most prominent feature of data recorded under potentiostatic control at overpotential $E = 400$ mV was well pronounced “hidden negative resistance” [3,31] shown in Fig. 1 recognized by the large arc in the left half-plane of complex coordinates with real positive ends at high and low frequency limits.

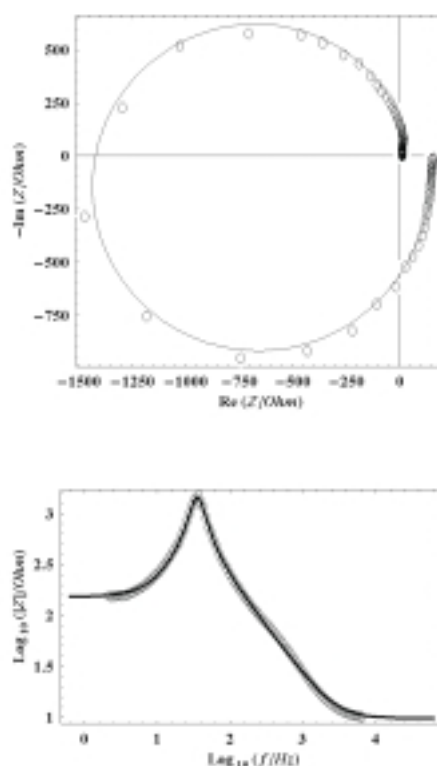


Figure 1. Impedance plots at $E = 400$ mV before anodic pre-polarization. Circles – experimental data; solid line – fitted $Z(s)$ function recalculated to zero-pole representation according to Eq. (3) with parameters for set I in Table 1. Data showing negative differential resistance. a. complex impedance coordinates: $-\text{Im}(Z)$ vs. $\text{Re}(Z)$. b. Bode amplitude coordinates: $\log(|Z|/\text{Ohm})$ vs. $\log(f/\text{Hz})$.

The impedance plots were featured by scattered data points (Fig. 1a) and sharp maximum of the impedance magnitude typical for resonant-type response (Fig. 1b). The same electrode with additional resistance added in series lost its stability and run into sustained oscillations as earlier reported [57,58] and similar loss of stability was observed under gc (control of the current). When the electrode was shortly pre-polarized at more anodic overpotential the negative differential resistance disappeared and the large arc switched to the right half-plane with its data points still heavily scattered showing again resonant-type response but electrode stable under both pc and gc, as shown in Fig. 2 a and b.

Similar observations were reported in the past for copper dissolution in phosphoric and acetic acids [59,60].

Because the reliability of eis data showing negative differential resistance was sometimes called into question by other authors [61–63], it seemed reasonable to prove their validity with Kramers-Kronig (KK) transformation [41]. This was done for data in admittance representation according to the claim of Gabrielli *et al.* [64] of KK validity tests relying on stability conditions and the postulate that data used in KK transformation should be in a form representing stable control.

With data validated in this way their analysis with standard methods of Complex Nonlinear Least Squares (CNLS) fits [24–27] could be safely attempted.

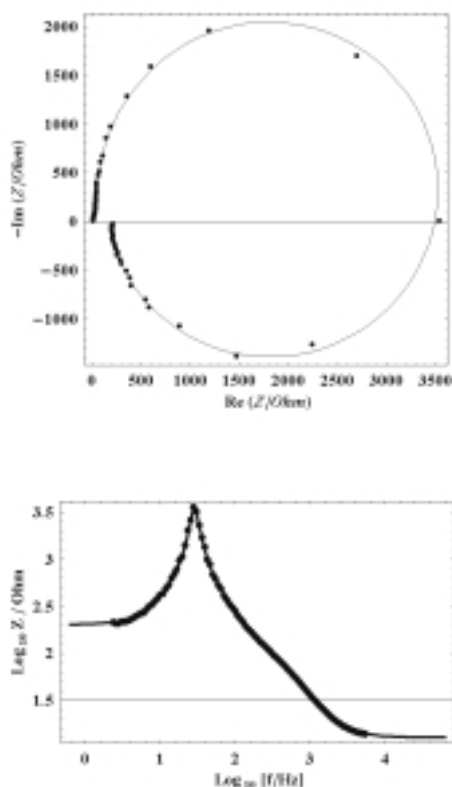


Figure 2. Impedance plots at $E = 400$ mV after anodic pre-polarization. Dots – experimental data, solid line – fitted function with parameters for set II in Table 1. Data showing only positive differential resistances. a. complex impedance coordinates: $-\text{Im}(Z)$ vs. $\text{Re}(Z)$. b. Bode amplitude coordinates: $\log(|Z|/\text{Ohm})$ vs. $\log(f/\text{Hz})$.

RESULTS AND DISCUSSION

Analysis involving zero-pole representation. Direct application of CNLS procedures using eqc involving series-parallel combination of R, C elements as postulated by Agarval *et al.* [65] for “measurement models” and by Boukamp in his “linear KK transformation” [66] failed due to various numerical problems and over-sensitivity to starting parameters [67]. It turned out that the most suitable fitting model was simply mathematical function in the form of a rational function of frequency, $f(s)$, $s = i\omega$, *i.e.* the ratio of polynomials of variable s of the high enough order. The minimum order n of polynomials and fitted rational function of complex frequency is chosen, somewhat arbitrarily, as the one ensuring the fit satisfactory enough. This corresponds to the minimum number of capacitances (more precisely: time constants $\tau_i = 1/(R_i C_i)$, $i = 1..n$) used in eqc in case of modelling and fitting with suitable eqc [1].

$$f(s) = \frac{N_n(s)}{D_n(s)} \quad (1)$$

$N_n(s)$ and $D_n(s)$ are polynomials of n -th degree in the numerator and denominator respectively of the fitted function $f(s)$. For our purposes it was sufficient to use 3rd order rational function of the final form as in Eq. (2) and fitted were parameters $R_s, a_2, a_1, a_0, b_2, b_1$ and b_0 .

$$Z(s) = R_s \frac{s^3 + a_2 s^2 + a_1 s + a_0}{s^3 + b_2 s^2 + b_1 s + b_0} \quad (2)$$

From this function the traditional R,C eqcs as well as zero-pole representation as in Eq. (3) could be easily recalculated [67] with the number of zeros, poles or capacitances in eqs equal to the order n of fitted rational function, *i.e.* 3 in this case.

$$Z(s) = R_s \frac{(s - z_1)(s - z_2)(s - z_3)}{(s - p_1)(s - p_2)(s - p_3)} \quad (3)$$

where z_1, z_2, z_3 are zeros, p_1, p_2 and p_3 are poles of the impedance respectively. They have dimension of angular frequency and their number corresponds to the order of fitted function in Eq. (2). The physical sense of impedance zeros corresponds to characteristic frequencies (reciprocal time constants) of relaxation under pc, this of poles refers to corresponding frequencies (reciprocal time constants) of relaxation under gc. Serious advantage of representing impedance in terms of zeros and poles as in Eq. (3) is independence of zeros and poles of the size of the electrode with $1/R_s$ (high frequency limit of the admittance) being the single “extensive” parameter proportional to the surface area of the electrode.

While calculated (R, C) elements of the equivalent circuit revealed some interesting properties of eis data in Fig. 1 and 2 [67], the most important and interesting conclusions are related to the values of zeros and poles in Eq. (3) compiled in Table 1. It is immediately seen that all zeros were negative real numbers and out of three poles, one was negative real and other two were complex conjugate with positive real part. As was shown by Naito *et al.* [54] poles and zeros of the electrode impedance are equal to eigenvalues of the Jacobi matrix under gc and pc respectively and this equality sets up the formal link between the theory of the eis [1,2,4] and the system dynamics and bifurcation theory [3,43,68]. Negative values of zeros in Table 1 tell on the electrode stability under pc. Positive poles or, in case of complex conjugate poles, their real part, tell on electrode instability under gc and complex conjugate values tell on oscillatory response, relaxation for negative and oscillatory divergence for positive real part.

Table 1. Zero-pole representation according to Eq. (3) of the eis data shown in Fig. 1 (set I) and in Fig. 2 (set II). Dataset I + R_{ad} is for dataset I with resistance $R_{ad} = 2000$ Ohm added in series. Dimensions of z_i and p_i : rad s^{-1} .

Dataset\parameter	R_s/Ohm	z_1	z_2	z_3	p_1	p_2	p_3
I	9.8	-2645	-193	-8.77	-225.4	$7.92-34.8i$	$7.92+34.8i$
II	12.8	-2618	-182	-6.98	-255.1	$-3.47-28.5i$	$-3.47+28.5i$
I + R_{ad}	2009.8	-227.4	$2.26+36.7i$	$2.26-36.7i$	-225.4	$7.92-34.8i$	$7.92+34.8i$

Discussion and conclusions. Conclusion on electrode stability under pc and gc may appear not quite convincing when based merely on its impedance function in frequency domain. Most conclusive are certainly responses to potential and current steps in time domain. In Fig. 3 there are shown these calculated responses for impedance function as in Eq. (3) with parameters in Table 1 representing data in Fig. 1 (dataset I) and in Fig. 2 (dataset II). These plots show that impedances in Figs. 1 and 2 represent electrodes stable under pc (Figs. 3 a, c) as proves asymptotic convergence of the current response. In Fig. 3a there is short part of the plot shown in the inset with negative current and this is the reminiscence of the negative differential resistance seen also as eis data points in Fig. 1a in the left half-plane of impedance coordinates, *i.e.* in the region of $\text{Re}(Z) < 0$. This is not the case for Fig. 3c corresponding to eis data in Fig. 2, where only positive differential resistance values were recorded. For comparison of frequency domain data in Figs 1 and 2 and time domain data in Figs. 3 a, c it has to be considered that high frequency parts in Figs. 1 and 2 correspond to initial, short time parts of plots in Figs. 3 a, c. The minima of the current shown in insets, negative in Fig. 3a and positive in Fig. 3c, correspond to “resonant” peaks in Figs. 1b and 2b and scattered points in Figs. 1a and 2a.

Under gc data set II represents stable behaviour (Fig. 3d) and dataset I represents instability manifested as oscillatory divergence or start of the limit cycle (Fig. 3b).

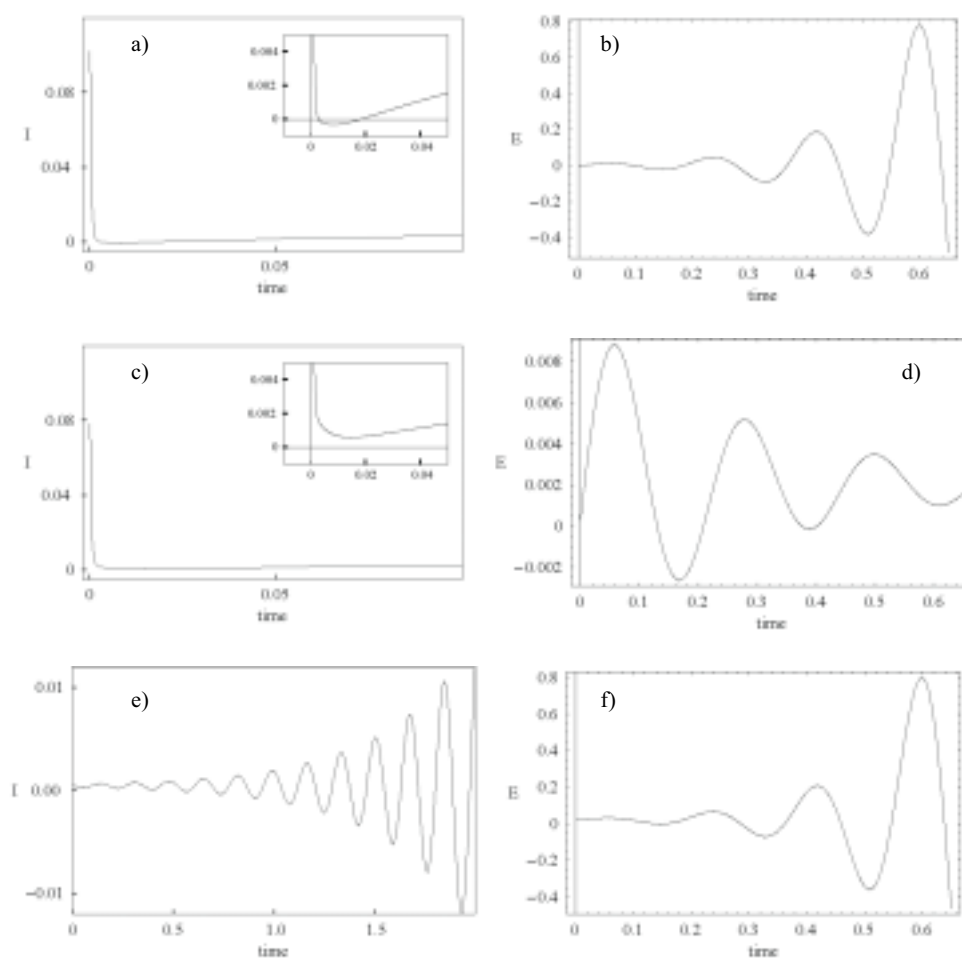


Figure 3. Potential-step ($\Delta E = 1$ V) current responses (a, c, e) and current-step ($\Delta I = 10^{-5}$ A) potential responses (b, d, f) calculated for impedances in zero-pole representation as in Eq. (3). (a, b) – dataset I in Table 1; (c, d) – dataset II in Table 1. (e, f) – dataset I with additional resistance 2000 Ohm added in series.

Additional resistance $R_{ad} = 2000$ Ohm added in series (Table 1, dataset I + R_{ad}) resulted in step responses shown in Figs. 3 e, f showing oscillatory divergence both under pc and under gc. This is effect of added series resistance resulting in change of values of impedance zeros to complex conjugate numbers with positive real part as shown in Table 1. While poles remain unchanged and are the same as for data set I, their positive real parts showing again instability under gc, new zeros turned now to complex conjugate with positive real parts showing loss of stability under pc and the periodic divergence to the limit cycle as revealed in experiments reported in [57,58].

This simple modelling of the effect of added series resistance on impedance zeros and resulting loss of stability under pc very well explains the somewhat mysterious role of the series resistance added deliberately to trigger sustained electrochemical oscillations [46] under pc. The effect of increasing series resistance can be conceived as continuous change of the control from ideal potential control using potentiostat (zero output resistance of polarizing source) to ideal current control using galvanostat (infinite output resistance of the polarizing source). This also indicates that systems like the one under study here can be stable under pc and unstable under gc but never can be stable under gc being unstable under pc.

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