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SYSTEM NON-LINEARITY COMPENSATION BY MEANS OF NON-LINEAR ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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ABSTRACT. Generally, for the evaluation of thermodynamic and kinetic parameters of an electrochemical system, an impedance spectroscopy method uses perturbation of small amplitude, in order to assures a linear behavior of the investigated process. When the experiment is strongly influenced by noise, a simple possibility to improve measurement quality is to increase the perturbation amplitude. Unfortunately, this easy way to increase the signal to noise ratio can generate non-linearity distortion impeding on the result quality. In this paper, a new procedure for non-linearity correction using different harmonics parameters was proposed and tested for a reversible electrochemical system.

INTRODUCTION

The investigation of an electrochemical system by dynamic methods can be performed using perturbation of large or small amplitude. The methods using large amplitude perturbation, steps or sweeps of potential or current, generally drive the electrode far from equilibrium where its response is usually a transient signal. The other approach consists in the use of a small amplitude step or, in the case discussed below, a sinusoidal perturbation, which brings the system in steady-state [1].

The main advantages of small amplitude methods are as follows:

- The experimental opportunity of carrying out high precision measurements, primary due to the steady-state regime, which allows the noise minimizing by mediation of successive measurements;
- Simpler mathematical treatment of electrode kinetics and mass transport due to low amplitude perturbation, typically under 5 mV applied voltage, when system response is linear;
- Easier separation of each elementary step contribution to the system response, due to experimental possibility to use perturbation within a large range of frequencies, usually between 0.001 and 100,000 Hz;

- The obtained information can be correlated with the imposed d.c. potential, which is an important feature when the investigated parameters are influenced by the applied potential, as is the case for the electrode reaction, double layer capacitance and, sometimes, even for ohmic resistance [2];
- The compensation of non-ideal behavior of the potentiostat and/or others electronic instrumentation included in the measurement network by means of Laplace plane analysis, facilitated by the system linearity [3].

The disadvantages of small amplitude techniques are mainly generated by the low value of the signal perturbation, determining a small amplitude response of the electrochemical system, which is highly susceptibility to be influenced by noise. Consequently, a sophisticated and expensive instrumentation becomes necessary.

Special alternatives of the electrochemical impedance spectroscopy were proposed to exploit the electrochemical system non-linearity in order to obtain information about its behavior. The most important are: rectification, second order techniques, intermodulation, demodulation and superior order harmonic analysis [1, 4].

Faradaic rectification uses the asymmetry between anodic and cathodic behavior of the electrochemical system in current controlled conditions, causing a modification of the continuous potential component and allowing the straightforward obtaining of the charge transfer coefficient, parameter otherwise difficult to obtain. Second order techniques examine the sinusoidal response signal, generated by systems asymmetry, and having the frequency twice higher as the perturbing one. The appearance of the second harmonic and the rectification component is illustrated by the following equation:

$$\sin(\omega t)^2 = \frac{1-\cos(2\omega t)}{2} \tag{1}$$

with the mention that, for a controlled potential technique, due to the electrochemical system particularity, in the resulting current intensity equation a quadrate of the perturbation term will appear.

Intermodulation techniques use a perturbation obtained by addition of two sinusoidal signals, with different pulsation, ω_M and ω_m. The system response is processed in order to obtain information about different pulsation signals, $\omega_M+\omega_m$ or $\omega_M-\omega_m$, their appearance being illustrated by the trigonometric equality:

$$\sin(\omega_M t)^2 - \sin(\omega_m t)^2 = \sin((\omega_M + \omega_m)t)\sin((\omega_M - \omega_m)t) \tag{2}$$

Demodulation techniques use also a perturbation containing two sinusoidal signals, with high and low pulsation values, and due to the non-linear behavior of the electrochemical system, the response signal will contain only the low pulsation component [5].

An other non-classical impedance spectroscopy method involves non-stationary impedance concept [6], where the components of the response signal change in time, demanding sophisticated equipment and mathematical processing, as for ex. the rotational Fourier transform [7].

The above mentioned impedance spectroscopy methods are used especially for kinetic measurements in electrocatalysis, corrosion, electrosorption, and also for analytical purposes [8]. The main disadvantage of these techniques consists of sophisticated, and therefore even expensive, instrumentation because in addition to the that necessary for linear impedance measurements, supplementary, a transfer function analyzer and high performance narrow band analogical filters are requested for each investigated harmonic.

Nevertheless, the presence of the non-linear distortion is not always desired for the electrochemical system investigation. A usual possibility to avoid it is the use of low amplitude-perturbing signal (lower than 5 mV/n, where n is the number of electrons involved in the electrochemical process). Unfortunately, a low amplitude value of perturbing signal is somehow in contradiction with the requirement of a large signal to noise ratio. Therefore, instead of improving the measurement quality due to amelioration of the system linearity, a too low perturbation will have a contrary effect because the response will be dominated by noise, basically a random signal.

The aim of the present paper is to find an algorithm to compensate the effect of non-linearity distortion on the system response components, in order to calculate those values as in the case of linear behavior, but using a much larger amplitude perturbation.

Non-linearity induced distortion

A steady-state theoretical voltammogram for a reversible electrochemical system is presented in figure 1, illustrating the influence of the d.c. component of the applied potential, E_{cc}, on the time dependence of the current intensity, when a sinusoidal perturbation is imposed. More important, is suggesting the influence of applied d.c. component on the occurred distortion for symmetrical transport condition (equal limiting currents). It can be seen that, for a d.c. potential closed to the half wave potential ($E_{1/2}$), due to the linearity of the electrochemical system, a slight distortion can be evidenced, containing just odd harmonics. At a different d.c. potential value, the response signal is highly distorted, containing both odd and paired harmonic frequencies.

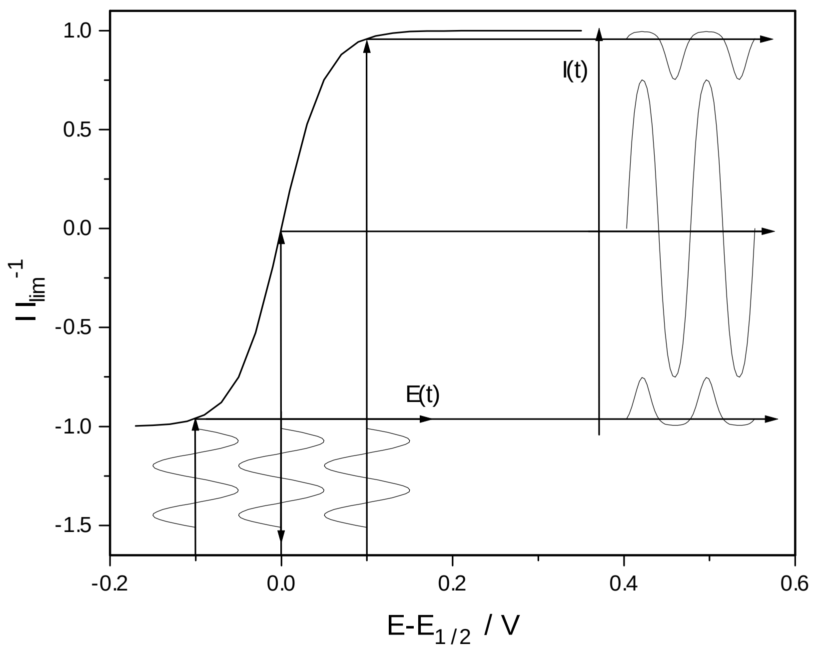

Figure 1. Dependence of the ratio between current intensity and its limiting value on the d.c. component of the applied signal.

Two types of sinusoidal signal distortion can be revealed. If the transfer function of the electrochemical system is linear the output signal is undistorted, containing therefore just the fundamental (first) harmonic frequency. Unlike this situation, if the transfer function in the investigated domain is non-linear, only paired harmonics will be generated. In addition, if the transfer function is asymmetric the odd harmonics will be present, modifying the d.c. current component.

The linearity of an electrochemical system is established if, in potential controlled conditions, for any arbitrary potential, E, the equality:

$$I(E+\Delta E)=I(E)+I(\Delta E) \qquad (3)$$

is verified for any potential perturbation, ΔE. In similar situation, the symmetry condition is:

$$I(E+\Delta E)=-I(\Delta E-E) \qquad (4)$$

As revealed by figure 1, the linearity condition is difficult to be fulfilled, unless the small amplitude perturbation is applied, whereas the symmetry condition is even harder to be respected, unless d.c. potential near half-wave potential and low perturbation are used.

So, if a large enough sinusoidal perturbation is used, the harmonics measurement can provide an alternative method for obtaining information about thermodynamic and, especially, kinetic parameters of the electrochemical system, using a suitable mathematical model. Unfortunately, an other important effect of the non-linear behavior of the electrochemical system is the alteration of the information carried by the fundamental harmonic, both impedance absolute value and delay being affected.

Harmonic parameter evaluation

Considering that the electrochemical system is perturbed in potential controlled conditions, when the time dependence of the potential is given by:

$$E(t) = E_{cc} + \Delta E \sin(\omega t) \quad (5)$$

where E_{cc} is the d.c. component and ΔE the amplitude of perturbing potential signal, and ω is the pulsation. The resulting current intensity is given by:

$$I(t) = I_{cc} + \Delta I_{ca1} \sin(\omega t + \phi_1) \quad (6)$$

for low amplitude perturbation, or:

$$I(t) = I_{cc} + \Delta I_{ca1} \sin(\omega t + \phi_1) + \Delta I_{ca2} \sin(2\omega t + \phi_2) + ... + \Delta I_{can} \sin(n\omega t + \phi_n) \quad (7)$$

if the perturbation is large enough to consider the electrochemical system outside the linearity domain. In above-mentioned equations, I_{cc} is the d.c. and $\Delta I_{ca\,n}$ the amplitude of n-th harmonic components of the current intensity, ϕ_1 is the phase of the first harmonic current intensity referenced to potential phase and $\Delta\phi_n=\phi_n-\phi_1$ is the delay between the n-th and the first harmonics components of current intensity.

For the determination of various harmonics parameters two approaches can be considered: analogical signal processing, i.e. using several phase lock amplifiers in order to obtain the component of given phase and frequency [9]; digital processing, when a data array representing the current and potential values are used for evaluation of the impedance parameters. The increasing use of the later solution is caused by flexibility, accuracy and, not at least, to lower prices of that solution caused especially by the huge progress of personal computers industry. Digital treatment can be performed in various ways, but more frequent the Fourier transform procedure is used.

The use of the Fourier transform is based on the idea that any periodic signal, like above I(t) function, can by presented as a superposition of sinusoidal signals, with different frequency in arithmetic progression. Using the fundamental frequency, the smallest, adding the harmonic frequencies, both odd and paired, any arbitrary periodic signal can be reconstructed, so information contained by the amplitudes and phases of the different harmonics can be used for quantitative evaluation [10]. The Fourier transform definition is:

$$F(I(t)) = I(\omega) = \int_0^{\infty} I(t)\exp(-j\omega t)dt \tag{8}$$

where ω is the pulsation of transformed signal, I(ω) and j is the complex operator.

It can be mentioned that non-linear fitting procedures, e.g. Levenberg-Marquardt analysis, or even a multidimensional linear fitting procedures, subsequent to the fitting model's linearization, can be used successfully for the evaluation of various harmonics parameters and the estimation of system's non-linearity.

RESULTS AND DISCUSSIONS

The case of a reversible electrochemical system under potential controlled steady-state conditions will be considered. Therefore, the comparison between the calculated results and the experimental ones must be done just for low frequency measurements. Also will be examined just the case of symmetric mass transport when anodic and cathodic currents have the same limiting values. The simulation of the system behavior was performed using LabVIEW™ graphic programming media due to the important data analysis facilities offered.

In these conditions for the electrode process:

$$O + n e^{-} \leftrightarrow R$$

the equilibrium potential is given by:

$$E(t) = E_{1/2} + \frac{RT}{nF}\ln\left(\frac{1+\dfrac{I(t)}{I_{\lim}}}{1-\dfrac{I(t)}{I_{\lim}}}\right) \tag{9}$$

where: I_{lim} is the limiting current intensity, $E_{1/2}$ is the half-wave potential and R,T and F have theirs usual meanings. From that, the theoretical steady-state transfer function can be derived:

$$\frac{I(t)}{I_{\lim}} = \frac{\exp\left(\dfrac{nF}{RT}\left(E(t)-E_{1/2}\right)\right)-1}{\exp\left(\dfrac{nF}{RT}\left(E(t)-E_{1/2}\right)\right)+1} \tag{10}$$

and was presented in figure 1 for one electron transfer and 25° C.

Using the non-linear Levenberg-Marquardt fitting procedure, with a multi-sinusoidal regression model, as in equation 7, up to 20 harmonics amplitude and delay can be obtained. This is equivalent with the solve of the next integral equations for the continuous component of the current intensity:

$$I_{CC} = I_{\lim} f_o \int_0^{\frac{1}{fo}} \frac{\exp\left(\frac{nF}{RT}\left(E(t)-E_{1/2}\right)\right)-1}{\exp\left(\frac{nF}{RT}\left(E(t)-E_{1/2}\right)\right)+1}\,dt \qquad (11)$$

and for complex harmonic current intensity:

$$I_{ca\,n} = I_{\lim} \int_0^{\frac{1}{fo}} \frac{\exp\left(\frac{nF}{RT}\left(E(t)-E_{1/2}\right)\right)-1}{\exp\left(\frac{nF}{RT}\left(E(t)-E_{1/2}\right)\right)+1} \exp\left(-\,j(2\pi f_o n)t\right) dt \qquad (12)$$

that allows calculation for each individual harmonic of the amplitude, ΔI_{can}, and the phase, ϕ_n, with:

$$\Delta I_{ca\,n} = \sqrt{\mathrm{Re}\{I_{ca\,n}\}^2 + \mathrm{Im}\{I_{ca\,n}\}^2} \qquad (13)$$

$$\phi_n = \tan^{-1}\left(\frac{\mathrm{Im}\{I_{ca\,n}\}}{\mathrm{Re}\{I_{ca\,n}\}}\right) \qquad (14)$$

The used symbols are: f_o the fundamental frequency, and functions Re and Im denotes the real and imaginary components of the harmonic current intensity.

In figure 2 are presented the influence of the sinusoidal potential amplitude (the values are presented in the legend) on the estimated continuous current component, on the left, and on the absolute value of impedance, on the right. The presented data are simulated in the above-mentioned conditions, considering also that I_{lim}=100 mA. For the numerical integration of equations 11 and 12, an array of 2^{12} = 4096 points in a single period sinusoidal signals was used. In the figures are presented the relative potentials, refered to the half-wave potential, $E_{1/2}$, for a one electron transfer process.

It can be remarked that for low amplitude values, slightly exceeding the linearity limit, the electrochemical system response denotes moderate differences from the linear behavior. Whereas, for large amplitude perturbation the occurred errors can be very important, as in the case of the impedance even impeding on the correct magnitude order determination [11].

These differences, attributed to the harmonic component formation, can be quantified by the harmonic parameter values.

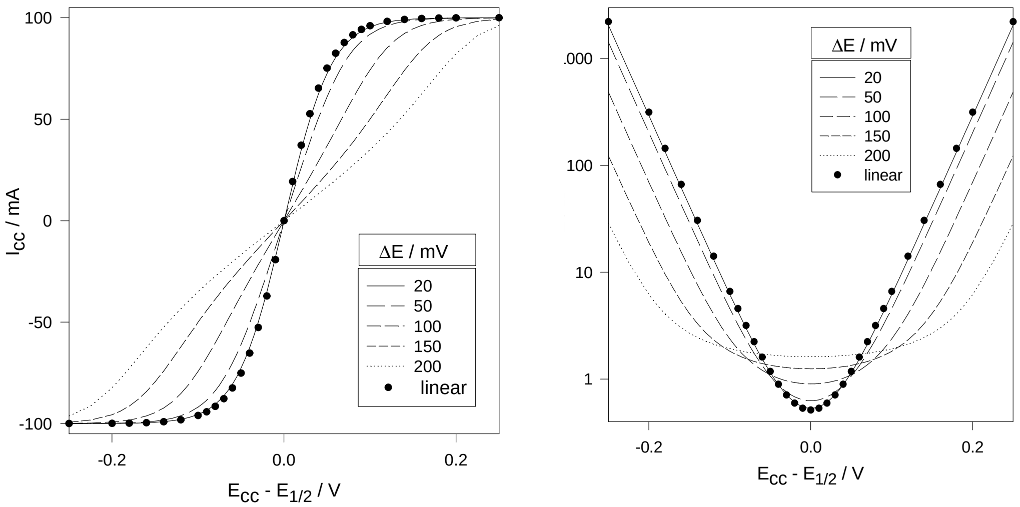

Figure 2. Influence of sinusoidal potential amplitude on the estimated continuous current component (on the left), and on the impedance absolute value (on the right).

For exemplification, in figure 3 are presented the amplitude of odd and paired harmonics for ΔE=0.1 V amplitude perturbation. In order to reveal the sign information, given by the trigonometric function subsequent to the amplitude, in figure 4 are presented the first five harmonics. It should be mentioned that the F function denotes sine for paired and cosine for odd harmonics.

It can be mentioned that amplitudes of a high order harmonic rapidly decline under the measurement limits, that can not exceed four orders of magnitude, especially for continuous component far from half-wave potential. Also, the numbers of the potential where the harmonic amplitude fall to zero, are depending on the harmonic order and could be easily calculated by simple decrementation of the harmonic order.

The amplitude and delay of an arbitrary order current equations, found by means of simulated data analysis, as a function of applied continuous and sinusoidal potential components was previously reported [12].

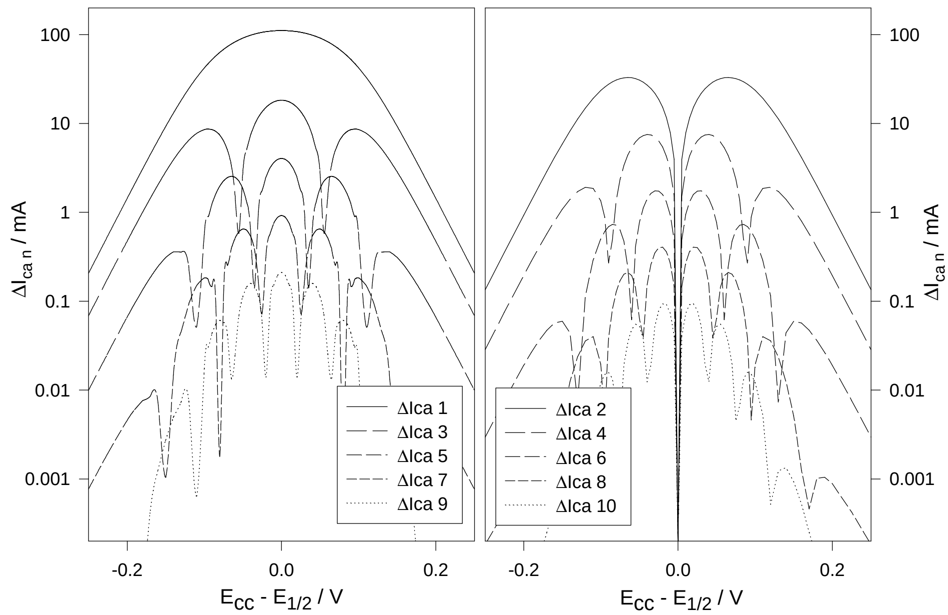

Figure 3. Influence of the applied continuous potential component on the estimated amplitude of sinusoidal current, for odd (on the left), and paired (on the right) harmonics (see the legend.

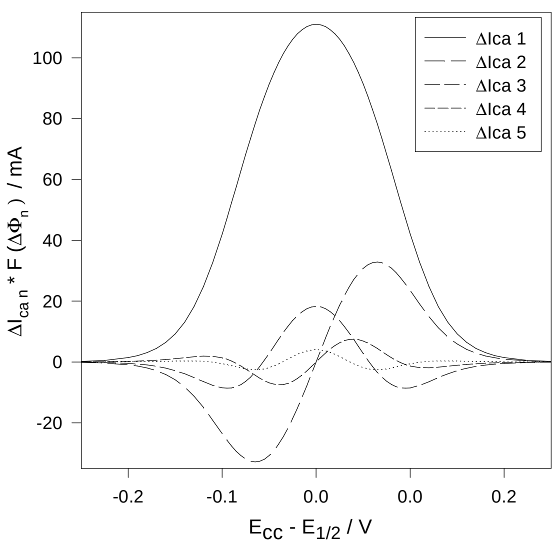

Figure 4. Influence of applied continuous potential component on the estimated amplitude of sinusoidal current harmonics (see the legend).

Inspired by that and using a multidimensional fitting procedure based on “trial and error” principle, the following equations were found, allowing the calculation of the continuous and sinusoidal current intensity components:

$$I_{cc,lin} = I_{cc} + \Delta I_{ca2}\sin(\Delta\phi_2) + \Delta I_{ca4}\sin(\Delta\phi_4) + ... + \Delta I_{ca2n}\sin(\Delta\phi_{2n}) \quad (15)$$

$$\Delta I_{ca1,lin} = \Delta I_{ca1} + 3\Delta I_{ca3}\cos(\Delta\phi_3) + ... + (2n+1)\Delta I_{ca2n+1}\cos(\Delta\phi_{2n+1}) \quad (16)$$

From these equations the absolute value of impedance could be calculated as:

$$Z = \frac{\Delta E}{\Delta I_{ca1,lin}} \quad (17)$$

where “lin” index from subscript of $I_{cc,lin}$ and $\Delta I_{ca1,lin}$ terms, denotes the corrected value, as their determination was performed using a small amplitude perturbation, when the linear behavior condition is fulfilled.

For the validation of equation (15) and (16), relative errors of continuous component and absolute impedance were calculated and presented in figure 5. It must be mentioned that, even if only the first twenty harmonics were used the results for impedance correction are very good, with errors not exceeding 1% in any situation, even for larger amplitude perturbation of 0.2 V. In the absence of the non-linearity correction the errors

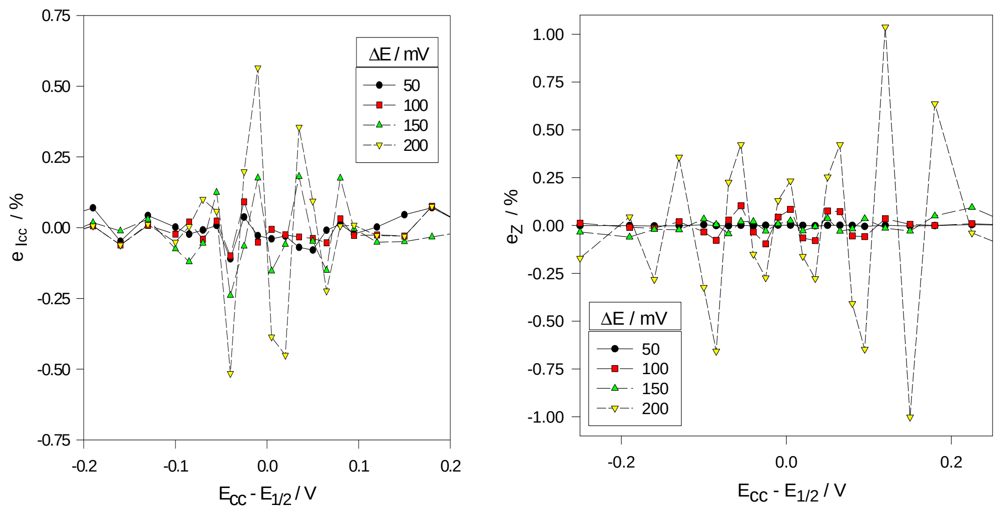

Figure 5. Determined relative error for continuous current component (on the left) and absolute impedance values (on the right) for different values of the applied continuous potential component.

can exceed 6000 %. In the case of continuous component correction the results are even better, partly due to a less important effect of non-linearity on the continuous current component, as revealed by figure 2.

Despite the spectacular results, the practical application of equation (15) and (16) is limited by experimental possibility of obtaining information about the harmonics generated by the system non-linearity. The use of digital instrumentation, based on “Laboratory Virtual Instrumentation” concept launched by National Instruments, and a wide range of data acquisition, processing and analysis functions, seems to be the optimum solution for impedance spectroscopy measurements, especially if the information about the system’s non-linearity is required.

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