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Short Communication

Polynomial description of dynamic impedance spectrogram—Introduction to a new impedance analysis method

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ABSTRACT

This paper presents a polynomial description of spectrograms obtained using Dynamic Electrochemical Impedance Spectroscopy. A method to fit the polynomial degree correctly is discussed. A simple electrical system of a diode connected in parallel with a capacitor was used for testing. Dynamic impedance measurements during potentiodynamic polarization were conducted. This paper presents an alternative analysis method that allows the determination of system electrochemical characteristics. This method was compared to classical analysis based on equivalent circuit fitting. An alternative method of analysis yielded many advantages in describing impedance results—the potential to obtain an infinite number of impedance spectra over a various range and the possibility to show the resistance and capacitance characteristics as a function of frequency and control of electrochemical energy sources. The polynomial description marks a step forward in analysis automation, facilitating easy and reliable automation and control of electrochemical energy sources.

1. Introduction

Electrochemical Impedance Spectroscopy (EIS) is currently one of the leading research techniques in the evaluation of physicochemical processes [1,2]. According to the database of the Institute of Scientific Information (ISI), 13,000 articles using EIS have been published over the last five years. These articles demonstrated the usefulness of this technique in many scientific fields such as electrochemistry, corrosion or research on fuel cells and electrochemical batteries or supercaps.

Analyzing data obtained from EIS challenges even experienced researchers. Measurements conducted by EIS help verify basic assumptions, thanks to referring to the course of the investigated physicochemical process [3]. Experimental data obtained in this way are analyzed by fitting the equivalent circuit. Correct fitting requires elements of the equivalent circuit to describe the physicochemical processes in the tested system properly [4]. For cases in which theoretical and experimental results differ, a new model is advanced and the whole procedure is repeated [4]. The χ^2 parameter establishes the reliability of the model assumed [5]. The analysis based on the use of an equivalent electrical circuit is currently the only method used to analyze impedance results. However, equivalent circuits do not always reliably represent the system studied and single value of χ^2 cannot be regarded as an absolute, unambiguous measure of the quality of the match. It was stated by Orazem and Tribolet, that "the numerical value of the χ^2 statistic for a weighted regression depends on the estimated variance of the data. The numerical value has no meaning if the variance of the data is unknown." [5] Authors also discussed problem with impedance data fitting in previous works [6–8].

So far, results obtained using the dynamic version of the classical impedance method approach have been analyzed in the same way [8,9]. Due to the possibility of acquiring the impedance spectrum in a very short time [10], the Dynamic Electrochemical Impedance Spectroscopy (DEIS) approach determines impedance changes in a system as a function of a controlled independent variable [11], e.g. impedance spectrogram can be obtained for controlled potential [12], for controlled current [13] etc. Of course, all other system parameters should remain unchanged during this time. Obtaining a set of impedance spectra as a function of one independent variable provides more information than an analysis of a single impedance spectrum. It makes DEIS a useful and powerful method with broad application, e.g. such as monitoring and diagnosis of electrochemical energy source [8,9]. A detailed theoretical and practical description of DEIS has been previously presented in a number of publications [8,14,15].

This paper presents an alternative way to describe and analyze impedance spectra obtained via DEIS. These results were presented as a function of the independent variable, which in turn enabled the

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presentation of frequency characteristics as a function of that same variable. Presenting impedance graphs as a set of polynomials and not as a set of individual impedance spectra facilitated the production of smoothed impedance spectra while eliminating gross errors. These graphs also enabled the analysis of infinite impedance spectra studied over the range for a given variable.

The search for new, more explicit analysis methods and impedance description results is necessary to develop dynamic impedance measurements further. The polynomial description method is a relatively simple approach, but yielded many advantages in the description of impedanceographs and created new possibilities in the analysis of impedance spectrogram. Authors present new methodology of impedance spectrogram analysis, departing from the analysis of individual impedance spectra. This is a novel approach not yet described previously in the literature. The polynomial description enables the implementation of DEIS for automation, control, diagnostics, and monitoring of electrochemical energy sources. Faster and more reliable electrochemical characterization of electrochemical systems can be achieved.

2. Materials and methods

DEIS measurements were conducted in a two-electrode system during potentiodynamic polarization. The measurements were made on a simple electronic circuit consisting of a 10 μF capacitor connected in parallel with the diode. In electrochemical practice, the analysis of impedance spectra by using such a simple RC circuit does not take place, because there is always a component related to the electrolyte resistance. However, the use of polynomial notation of the spectrogram facilitates possibility of performing mathematical operations such as addition, subtraction, differentiation, integration, etc. In the case of more complex electrochemical processes, spectrograms can be simplified by using described operations.

The voltage varied from 0.45 to 0.65 V with a linear change rate of 1 $mV{\cdot}s^{-1}$. During the linear voltage change, the DEIS measurement was performed simultaneously. The multisinusoidal perturbation signal consisted of 31 elementary sine waves with frequencies varied from 1.1 Hz to 19 kHz. Individual frequencies are chosen as a unique prime number or multiplication of this number to avoid any influence of harmonics. Phase shifts and amplitude values were optimized so that the total amplitude of the perturbation signal did not exceed 15 mV. The analyzing window of the Short-time Fourier Transform is dependent on the lowest used frequency. Acquired data was analyzed with 1 s analyzing window. The sampling rate was dependent on the demands to minimum 3 times greater number of samples than highest used frequency, and for obtaining presented results it was set to 76 800 samples per second.

3. Results and discussion

3.1. Dynamic impedance measurements

A description of the expected electrochemical system behavior variability by means of a single imitation spectrum (impedance or admittance) is inadequate. In this case, the description was introduced by means of a spectrogram, i.e. a set of spectra interconnected by the variability of the object's behavior. The evolution of the examined object is a deterministic process that relates changes in immittance with the independent variable (time, potential, current) characteristic of the way the experiment is conducted. Initially, the immittance value must be estimated for the nodes of values of the independent variable before describing changes to the immittance of the system. The length of the segments used for this purpose affects the deviation of the pseudo-stationary approximation of the object description from its actual behavior. The segment estimates of the immittance spectrum construct a set known as a spectrogram. For each spectrum frequency, a specific dependence on the independent variable is observed, defining the isofrequency curves.

Single spectra make it possible to determine the instantaneous values of the model parameters, which is a traditional approach to spectrogram analysis. On the other hand, due to the existence of a deterministic relationship between the isofrequency curve values, an alternative approach of polynomial analysis is possible.

In order to illustrate and introduce the new method of mathematical notation of spectrograms, the experimental results presented in Fig. 1a were used.

The graph shown in Fig. 1a reflects changes in the impedance of the equivalent circuit consisting of a capacitor connected in parallel with the diode during a linear voltage change. The projection of complex admittance (Fig. 1b) shows the same results. Impedance and admittance changes were regular for this system. Each elementary impedance spectrum was extracted and analyzed classically. A theoretically and statistically selected electrical equivalent circuit is most often used for this purpose. Before data analysis, data compliance should be verified by Kramers-Kronig relations [16].

3.2. Polynomial impedance analysis

Here, the authors propose a novel method to analyze the impedance grams. The isofrequency points, marked by characteristic lines in the spectrograms, are visible on the impedance and admittance diagrams. Each point for the i-th frequency corresponds to the described potential E value given by the real $Z^{'}(2\pi f_i E)$ and imaginary $Z^{''}(2\pi f_i E)$ parts of the impedance. For the potential range $E_1 \le E \le E_2$ of impedance spectrogram, changes to the real part of the impedance $Z^{'}(f_1, E)$ and the imaginary part of the impedance $Z^{''}(f_1, E)$ as a function of the potential are presented in the form of polynomials:

$$f_1 \rightarrow \left\{ \begin{array}{l} Z^{'}(f_1, E) \approx a_1^{'} + b_1^{'}E + c_1^{'}E^2 + d_1^{'}E^3 + \cdots \\ Z^{''}(f_1, E) \approx a_1^{''} + b_1^{''}E + c_1^{''}E^2 + d_1^{''}E^3 + \cdots \end{array} \right\}$$

$$f_i \rightarrow \left\{ \begin{array}{l} Z^{'}(f_i, E) \approx a_i^{'} + b_i^{'}E + c_i^{'}E^2 + d_i^{'}E^3 + \cdots \\ Z^{''}(f_i, E) \approx a_i^{''} + b_i^{''}E + c_i^{''}E^2 + d_i^{''}E^3 + \cdots \end{array} \right\}$$

$$f_n \rightarrow \left\{ \begin{array}{l} Z^{'}(f_n, E) \approx a_n^{'} + b_n^{'}E + c_n^{'}E^2 + d_n^{'}E^3 + \cdots \\ Z^{''}(f_n, E) \approx a_n^{''} + b_n^{''}E + c_n^{''}E^2 + d_n^{''}E^3 + \cdots \end{array} \right\}$$

An analogous mathematical description can be used for impedance data in another projection, such as complex admittance or capacitance. Weighted polynomial description was used for presented example. The purpose of introducing weights into the procedure of matching polynomials of an appropriate degree, to raw impedance or admittance data, is to take into account the effect of variability of measurement accuracy depending on the magnitude of measured value. On the other hand, the values of the electrochemical systems' immmitances depend on the frequency and often the general form of such a relationship is similar for typical measurement conditions. Therefore, it is possible to create at least a rough estimate of weight function for the analysed spectrograms. In this demonstration example, such a function was constructed based on the difference between the experimental data and the theoretically derived values for each potential and frequency value, constituting the spectrogram domain. Such an operation requires, of course, the assumption of an equivalent circuit describing the tested electrochemical object.

In the case of an attempt to describe the immittance using the polynomial approximation, it should be noted that the calculation of the polynomial coefficients is usually badly conditioned when the degree of the polynomial is large or the distribution of approximation nodes is incorrectly selected. For this reason, it was decided to limit the increase of the degree until the above effect is revealed. In the case of software package used in actual evaluations it can be observed by monitoring the value of conditional number of decomposed Vandermonde matrix.

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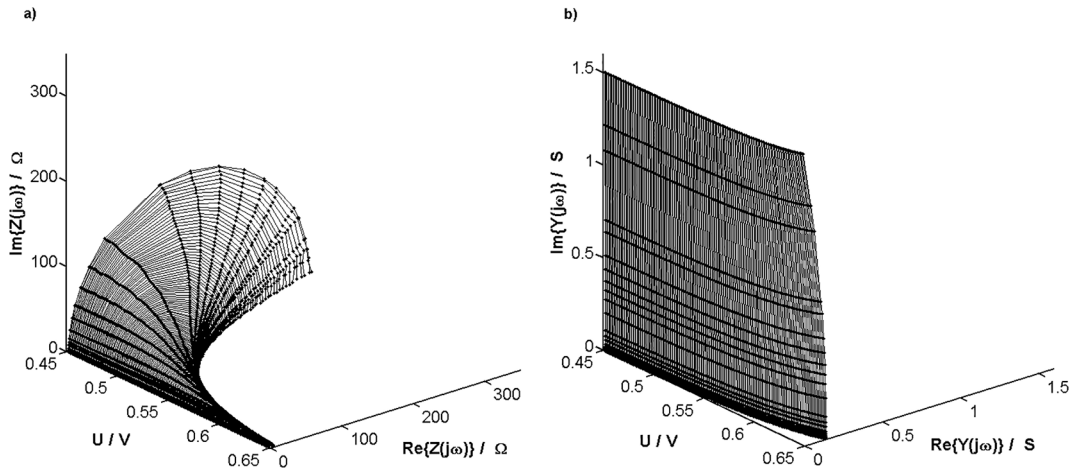

Fig. 1. Results obtained using the DEIS method for the system during voltage changes from 0.45 to 0.65 V shown as a) impedance and b) admittance, graphs. The rate of change = 1 mV·s^{-1}.

3.2.1. Selection of the polynomial degree

Of course, the order of the polynomial depends on the criterion adopted to match the polynomial with experimental data. The authors propose using the correlation coefficient r^2 as the criterion. Fig. 2a shows polynomial matching to the real part of admittance, which equaled the reciprocal of the resistance and the fitting for five different polynomial degrees—3rd, 4th, 5th, 6th, and 7th for the exemplary frequency chosen. The polynomial matching that resulted from the mathematical description of the function is the least "certain" for the boundary values where the deviation of the polynomial function from the measurement points can be seen. For single points for voltages close to 0.45 V (seen in Fig. 2a), the relative error of the values adjusted to the measurement values for the lower polynomial degrees was several hundred percent. However, the fitting was very precise over the entire tested range for higher degree polynomials (6th and 7th).

Fig. 2b shows r^2 as a function of frequency for all fitted polynomials. The last two frequencies deviate significantly from the quality of the fit, clearly shown in Fig. 3a. These polynomials have completely different courses, uncharacteristic for the tested elements, what can indicates for the hardware limitations for the highest frequency measurements. Isofrequency dependencies are not available, when individual impedance spectra are analyzed. The polynomial degree cannot increase infinitely, especially when further mathematical operations on polynomials are planned. Therefore, the lowest polynomial degree that did not improve the r^2 for each frequency by at least 1 * 10^{-6} was chosen. The 6th polynomial degree met the criteria described above and was used for analysis. The polynomial degree selection also depended on various relationships and other polynomial selection criteria may be necessary for more complex changes. Very detailed study on data modeling by Lasia [17] presents alternative fitting criteria, such as weighted sum of squares, what can be better criterion for more complex impedance results. In next steps of development of polynomial spectrogram analysis different approaches will be verified.

3.2.2. Comparison of classical and polynomial impedance analyses

The impedance results were analyzed by two different methods: the

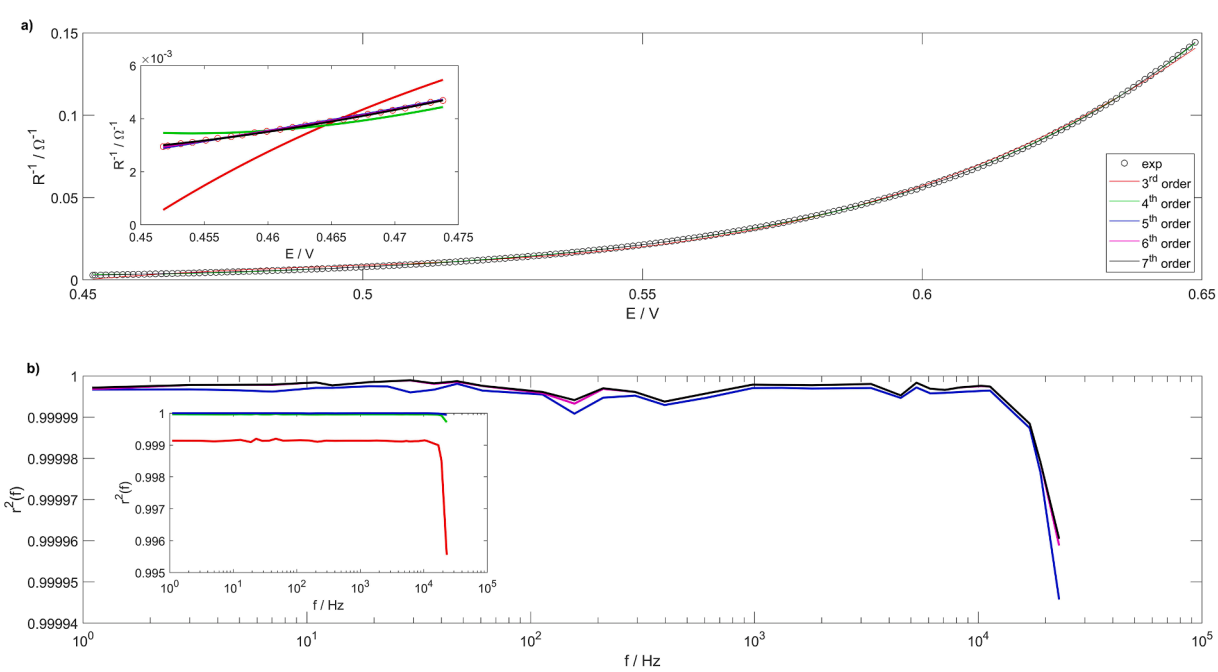

Fig. 2. a) Fitting 3rd, 4th, 5th, 6th, and 7th order polynomials to the real admittance part at a frequency of 1.1 Hz. b) Correlation coefficients for all polynomials fitted to the real part admittance over the entire frequency range.

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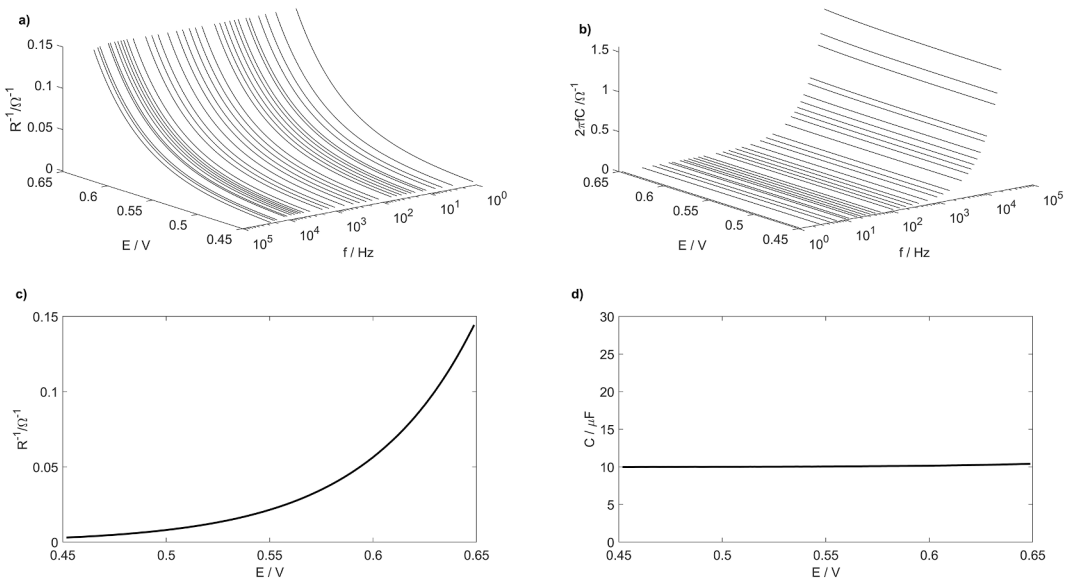

Fig. 3. Comparison of resistance and capacitance results for a), b) polynomial analysis, and c), d) classical analysis using an equivalent circuit.

classical frequency method and the new polynomial analysis. For the simple circuit that consisted of a diode and a capacitor, a polynomial analysis of the admittance spectrogram in Fig. 1b was performed and gave direct results in the form of the resistance reciprocal and capacitance. Sixty-two polynomial waveforms were obtained, twice the number of frequencies used in the excitation signal. Thirty-one polynomial equations for both the real (Fig. 3a) and imaginary (Fig. 3b) portions of the admittance as a function of potential change are shown. Using the classical analysis method and an RC equivalent circuit determined the resistance change (Fig. 3c) and capacitance (Fig. 3d) in the function of the potential change for each impedance spectrum presented in the impedance spectrogram in the function of potential shown in Fig. 1

The resistance of the electrical circuit should not depend on the frequency. In Fig. 3a, the influence of the measurement system is visible at a certain high-frequency range. Analysis of isofrequency dependencies can provide guidelines for determining the usable range of the frequencies tested, what can be supplementary to results obtained by Kramers-Kroning verification. Polynomial correlation analysis gives possibility to obtain frequency dependence of R and C values of investigated system, which is impossible for the impedance analysis with the use of equivalent circuit. The possibility of obtaining electrical parameter dependences based on the frequency creates new possibilities for the analyses of electrochemical processes.

The polynomial description offers many advantages and facilities. First, the polynomial interpolation smooths the spectrogram and helps create individual impedance spectra. Analysis of reproduced spectra with an equivalent circuit helps eliminate gross errors. Secondly, for each potential value in the $E_1 \leq E \leq E_2$ interval, it is possible to determine an elementary impedance spectrum, which allows the acquisition of an infinite number of impedance spectra. Fig. 4 shows spectral reproduction over the entire range of the potentials for the selected polynomial degree matching. Additionally, for a narrow voltage range (0.5–0.51 V), an impedance diagram with higher impedance spectra was acquired thanks to the use of a polynomial description. Only 10 impedance spectra were obtained from the range of voltages tested and shown in the impedance diagram (Fig. 1a). This is an added advantage of polynomial analysis in that it allows us to compute the impedance spectrum for each selected potential value and provides a powerful tool for studying dynamic electrochemical processes.

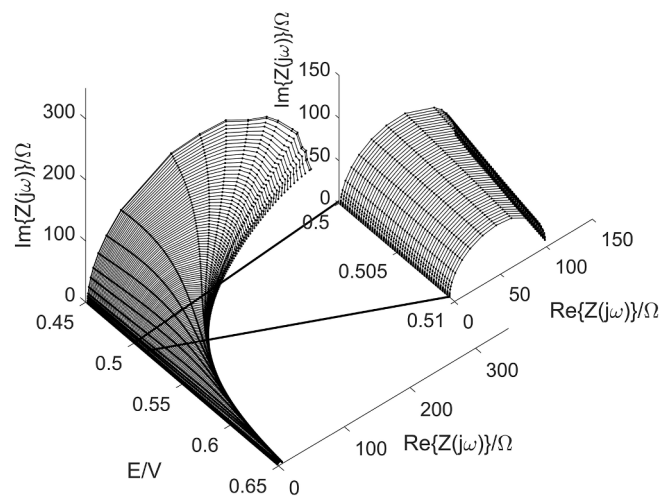

Fig. 4. Reconstruction of the impedance spectrogram over the entire range from polynomial relationships.

4. Conclusions

Dynamic electrochemical impedance spectroscopy monitors impedance characteristic changes as a function of the independent variable. This allows use of polynomial analysis for results obtained and acquisition of the electrochemical characteristics from a particular system. This improves several things—the potential for obtaining an infinite number of impedance spectra in a specific range and the possibility of acquiring resistance and capacitance characteristics as a function of frequency. In addition, reproducing impedance spectra while eliminating gross experimental errors aids impedance analysis automation. In addition, future polynomial spectrogram recordings will enable easy automation and control of electrochemical energy sources (e.g. fuel cells or supercaps). The polynomial data is simple and enables diagnostics and monitoring of the investigated objects.

The polynomial notation creates the potential for carrying out a series of simple mathematical operations on impedance spectrograms. Multinomial notation of spectrograms enables addition, subtraction, multiplication, division, convolution multiplication, integration, and differentiation. These arithmetic operations on polynomials are

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alternatives to digital integration and differentiation and create new automation, diagnostics, and monitoring possibilities of electrochemical energy sources. These operations can be used for more sophisticated analysis purposes, e.g. differential-integral analysis presented.

This work is introductory and describes a new approach to spectrogram analysis. The polynomial analysis is a consequence of the descriptions of dynamic spectra and mathematical operations. These assumptions were confirmed using a simple equivalent circuit example. Based on the impedance result analyses, a polynomial fit criterion was developed using two alternative analysis methods.

CRediT authorship contribution statement

K. Darowicki: Conceptualization, Methodology. **A. Zielinski:** Software, Formal analysis, Visualization, Writing - review& editing. **M. Mielniczek:** Investigation, Visualization, Writing - review& editing, Funding acquisition. **E. Janicka:** Investigation, Validation. **L. Gawel:** Software, Formal analysis, Validation.

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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