



## Full Communication

# Polynomial analysis as a new way of describing dynamic impedance spectra – Differential and relative impedance spectra

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## ABSTRACT

Model measurements of an equivalent electrical system were carried out using the technique of Dynamic Electrochemical Impedance Spectroscopy. The measurement took the form of potentiodynamic changes imposed on the tested system. Using the possibility of continuous impedance measurements, an attempt was made to develop an original and innovative method of analyzing impedance spectrograms, which is termed polynomial analysis. As a result of this approach, it is possible to generate two novel impedance spectra from the primary impedance spectrogram. The innovation lies in the use of simple polynomials to describe a set of spectra, and then performing differential and division operations, which result in differential- and relative-impedance spectra. Among other things, differential spectra have the ability to track the rate of change in impedance as a function of an independent variable. By contrast, relative impedance spectra eliminate surface influence, which opens the way to the direct comparison of physicochemical processes and more.

## 1. Introduction

Electrochemical impedance spectroscopy (EIS) is currently one of the main research methods used in electrochemistry. The development of this technique dates back to the second half of the last century. The first, very important, and comprehensive works on theory, measurement techniques and methods of analysis were by Macdonald [1] and Barsukov [2]. Gabrielli [3] summarized various applications of the EIS method in a concise, but very helpful way, together with a discussion of the results obtained. Mansfeld and Lorenz [4] and Mansfeld et al. [5] focused on the use of impedance tests in corrosion engineering. A broad overview of the application of the EIS method in fuel cell research can be found in the book *Electrochemical Impedance Spectroscopy in PEM Fuel Cells* [6]. Lasia's work [7] is notable for its very insightful and elegant mathematical description of the impedances of various electrochemical processes. Many other valuable reports on other applications of EIS have been published. All these works and studies are connected by a basic assumption of the stationarity of the studied processes.

A new trend in impedance research is Dynamic Electrochemical Impedance Spectroscopy (DEIS), which considers the possibility of studying non-stationary processes. This technique was developed by Darowicki et al. [8–11], Park [12], and Gerengi et al. [13]. Several

articles have been published recently, outlining the current areas of application of the DEIS technique [14–17], especially in the field of fuel cells [18,19], batteries [20], and corrosion processes [21].

Classically, spectrogram analysis comes down to the analysis of elementary sequences of impedance spectra. Individual elementary impedance spectra are usually analyzed using the correlation method, which requires the prior definition of an equivalent electrical circuit. In this way, the dependence of individual electrical elements of the equivalent circuit as a function of the independent variable can be obtained. In this case, there is the question of the correct selection of the equivalent electrical circuit. This classical approach can be replaced by an alternative method, which is polynomial analysis. The use of polynomials to describe spectrograms has already been presented by Darowicki and co-workers [22]. This method consists in using a set of polynomials to describe classical impedance diagrams. Two polynomials are created for each measurement frequency in the examined range of changes of the independent variable. The first corresponds to changes in the real part of the impedance while the second describes changes in the imaginary part of the impedance.

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$$\text{For every measured frequency } f_i \rightarrow \begin{cases} Z^+(f_i, x) \approx a'_1 + b'_1 x + c'_1 x^2 + d'_1 x^3 + \dots \\ Z^-(f_i, x) \approx a''_1 + b''_1 x + c''_1 x^2 + d''_1 x^3 + \dots \end{cases} \quad (1)$$

The polynomial description of impedance changes creates many new possibilities for analysis. In this paper, we will present differential-impedance spectrograms and relative-impedance spectrograms. These concepts are original and have not been discussed previously. Therefore, to illustrate the conversion procedures and the significance of the presented analytical proposal, impedance measurements of a model electrical system were carried out under dynamic conditions, as an example. This approach has an additional value, as it allows for verification of the quality of the measurement results obtained under dynamic conditions.

## 2. Materials and methods

Model RC electrical systems are commonly used to test impedance measurement systems under static conditions. The same can be done for dynamic measurements. The model electrical system designed for dynamic tests consisted of a Schottky diode connected in parallel with a capacitor. The diode resistance is identified with the charge transfer resistance  $R_{CT}$ , while the capacitor  $C_{DL}$  represents the capacitance of the electrical double layer. A resistor  $R_E$  representing the resistance of the electrolyte is connected in series to this system. This arrangement is shown in Fig. 1.

The model, a non-linear electrical system, was polarized in the direction of diode conduction with  $\frac{dE}{dt} = 1 \text{ mV/s}$ . The applied DC voltage changes were identified with the potential changes. The obtained polarization relationship is shown in Fig. 2.

The polarization relationship is described by the equation:

$$\ln i_{DC}(E) = \ln i_{DC}(E_S) + b(E - E_S) \quad (2)$$

where  $b = 18 \text{ V}^{-1}$  is the diode voltage coefficient. The resistance of the diode  $R_{CT}^{DC}$  determined in DC changes with the change of applied potential is as follows:

$$\frac{1}{R_{CT}^{DC}(E)} = \frac{i_{DC}(E)}{dE} = b i_{DC}(E_S) \exp b(E - E_S) = 18 i(E) \quad (3)$$

Due to the polarization, a capacitive direct current flows through the system:

$$i_{DC}^C = C_{DL} \frac{dE(t)}{dt} = 24.610^{-9} \text{ A} \quad (4)$$

$i_{DC}^C$

Over the entire range of tested potentials, the DC charging current of the capacitor  $i_{DC}^C$  was negligibly small. The ohmic drop on the electrolyte resistance  $R_E i_{DC}(E)$  was also negligibly small. Therefore, it was not necessary to correct the current–potential characteristics by the value of

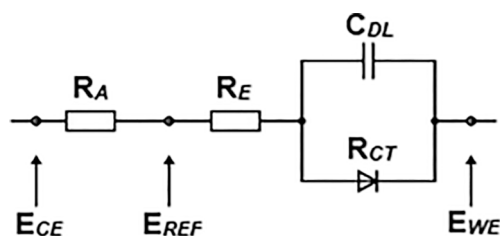


Fig. 1. Model electrical system used in dynamic impedance measurements.  $R_{CT}$  – charge transfer resistance,  $C_{DL} = 24.6 \mu\text{F}$  – double electrical layer capacitance,  $R_E = 2.0 \Omega$  – electrolyte resistance. Points marked on the graph indicate electrode connection points:  $E_{CE}$  – counter electrode,  $E_{REF}$  – reference electrode,  $E_{WE}$  – working electrode. The resistor  $R_A$  connected in series was used as a fuse to prevent a short circuit between the counter and reference electrodes.

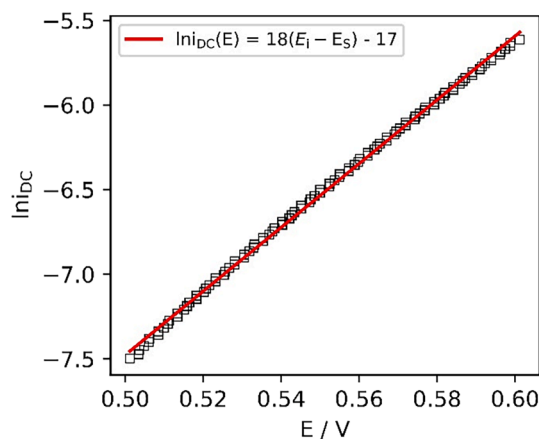


Fig. 2. Polarization dependence of a model electrical system.  $E$  – potential,  $i_{DC}(E)$  – direct current.

ohmic drop and the capacitive direct current.

## 3. Results and discussion

### 3.1. Impedance spectrogram

The model electrical system was polarized as in the DC measurements. The DC potential was changed from  $E = 0.5 \text{ V}$  to  $E = 0.6 \text{ V}$  at a rate of  $\frac{dE(t)}{dt} = 1 \text{ mV/s}$ . A package of 24 elementary voltage signals with selected frequencies and fixed amplitudes was superimposed on the constant potential:

$$E(t) = E_S + \frac{dE(t)}{dt} + \sum_{i=1}^{24} \delta E_i \exp 2\pi f_i t \quad (5)$$

where  $\delta E_i$  is the amplitude of the  $i$ -th voltage perturbation signal.

The current response of the model electrical system is represented by the equation:

$$i(E) = i(E_S) + i_{DC}(E) + \sum_{i=1}^{24} \delta i_i \exp 2\pi f_i t + \varphi_i \quad (6)$$

where  $\delta i_i$  is the amplitude of the  $i$ -th elementary current perturbation signal, and  $\varphi_i$  is the  $i$ -th phase angle.

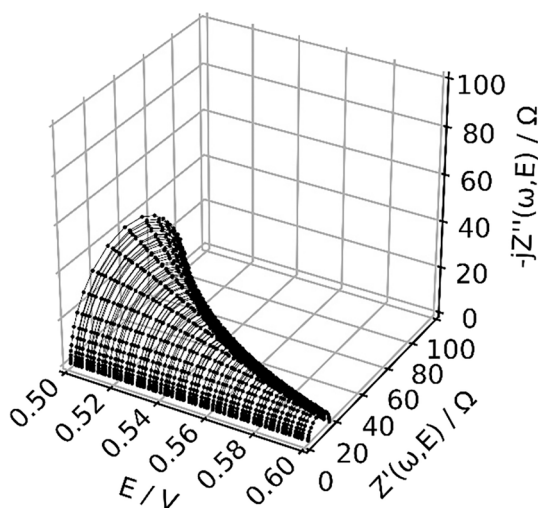
Measurement frequencies ranged from 3 Hz to 4.5 kHz. This range of frequency changes corresponded to a range of amplitude changes from 15 mV to 1 mV. The decomposition of a package of sinusoidal excitations and a package of current responses using the short-time Fourier transform allows the determination of the impedance spectrogram shown in Fig. 3. The procedure for measuring instantaneous impedance spectra has been presented in detail in earlier publications describing applications of dynamic electrochemical impedance spectroscopy [23,24].

The impedance potential spectrogram is composed of many elementary impedance spectra. Single impedance spectra represent the state of the model electrical system for specific potentials. The impedance decreases as the potential increases. The exponential dependence of impedance changes as a function of potential is visible. Each elementary impedance spectrum is determined for the potential  $E_i$  and can be analyzed based on the relationship:

$$Z(2\pi j f, E_i) = R_E + \frac{R_{CT}^A(E_i)}{1 + 2\pi j f R_{CT}^A(E_i) C_{DL}} \quad (7)$$

where  $R_{CT}^A(E_S)$  is the charge transfer resistance determined for the initial potential  $E_S$ .

Conducting a correlation analysis of the experimental spectra and the theoretical equation (7) makes it possible to determine the validity of the proposed measurement technique. It is a universal methodology



**Fig. 3.** The impedance spectrogram of the model electrical system  $R_{E|CDL,R_{CT}}(E)$  determined in the potential range from  $E = 0.5$  V to  $E = 0.6$  V. The rate of change of potential  $\frac{dE}{dt} = 1$  mV/s.

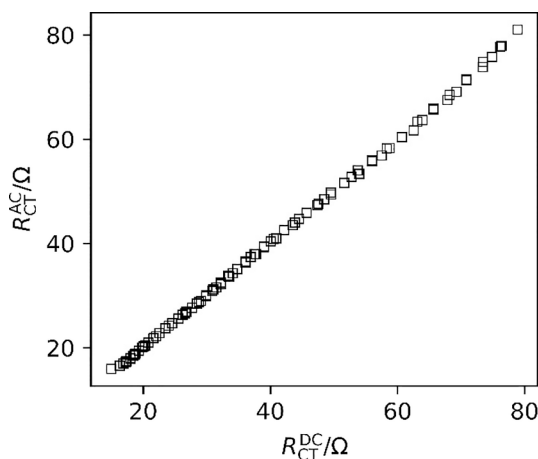
for the verification of measurement quality under dynamic conditions. **Fig. 4** shows changes in resistance  $R_{CT}^{AC}(E)$  determined based on impedance measurements in relation to the value of  $R_{CT}^{DC}(E)$  determined using DC measurements.

The relationship between  $R_{CT}^{AC}(E)$  and  $R_{CT}^{DC}(E)$  is perfectly convergent at the level of the correlation coefficient  $r^2 = 0.999$ . Therefore, the conducted analysis confirms the correctness of the measurement procedures and the coherence of the DC and impedance measurements.

Changes in impedance in relation to the potential are deterministic and monotonic. Therefore, it is possible to use a different approach to analyze impedance spectrograms which involves the use of a polynomial description. The first stage of this analysis is the transition from the domain of complex numbers representing the analyzed spectrogram to the polynomial domain.

For each frequency  $f_i$ , changes in the real part of the impedance  $Z'(E, f_i)$  as a function of the potential and changes in the imaginary part of the impedance  $Z''(E, f_i)$  in relation to the potential can be approximated by the Taylor series.

For the  $i$ -th frequency  $f_i$  we obtain the series:



**Fig. 4.** Changes in resistance  $R_{CT}^{AC}(E)$  determined from DEIS measurements in relation to the resistance  $R_{CT}^{DC}(E)$  determined from DC measurements.

$$Z'(E, f_i) \approx Z'(E_s, f_i) + \left( \frac{dZ'(E, f_i)}{dE} \right)_{E_s} (E_i - E_s) + \frac{1}{2!} \left( \frac{d^2 Z'(E, f_i)}{dE^2} \right)_{E_s} (E_i - E_s)^2 + \frac{1}{3!} \left( \frac{d^3 Z'(E, f_i)}{dE^3} \right)_{E_s} (E_i - E_s)^3 + \dots \quad (8a)$$

$$Z''(E, f_i) \approx Z''(E_s, f_i) + \left( \frac{dZ''(E, f_i)}{dE} \right)_{E_s} (E_i - E_s) + \frac{1}{2!} \left( \frac{d^2 Z''(E, f_i)}{dE^2} \right)_{E_s} (E_i - E_s)^2 + \frac{1}{3!} \left( \frac{d^3 Z''(E, f_i)}{dE^3} \right)_{E_s} (E_i - E_s)^3 + \dots \quad (8b)$$

The number of terms in the series depends on the chosen criterion of matching the polynomials to the experimental results. In our experiment, the value of the correlation coefficient was taken to be  $r^2 = 0.999$ . Adoption of this criterion implied the use of the fifth-order series to describe changes in impedance in relation to potential.

Determination of impedance polynomials enables the reconstruction of the whole impedance spectrum for the range of tested potentials. The essential value of the polynomial description is the ability to perform mathematical operations (such as differentiation or division) on spectrograms.

### 3.2. Differential-impedance spectrogram

In many cases, as well as the value of the impedance of the tested electrochemical system, the rate of impedance change can be of interest. We deal with this situation when we are interested in changes in the impedance of an electrochemical cell due to changes in current consumption. Other examples are changes in the impedance of organic coatings as a function of exposure time or changes in the impedance of passivated metals and alloys as a function of potential. In such cases, it is reasonable to determine differential-impedance spectrograms.

The fitting of *iso*-frequency polynomials is the starting point for the differentiation operation. Given polynomials of a certain degree, in our case fifth order, we differentiate them with respect to the independent variable. This leads to new polynomials for both the real and imaginary impedance parts.

For the  $i$ -th frequency  $f_i$  we get the differential series:

$$\frac{dZ'(E, f_i)}{dE} \approx \left( \frac{dZ'(E, f_i)}{dE} \right)_{E_s} + \frac{2}{2!} \left( \frac{d^2 Z'(E, f_i)}{dE^2} \right)_{E_s} (E_i - E_s) + \frac{3}{3!} \left( \frac{d^3 Z'(E, f_i)}{dE^3} \right)_{E_s} (E_i - E_s)^2 + \dots \quad (9a)$$

$$\frac{dZ''(E, f_i)}{dE} \approx \left( \frac{dZ''(E, f_i)}{dE} \right)_{E_s} + \frac{2}{2!} \left( \frac{d^2 Z''(E, f_i)}{dE^2} \right)_{E_s} (E_i - E_s) + \frac{3}{3!} \left( \frac{d^3 Z''(E, f_i)}{dE^3} \right)_{E_s} (E_i - E_s)^2 + \dots \quad (9b)$$

Based on the polynomials (9a) and (9b), it is possible to return to single impedance spectra determined for individual potential values in the  $\Delta E = (E_i - E_s)$  range. This operation makes it possible to obtain new differential spectrograms for a given system. Such an operation was not possible under the conditions of classical EIS measurements, because in this case we only obtain one spectrum. Of course, we could have a set of spectra and could then apply the presented approach, but the main goal of the polynomial analysis is to use it in conjunction with continuous impedance data. The differential-impedance spectrogram of the model electrical system created in this way is shown in **Fig. 5**.

**Fig. 5** shows the convergence of the differential spectrogram and the primary spectrogram. This similarity is due to the exponential dependence of the charge transfer resistance on the potential. For the model electrical system, a single impedance spectrum determined for a specific

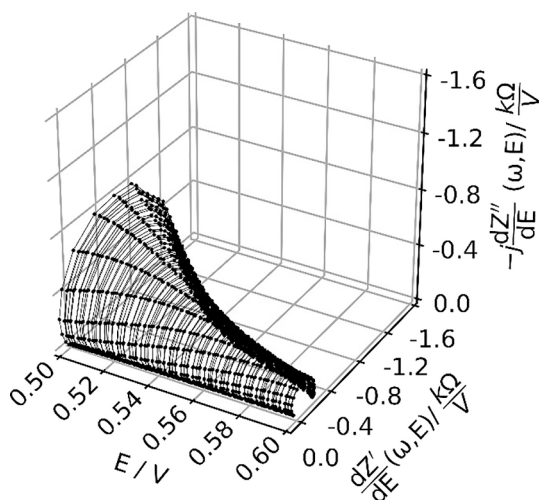


Fig. 5. Differential-impedance spectrogram of a model electrical system  $R_E[C_{DL}R_{CT}(E)]$  determined in the potential range from  $E = 0.5$  V to  $E = 0.6$  V. The rate of change of potential  $\frac{dE}{dt} = 1$  mV/s.

potential  $E_i$  is given by the equation:

$$\frac{dZ(2\pi jf, E_i)}{dE} = \frac{\left(\frac{dR_{CT}^{AC}(E)}{dE}\right)_{E_i}}{[1 + 2\pi jf C_{DL} R_{CT}^{AC}(E_i)]^2} \quad (10)$$

The minus sign on the axis of the figure is associated with decreasing impedance as the potential increases. The analysis of changes in the differential impedance spectrogram makes it possible to determine which electrical element of the equivalent circuit depends on the potential and which is independent of the potential. However, the main information is the rate of change of the impedance of a given process relative to an independent variable. In the presented case, this variable is potential.

### 3.3. Relative-impedance spectrogram

The determination of the differential spectrogram creates further opportunities to process the impedance measurements obtained by the DEIS method. For example, it is possible to determine the relative-impedance spectrogram.

Comparing absolute impedances or their changes as a function of an independent variable does not always provide us with sufficient information. Comparing changes in the impedance of anti-corrosion organic coatings as a function of time is a complex issue due to the low reproducibility of measurement results. It is difficult to prepare sets of coatings with ideal initial impedances. Comparing changes in the impedance of different fuel cells or electrochemical cells is also unjustified due to lack of knowledge of the actual electrode surfaces. Evaluation of the impact of the surface on the intensity of electrochemical processes is essential. Usually, we only have a geometric surface area, which does not reflect the electrochemical surface. Equally often, it is not possible to determine the electrochemical surface using physicochemical methods or this is complicated. However, the influence of surface area is always crucial.

If any electrical parameter  $X$  describing a given process, such as capacitance, resistance, Warburg coefficient, etc., depends on the surface, then this creates a problem. Note, however, that the determination of  $\frac{dX}{dE}$  eliminates the influence of the surface area. These issues explain the idea behind determining relative-impedance spectrograms. The polynomial method presented in this publication offers the possibility of determining relative-impedance spectrograms.

Having a set of basic polynomials (8a) and (8b) and a set of differential polynomials (9a) and (9b) for any fixed potential  $E_i$  and each

measurement frequency  $f_j$ , it is possible to convert:

$$\frac{dZ(2\pi jf, E_i)}{Z(2\pi jf, E_i)dE} = \frac{\left(\frac{dR_{CT}^{AC}(E)}{dE}\right)_{E_i}}{R_{CT}^{AC}(E_i) [1 + 2\pi jf C_{DL} R_{CT}^{AC}(E_i)]} \quad (11)$$

Spectra of relative impedance determined in this way for different potentials create a relative-impedance spectrogram, as shown in Fig. 6.

For each potential and extremely low frequencies, the relative impedance of the model electrical system is real and is equal to:

$$\lim_{f \rightarrow 0} \frac{dZ(2\pi jf, E_i)}{Z(2\pi jf, E_i)dE} = \frac{\left(\frac{dR_{CT}^{AC}(E)}{dE}\right)_{E_i}}{R_{CT}^{AC}(E_i)} = -b \quad (12)$$

For extremely low frequencies, the relative impedance does not depend on changes in potential. On the other hand, for extremely high frequencies, the relative impedance of the tested electrical system is imaginary and is equal to:

$$\lim_{f \rightarrow \infty} \frac{dZ(2\pi jf, E_i)}{Z(2\pi jf, E_i)dE} = \frac{1}{2\pi jf \frac{R_{CT}^{AC}(E_i)C_{DL}}{\left(\frac{dR_{CT}^{AC}(E)}{dE}\right)_{E_i}}} = \frac{1}{2\pi jf \frac{R_{CT}^{AC}(E_i)C_{DL}}{b \exp(b(E_i - E_s))}} \quad (13)$$

For extremely high frequencies, the relative impedance measured is given by the imaginary component. The value of the imaginary component of the relative impedance depends not only on the capacitance of the electrical double layer but also on the charge transfer resistance.

## 4. Conclusions

A relative-impedance spectrogram is a new concept dedicated to the comparison of electrochemical processes by eliminating the surface area effect. It is different to the single impedance spectra obtained by the EIS method, and is also different to DEIS primary impedance spectrograms or DEIS differential impedance spectrograms.

The simplicity of polynomial analysis, which makes use of elementary mathematical operations and innovative measurement technology, makes it possible to take a new look at the concepts of impedance, admittance, and complex capacitance.

The combination of dynamic electrochemical impedance spectroscopy with polynomial analysis offers a lot of new information and possibilities. The main advantage of the discussed approach is the relativity

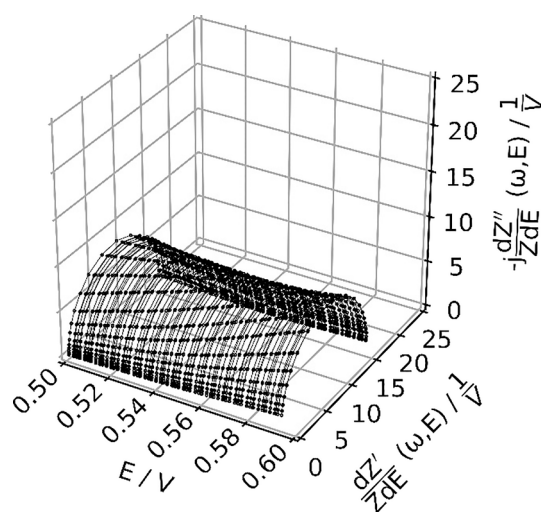


Fig. 6. The relative-impedance spectrogram of the model electrical system  $R_E[C_{DL}R_{CT}(E)]$  determined in the potential range from  $E = 0.5$  V to  $E = 0.6$  V. The rate of change of potential  $\frac{dE}{dt} = 1$  mV/s.

of the obtained data, which makes it possible to make the examined processes independent of the influence of the surface area. In addition, using the polynomial analysis procedure, differential-impedance spectrograms can be obtained. Their differential characteristics make it possible to determine the rate of impedance changes as a function of a particular variable, which permits a more in-depth understanding of the kinetics of a given process. Using relative-impedance spectra, it is possible to directly and quickly compare electrochemical systems such as fuel cells and supercapacitors, as well as previously researched and widely discussed systems such as protective coatings and specific corrosion processes.

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## CRediT authorship contribution statement

**Kazimierz Darowicki:** Conceptualization, Methodology, Writing – review & editing. **Szymon Wysmulek:** Software, Formal analysis, Investigation, Writing – original draft, Visualization. **Anna Karólkowska:** Software, Validation, Visualization.

## 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.

## Data availability

Data will be made available on request.

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