

Differential analysis of dynamic immittance spectra

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ARTICLE INFO

Keywords:

Dynamic electrochemical impedance spectroscopy
Equivalent circuit modelling
Differential impedance analysis

ABSTRACT

This work presents a new approach to the analysis of immittance spectrograms of systems characterised by non-stationarity. The possibility of linking the evolution of the immittance response with changes in the parameters describing the system is achieved by introducing a spectrum in differential form. By using the above procedure, it becomes possible to separate elements with a dependence (or lack thereof) from an independent variable appearing in the dynamic electrochemical impedance method. The work illustrates the usefulness of this approach for the elementary components used to model the behaviour of electrochemical systems.

1. Introduction

The electrochemical impedance spectroscopy (EIS) technique [1] is one of the basic tools in modern electroanalysis [2,3]. One of the promising directions in EIS development is the variant that allows the analysis of time-dependent responses by means of several different methodologies [4]. A common feature of the approaches taken by Bondarenko [5] and Darowicki [6] is the use of a multi-frequency perturbation signal and its analysis by means of short-time Fourier transformation. The above-mentioned approach, referred to as dynamic electrochemical impedance spectroscopy (DEIS), makes it possible to obtain a set of impedance spectra describing changes in the electrochemical system [7], treated as one maintaining piecewise stationarity for time segments subjected to transformation [8].

The issue of stationarity of the tested system is associated with the need to preserve the invariability of its properties during the measurement period. In the case of typically non-stationary electrochemical systems correction procedures can be used, taking into account the temporal evolution of system behaviour [9]. On the other hand, it is possible to ease the stationary requirement by reducing the measurement time, to which a sufficiently small change in the properties of the object (pseudo-stationarity) can be assumed. The above goal is achieved by parallelizing the impedance measurement for several frequencies, which effectively shortens the total measurement time.

Extended information on the behaviour of the system can be extracted from the impedance changes as a function of a specific independent variable. The paper [11] presents the possibility of application of differential impedance analysis for results obtained by impedance differentiation versus frequency.

DEIS experimental conditions automatically impose the presence of an additional variable (usually potential or current), creating constraints on the behaviour of the examined system. The new method of analysis is based on the assumption that the impedance (or generally immittance) as a function of an independent variable will behave differently, depending on whether or not the elements of the equivalent circuit depend on the above variable.

In this work, the authors present the theoretical foundations of a new approach to the analysis of immittance spectra, taking into account the use of differential dependencies of immittance versus potential, treated as independent variable, used in DEIS experiments.

2. Theory

The general term immittance G refers to a family of electrical system transfer functions defined in the frequency domain. The most frequently used are impedance Z , and its inverse, admittance Y . While both of the above quantities are well suited for conductive systems, in the case of electrochemical power sources technology [12] (super-capacitors, fuel cells) it may be convenient to use the complex capacitance C , defined by relation:

$$C = C' + jC'' = \frac{1}{j\omega Z} = -\frac{Z''}{\omega(Z'^2 + Z''^2)} + j\frac{Z'}{\omega(Z'^2 + Z''^2)} \quad (1)$$

where C' is the dielectric capacitance, and C'' the dielectric loss of the system, respectively.

The content of information in the immittance representation, expressed with use of any of the above quantities, increases significantly in the case of DEIS. As a result of a single experiment, a time-dependent

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data set (spectrogram) is obtained, and an additional correlation appears between the immittance values, due to presence of an independent variable, usually the potential or current. As a new quantity, a derivative of immittance is introduced relative to the potential independent variable:

$$\frac{\partial G(E, \omega)}{\partial E} = \frac{\partial G'(E, \omega)}{\partial E} + j \frac{\partial G''(E, \omega)}{\partial E} \quad (2)$$

which leads to the creation of a set of differential spectra, depending on the topology of the equivalent circuit, modelling the behaviour of the examined object. The differential spectrogram (2), due to its dependence on potential, can be used to analyse the behaviour of an object with mixed stationary/non-stationary (potential-dependent) behaviour.

Let's assume that the investigated system can be modelled by serial or parallel connection of resistive and capacitive elements. Moreover, in this simplified, theoretical approach only resistive component will exhibit dependence on potential. Depending on the topology of the equivalent circuit and the chosen immittance type, several differential representations can be derived. In the case of serial connection of elements, the differential impedance components are described by the formula:

$$\frac{\partial Z_s'(E, \omega)}{\partial E} = \frac{dR}{dE}, \quad \frac{\partial Z_s''(E, \omega)}{\partial E} = 0 \quad (3)$$

On the other hand, for parallel interconnection, the expressions for the real and imaginary parts take a more complicated form:

$$Z_p'(E, \omega) = \frac{R}{1 + \omega^2 R^2 C^2} \quad (4)$$

$$\frac{\partial Z_p'(E, \omega)}{\partial E} = \frac{\frac{dR}{dE}(1 + \omega^2 R^2 C^2) - R(2\omega^2 R C^2) \frac{dR}{dE}}{(1 + \omega^2 R^2 C^2)^2} = \frac{(1 - \omega^2 R^2 C^2)}{(1 + \omega^2 R^2 C^2)^2} \left(\frac{dR}{dE} \right) \quad (5)$$

$$\lim_{\omega \rightarrow 0} \frac{\partial Z_p'(E, \omega)}{\partial E} = \left(\frac{dR}{dE} \right); \quad \lim_{\omega \rightarrow \infty} \frac{\partial Z_p'(E, \omega)}{\partial E} = 0 \quad (6)$$

$$Z_p''(E, \omega) = \frac{\omega R^2 C}{1 + \omega^2 R^2 C^2} \quad (7)$$

$$\frac{\partial Z_p''(E, \omega)}{\partial E} = \frac{2\omega R C \frac{dR}{dE}}{(1 + \omega^2 R^2 C^2)^2} \quad (8)$$

$$\lim_{\omega \rightarrow 0} \frac{\partial Z_p''(E, \omega)}{\partial E} = 0; \quad \lim_{\omega \rightarrow \infty} \frac{\partial Z_p''(E, \omega)}{\partial E} = 0 \quad (9)$$

Depending on the RC connection topology, the obtained differential relationship allows determination of the resistance change either according to (3) for the serial variant, or by extrapolation of the low-frequency part of the spectrum to the real axis according to (6). The preferential utilization of the impedance form of the transfer function is also noticeable for this type of connection, in which case the processing and interpretation of the spectrogram has a simpler form.

An analogous interpretation in the context of complex capacitance involves Eqs. (10) and (11) for parallel and serial connections, respectively:

$$\frac{\partial C_p'(E, \omega)}{\partial E} = 0; \quad \frac{\partial C_p''(E, \omega)}{\partial E} = \frac{j}{\omega R^2} \frac{dR}{dE} \quad (10)$$

$$\frac{\partial C_s(E, \omega)}{\partial E} = \frac{j}{\omega Z_s^2(E, \omega)} \frac{\partial Z_s(E, \omega)}{\partial E} \quad (11)$$

In the parallel case (10), the spectrogram of the complex capacitance of the system is simplified to the imaginary component, representing the change of resistance value.

Based on Eqs. (3)–(11), it can be found that, depending on the data projection and connection topology used, in some cases the differential

spectrogram, containing only the real or imaginary part, should reflect the variability of the potential-dependent element without any influence of the independent one.

3. Results and discussion

The equivalent circuits described earlier reflect the important case of a blocking electrode and an electrode undergoing a faradaic process. To visualise the usability of the dependences (3)–(11) a numerical simulation was made for systems with RC and (RC) topology in accordance with the Boukamp notation. Calculations of spectrograms were made for conditions of linearly changing potential, selected in a way that visualises changes in the immittance response, resulting from the resistance change trend. A capacitor of $C = 100 \mu\text{F}$ was used as an element independent of potential, the characteristic of the Faradaic element (R) was constructed according to the following dependency:

$$R(E) = \exp\left(\frac{RT}{\alpha F i_0} \left(\frac{-\alpha F E}{RT}\right)\right) \quad (12)$$

with parameters $\alpha = 0.5$, $i_0 = 1 \cdot 10^{-3} \text{A}$, and the potential derivative appearing in formulae (5), (6) and (10) equal to:

$$\frac{dR(E)}{dE} = \frac{-1}{i_0} \exp\left(\frac{-\alpha F E}{RT}\right) = \frac{-\alpha F}{RT} R(E) \quad (13)$$

The simulation procedure reflects the conditions of a potentiodynamic DEIS experiment. The potential was changed by a step-wise ($\Delta E = 2 \text{mV}$) increase in its value. For each subsequent step, the dynamic resistance $R(E)$ value was determined in accordance with (12). The value of resistance together with a constant capacitance was used to determine the instantaneous immittance spectrum corresponding to a given potential value. As a result, for each changing potential value, the spectrum, being part of the spectrogram, was obtained. The resulting immittance spectrogram was subjected to differentiation in relation to the independent potential variable. In order to obtain a spectrogram consistent with the relationship (2), one of many available numerical differentiation algorithms can be used; the 3-point Lagrange approximation was applied in the discussed simulation.

Fig. 1 presents the immittance spectra for both methods of connection with the circuit transfer function expressed by impedance and complex capacitance.

The spectrograms presented in Fig. 1(b) and (c) correspond to the situation described by the dependencies (5), (8) and (11) respectively, in which the immittance expressions contain real and imaginary components. On the other hand, Fig. 1(a) and (d) illustrate the situation in which the immittance derivative contains only the contribution of the potential dependent quantity, according to Eqs. (3) and (10), respectively. These are cases with the transition function expressed by serial impedance and parallel complex capacitance. The additivity of differentiation operations results in the elimination of the component independent of the potential, and thus the separation of the element for which such a dependency exists.

In order to verify the theoretical relationships developed, a potentiodynamic DEIS experiment was performed. An electronic circuit consisting of a capacitor and a semiconductor diode connected in parallel was used as a model. The dynamic diode resistance depends on the voltage bias applied, the capacitance is taken as the quantity independent of it. The experimental impedance data were converted into a complex capacitance according to (1). Fig. 2(a) shows the spectrogram for a voltage range in which the exponential increase in diode current is observed. Differentiation in relation to the potential variable enabled the determination of the differential capacitance spectrogram, shown in Fig. 2(b). There is a visible dispersion of the real part of the spectrogram, whose expected value, according to relationship (10), should be zero. The source of deviations is both the uncertainty of impedance determination as well as the error introduced by the numerical differentiation process. It is of particular importance due to the

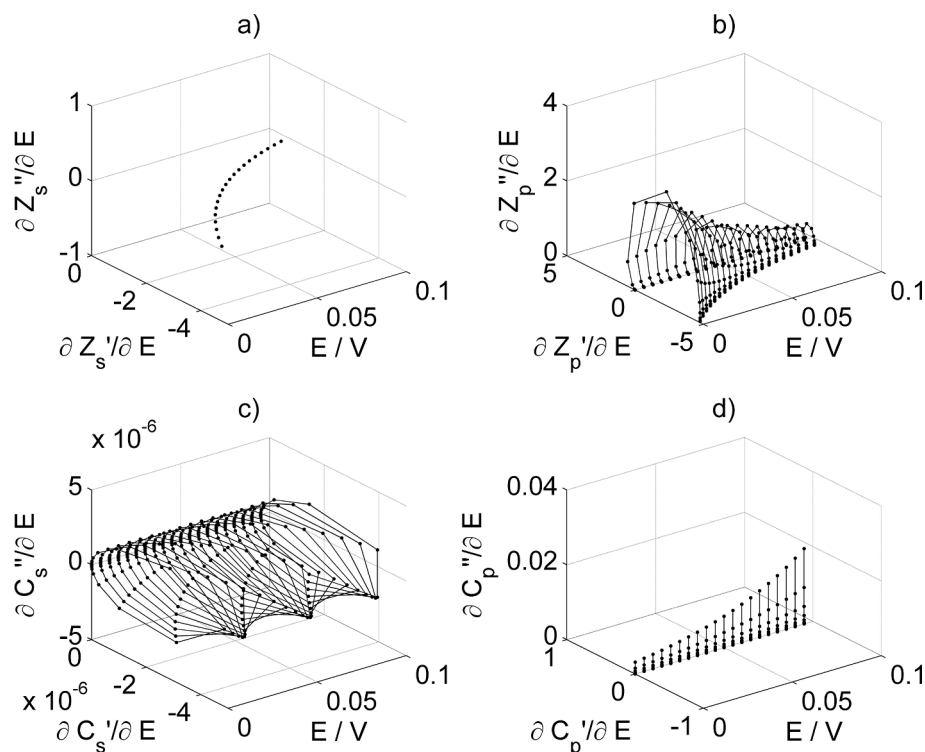


Fig. 1. Simulation of immittance spectrograms of circuits with serial and parallel connection of R and C elements. The capacitor is independent of potential, resistance is an exponential function of potential. (a) Differential impedance of a serial connection, (b) differential impedance of a parallel connection, (c) differential complex capacitance of a serial connection, (d) differential complex capacitance of a parallel connection.

relationship between the accuracy of the determination of differential spectra and the sampling step of current and voltage signals in the time domain, characteristic of the DEIS methodology, and constituting one of its main operating parameters. According to the relationship (10), the imaginary part of the complex capacitance should reflect changes in the dynamic resistance of the diode. For the selected frequency (circles in Fig. 2b) the imaginary values of complex capacitance were

determined. Fig. 2(c) shows a comparison of the values determined by means of spectrogram differentiation (circles) and the value defined by Eq. (10) by differentiating the value of resistance $R(E)$, obtained from matching subsequent spectra to the model (RC) (solid black line). A satisfactory correlation of both quantities is observed, confirming the correctness of the theoretical assumptions made.

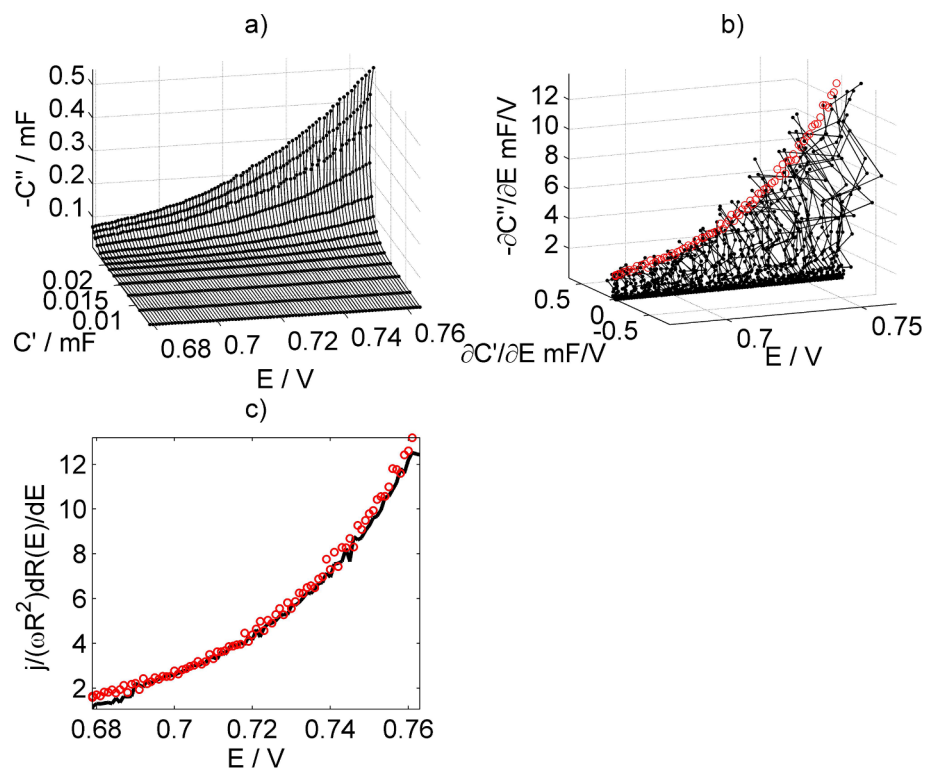


Fig. 2. (a) Complex capacitance spectrogram obtained during a potentiodynamic DEIS experiment on the electronic circuit consisting of parallel connection of a diode (with dynamic resistance dependent on potential) and a capacitor (without potential-dependent capacitance). (b) Differential capacitance spectrogram (-) with points (O) used to estimate resistance derivative, according to (10). (c) Estimation of the term appearing in formula 10 directly from the differential spectrogram (O) and from data obtained by fitting the consecutive spectra (Fig. 2(a) to the equivalent circuit (CR) 2(c)).

4. Conclusions

Dynamic electrochemical impedance spectroscopy allows monitoring of changes in the electrochemical system response as a function of an additional independent variable. This creates the possibility of defining new relationships that can be used to identify system components that depend on the above variable or do not show such dependence. By choosing one of the possible immittances of the tested object, it becomes possible to extract differential dependencies related to individual elements of the equivalent circuit without the influence of the others. This work has an introductory character, describing new methodology for analysing DEIS spectrograms. It is limited to considerations related to elementary connections of equivalent circuit elements. However, the presented assumptions indicate the possibilities of application of differential analysis in issues such as verification of correctness of modelling with the help of the Voigt system or identification of optimal working conditions for electrochemical energy sources, which will be the subject of the authors' future work.

CRediT authorship contribution statement

K. Darowicki: Conceptualization, Methodology, Resources, Writing - original draft, Writing - review & editing, Supervision. **A. Zieliński:** Methodology, Software, Formal analysis, Investigation, Data curation, Visualization, Writing - original draft, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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