Potentiodynamic electrochemical impedance spectroscopy for solid state chemistry

G. A. Ragoisha and A. S. Bondarenko

Physico-Chemical Research Institute, Belarusian State University, Minsk 220080, Belarus

ragoishag@bsu.by

Abstract. Potentiodynamic electrochemical impedance spectroscopy (PDEIS) employs virtual instruments for probing the interface and gives, in real time and in a single potential scan, the multidimensional spectra that characterise complex impedance of the interface as a function of frequency and the electrode potential, along with the potentiodynamic voltammogram. The built-in equivalent electric circuit analyser provides semi-automatic extraction of the potential dependencies of the double layer capacitance, components of Faraday impedance (charge transfer resistance and Warburg impedance) and some additional impedance elements from the impedance spectra extended for the variable potential. PDEIS has been applied to probe the electrochemical response of metal monolayers and nanostructures on various supports.

Introduction

The electrochemical response of the interface between a conductor, or semiconductor, and electrolyte exhibits the characteristic signatures of electronic, chemical and mass transfer processes in the frequency domain, which are the subject of the electrochemical impedance spectroscopy [1]. Electrochemical impedance spectra and the electric current vary with the electrode potential; thus the comprehensive characterisation of the interface by the electrochemical response comprises the voltammogram, that shows the dc current response, along with the dependence of real and imaginary ac impedance components on the frequency and the electrode potential. Because of the complexity of acquisition of the multidimensional electrochemical impedance dependencies, the common electrochemical impedance spectroscopy considers just their constant potential section, missing the information that comes from the dependence of the electrochemical impedance spectra on the potential.

This paper considers the potentiodynamic electrochemical impedance spectroscopy (PDEIS) – the technique that gives, in real time and in a single potential scan, the dependencies of the electrochemical impedance both on the frequency and the electrode potential, together with the potentiodynamic voltammogram. With this new technique the investigator can acquire and analyse both the dc and the ac electrochemical response using the experimental procedure very similar to the common acquisition of the potentiodynamic voltammogram.

Potentiodynamic electrochemical impedance spectroscopy

The precursor of PDEIS – Fourier transform electrochemical instrumentation [2] – uses the multi-frequency excitation superimposed onto a staircase dc potential ramp with the post-experiment Fourier transform decomposition of the total response into a number of individual frequency responses. Though the Fourier transform instrumentation provides some possibility for the simultaneous investigation of the frequency and potential dependencies of the electrochemical response, the post-experimental processing is inconvenient and the Fourier transform technique

imposes a severe restriction on the amplitude of the excitation that results in the limitation of the measurement accuracy, which is critical for the equivalent electric circuit analysis of the impedance spectra. The obstacle is the nonlinearity of the electrochemical system that requires the amplitude of the testing signal to be within 10 mV. This is sufficient for precise processing of a single frequency but the superposition of several frequencies degrades the quality of the response rapidly with the increase in the number of frequencies, even with the optimised component phases of the multi-frequency signal. For this reason we use consecutive probing with a stream of wavelets in a limited frequency range instead of integral multi-frequency probing [3], leaving the integral probing and analysis for preview scans in wider frequency ranges.

Frequency scanning with wavelets gives high accuracy but it is slow when implemented by common instrumentation. Therefore we had to develop fast virtual instruments for probing electrochemical systems and for the real-time analysis of the response.

The heart of the PDEIS spectrometer is the low-level optimised real-time data acquisition and control system [4] that provides a microsecond accuracy of the measurement, processing and control synchronisation without time penalties attributed to most real-time systems. The virtual instruments are entitled to control critical system resources, while Windows gets the control outside the time-critical stages. This symbiosis of the two centres of critical system resources control conciliates the temporal precision achieved on the low level with the availability of advanced high-level functions of the operating system that is normally not assigned to deal with real-time tasks. Besides this advantage over the true real-time operating systems, our virtual instrument concept benefits from direct control of the hardware by the CPU of the computer. Due to immediate processing of the measured data by the CPU, the virtual instruments need neither imbedded processor nor memory chips and counters on the interface board. High-precision time scale is maintained directly by the processor time-stamp counter (this feature is present in Pentium and later CPUs). The speed optimisation in this case complies with the optimisation of the instrument cost.

Fig. 1 shows a schematic diagram of the PDEIS spectrometer. The virtual instruments probe the ac and dc current response of the interface in the three-electrode electrochemical cell by means of the potentiostat that is controlled through digital and analog channels. The electrode potential of the working electrode is controlled versus the reference electrode (AgCl/Ag in this work). A platinised Pt counter electrode of high surface area is used to eliminate the counter electrode impedance from the measured impedance that comprises the electrochemical impedance and some uncompensated serial resistance considered in the equivalent electric circuit analysis. Typically from 20 to 30 frequencies were processed on each potential step of the staircase dc potential ramp, which was sufficient for the separation of Faraday impedance components (charge transfer resistance and Warburg impedance) from the impedance of the electric double layer and the serial resistance. The discreteness of the dc ramp was 1 mV with typical values of the steps from 1 to 5 mV. Larger steps and lower number of frequencies were used to achieve high scan rates in the preview mode, while the typical scan rate for the quantitative analysis of the spectra was from 2 to 5 mV/s. The probing complex ac signal with a maximum 10 mV amplitude was superimposed onto the dc ramp on each step and the response was analysed in real time. The processed spectral range (from several Hz to several kHz) was a compromise between the scan rate and the comprehensiveness of the acquired response.
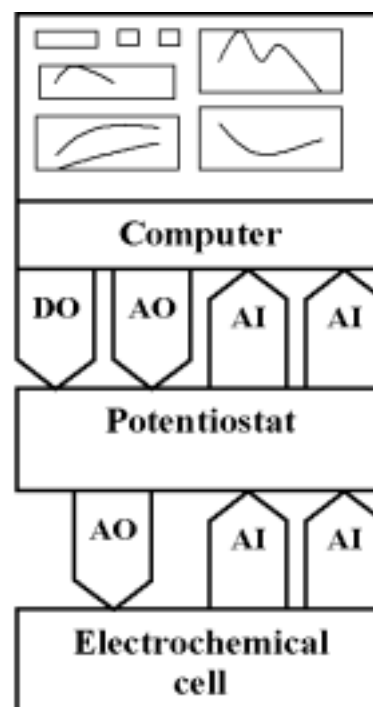

Fig. 1. Schematic diagram of the PDEIS spectrometer; DO – digital output, AO – analog output, AI – analog input.

Fig. 2 shows a typical view of the PDEIS spectrometer screen. Three graphs on the right are the constant potential sections of the 3D PDEIS spectrum presented in common electrochemical impedance spectroscopy coordinates. Nyquist plot shows the frequency dependence of the impedance implicitly as the imaginary impedance dependence on the real impedance. Imaginary impedance results from the elements of the equivalent electric circuit that shift the phase of the signal – capacitors (electric double layer capacitance, surface space charge layer capacitance and pseudo-capacitance of the processes conjugated with the charge transfer, e.g. adsorption), inductors, constant phase elements, specific electrochemical elements attributed to the diffusion, etc., while real impedance results from resistors (resistance of the electrolyte, charge transfer resistance) and the damping effect of the complex electrochemical elements, e.g. Warburg impedance. Bode plots beneath the Nyquist plot show explicitly the dependence of impedance magnitude and the phase shift on the frequency. During the potential scan the information in all those plots is renewed dynamically resulting in the animation of the plots. The film can be replayed after the scan or examined frame-by-frame. The same information is accumulated in the 3D spectrum on the left which can be displayed in three coordinate systems and viewed in different perspectives. In Fig. 2 the 3D spectrum of Ag nanostructures in the cyclic redox transformations on glassy carbon surface is shown in the form of the variable potential extension of the Nyquist plot, while the PDEIS spectrum of Ag nanoparticles on Au surface in Fig. 3 is shown in three different forms (variable potential extensions of Nyquist and Bode plots). The switching between the different representations of the PDEIS spectrum is achieved by clicking the corresponding button of the control panel on the screen beneath the spectrum.

The potentiodynamic voltammograms that are also shown in Figs. 2 and 3 were obtained from the same streams of data with the impedance spectra. Thus with PDEIS one can compare voltammograms and impedance spectra for just the same state of the electrode, which is important for variable, e.g. nanostructured systems.

Fig. 4 gives the idea of how much information is missing by the common potentiodynamic dc probing that ignores the frequency variance of the electrochemical response. Figs. 4 a, b, and c show the same PDEIS spectrum in different perspectives with the corresponding cyclic voltammogram. The cyclic voltammogram shows only a peak of the anodic oxidation of the new phase nuclei generated on Pt surface in the cathodic scan, while the PDEIS spectrum exhibits the exquisite 3D portrait of the same processes.

The power of PDEIS results from different potential and frequency dependencies of the complex impedance of various participants of the charge transfer on the interface, which enables the computation of parameters that characterise the interface by solving the impedance spectroscopy inverse problem.

In the present version of PDEIS we have implemented a semi-automatic analysis that processes the PDEIS spectrum frame-by-frame on the constant potential sections. The nonlinear fitting engine based on three different algorithms fits each frame of the spectrum to the corresponding equivalent electric circuit and determines the parameters that characterise the electric double layer, charge transfer resistance, the impedance attributed to the diffusion of the electrochemically active particles, the resistance of the electrolyte, the capacitance of the surface space charge layer (the extraction of this parameter from impedance spectra enables plotting of the semiconductor Mott-Schottky plots), pseudo-capacitance and pseudo-resistance of adsorption, etc.

Fig. 5 shows some examples of the equivalent electric circuit parameters dependencies on the potential for the interfaces that comply with relatively simple equivalent circuit shown in the insert to Fig. 5-a. R_s stands for the resistance of the solution, R_{ct} – charge transfer resistance, W – Warburg impedance (the specific electrochemical element that represents resistance and reactance of the diffusion), CPE – constant phase element. The later represents a non-ideal capacitor with a phase shift less then $\pi/2$ radians. The double-layer capacitance often comply with this element that mathematically represents the inadequacy of the system's description in terms of ordinary
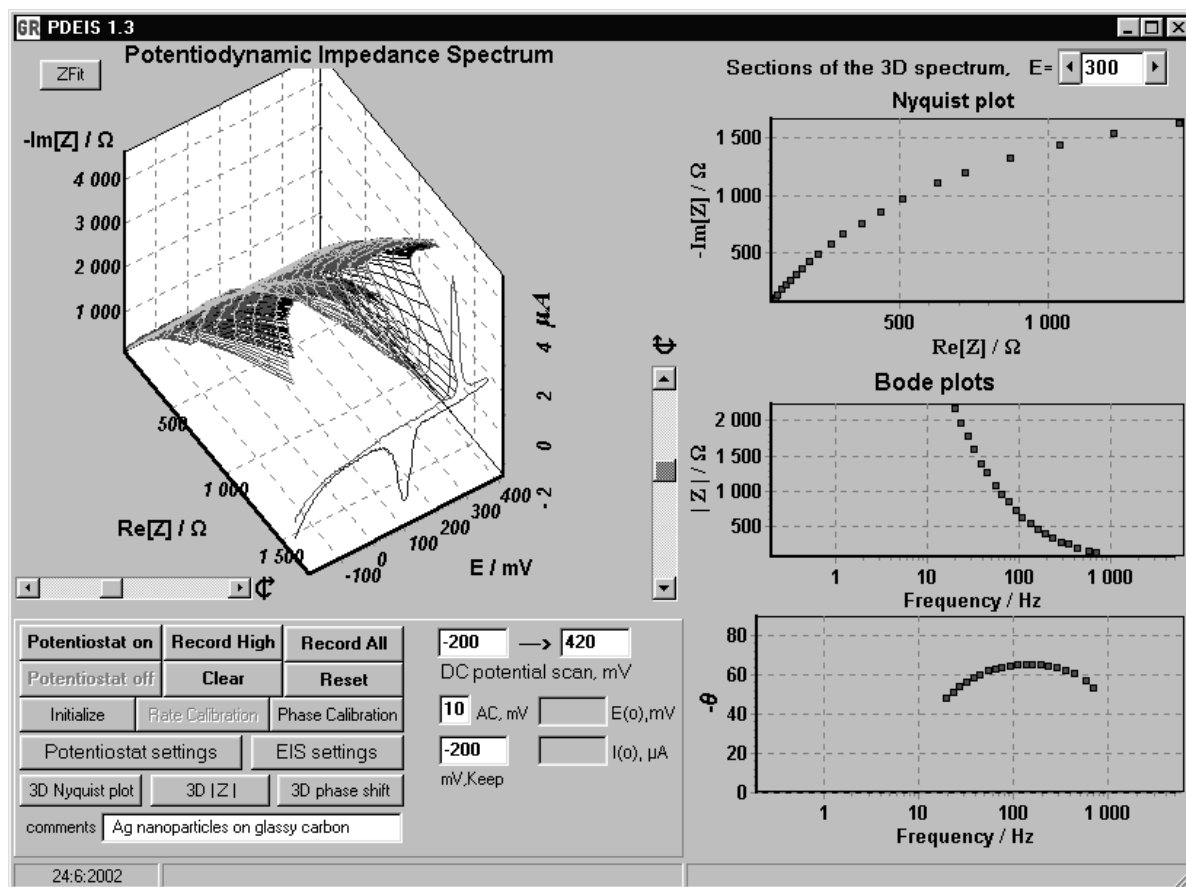
Fig. 2. The reproduction of the screen of the PDEIS spectrometer in cyclic redox transformations of Ag nanostructures on glassy carbon in 0.1 M HNO$_3$. The 3D spectrum on the left shows the impedance spectrum dependence on the potential together with the corresponding cyclic voltammogram shown on the transparent right front facet of the parallelepiped that embrace the PDEIS spectrum. The graphs on the right show the constant potential sections of the 3D spectrum.
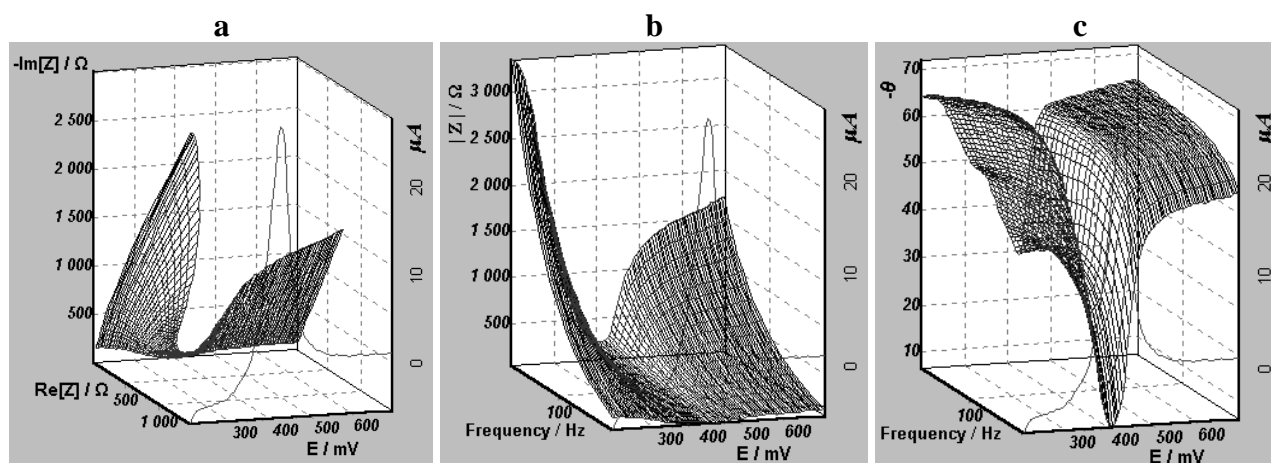

Fig. 3. Different representations of the PDEIS spectrum of Ag nanoparticles on gold support with the corresponding voltammogram
(a) imaginary impedance as a function of real impedance and the electrode potential;
(b) impedance magnitude as a function of the frequency and the electrode potential;
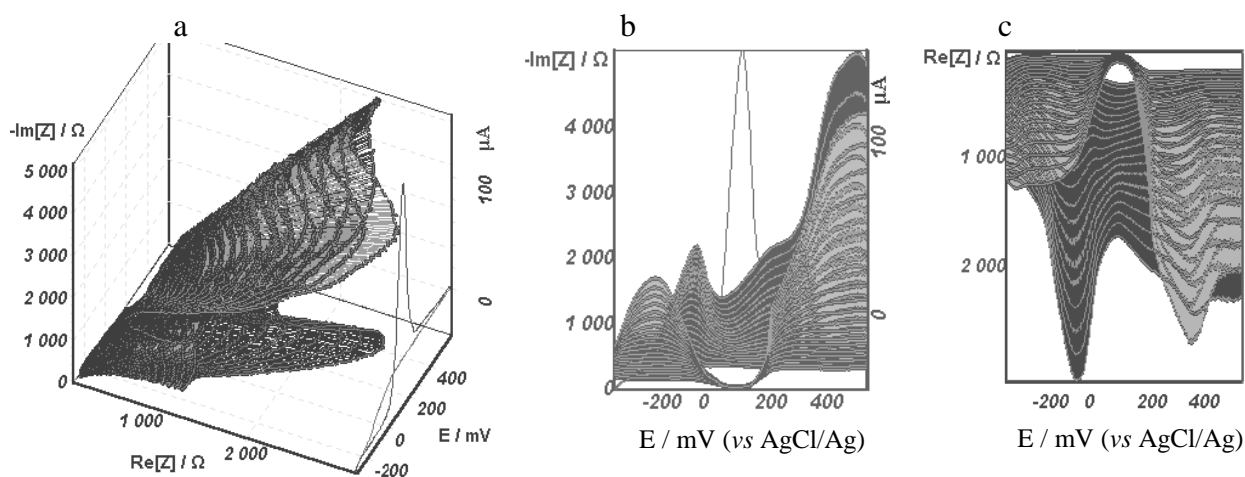(c) phase shift as a function of the frequency and the electrode potential;

Fig. 4. (a) 3D PDEIS spectrum of the interface between Pt and 10^{-2}M CuSO$_4$+0.1 M H$_2$SO$_4$ electrolyte and (b, c) the orthogonal projections of the same spectrum. The reproduction from the PDEIS spectrometer screen shows also the corresponding cyclic voltammogram. The brightness and contrast have been altered to compensate for missing colours of the originally colour graph.
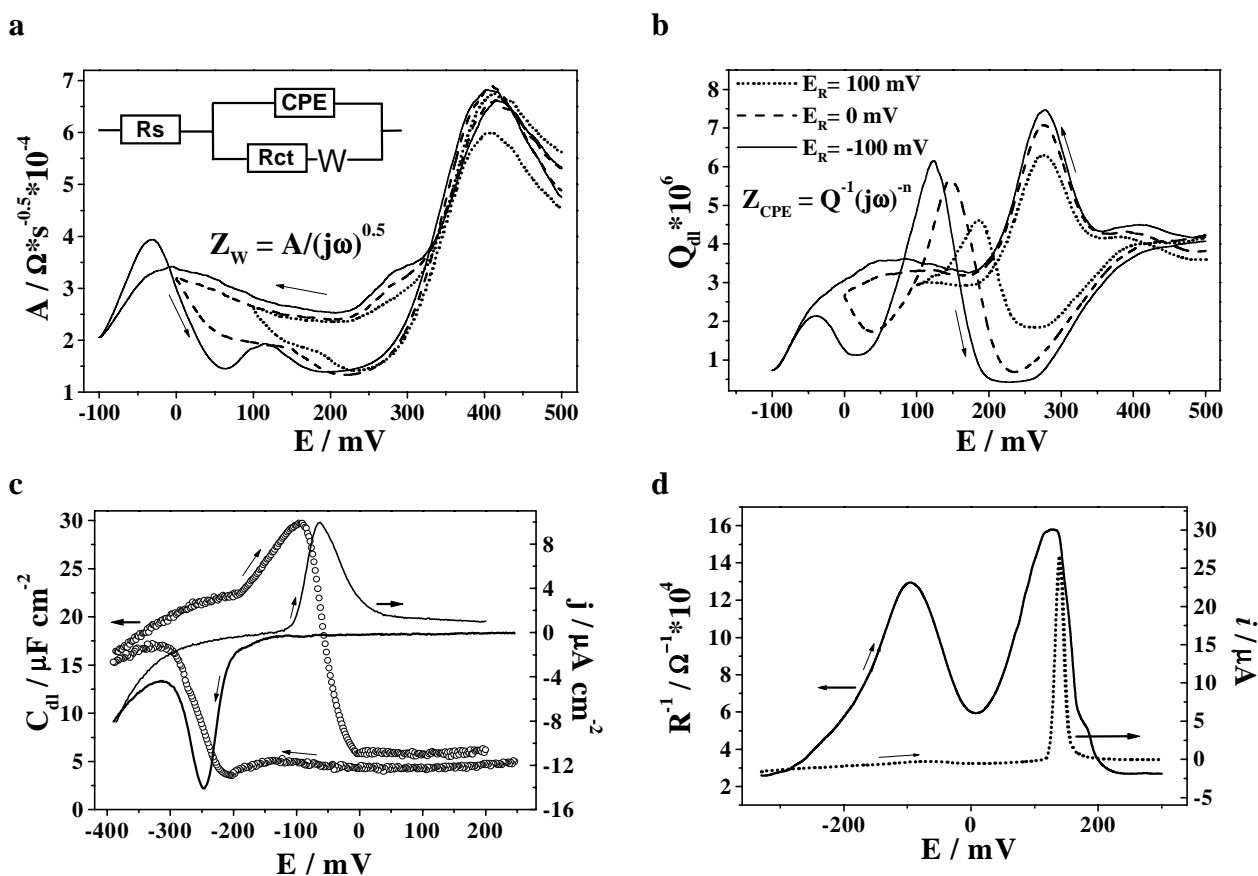

Fig. 5. The variation of the equivalent electric circuit parameters on the potential: (a) Warburg constant and (b) double layer pseudo-capacitance of the interface between Pt and 10^{-3}M CuSO$_4$+0.1 M H$_2$SO$_4$ (the equivalent circuit is shown in the insert, E$_R$ is the reversal potential in the cyclic potential scan); (c) double layer capacitance and the voltammogram of Te-electrode in 10^{-3}M PbNO$_3$+0.1HNO$_3$ during the underpotential deposition and electrochemical desorption of Pb monolayer; (d) the inverse charge transfer resistance and the voltammogram in the anodic destruction of the aggregates formed from Ag clusters on glassy carbon.

differential equations with constant coefficients [5]. The expression for the CPE impedance shown in the insert to Fig. 5-b is very similar to the impedance of the capacitor, with the exception that the exponent n is fractional. Q is the pseudo-capacitance when n is little below unity (the most common case) and transforms into real capacitance when $n=1$.

The double-layer capacitance and pseudo-capacitance dependence on the potential is a very sensitive indicator of the changes on the interface (Fig. 5-b,c). This dependence may correlate with the voltammogram in the electrochemical changes of the electrode surface but shows also features inaccessible to current studies, e.g. the capacitance of the double layer on a Te surface (Fig. 5-c [6]) shows characteristic changes in the underpotential deposition and desorption of Pb monolayer with an abrupt increase on the reverse scan just before the Pb monolayer electrochemical desorption that reveals hidden restructuring in the double layer. The Warburg constant (Fig. 5-a) and charge transfer resistance (Fig. 5-d) are also informative variables of the potentiodynamic experiment. Both are components of the Faraday impedance, the first reveals the electrochemical phenomena by the conjugate diffusion effects while the second reveals the charge transfer on its own. The charge transfer resistance in Fig. 5-d, e.g., reveals the hidden (in dc voltammetry) electrochemical activity of silver in the nanostructures that were assembled from electrochemically generated Ag clusters by the technique discussed earlier [7].

Summary

The advance of electrochemical impedance spectroscopy from the potentiostatic to the potentiodynamic mode improves the power of interfacial studies by the impedance technique substantially, due to the great amount of information contained in the dependencies of the equivalent electric circuit parameters on potential. PDEIS also provides fast acquisition and visualisation of the interface response to ac and dc current in a single potential scan.

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