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Determination of the charge transfer resistance of poly(3,4-ethylenedioxythiophene)-modified electrodes immediately after overoxidation☆

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ABSTRACT

Many electrochemical systems are intrinsically nonstationary and are affected by time-dependent phenomena. The requirement of stationarity in the classical version of impedance spectroscopy appears to be in conflict with the essential properties of the object, therefore a post-experimental mathematical/analytical procedure is necessary for the reconstruction of the “true” impedance values. In this study, it has been shown that the 4-dimensional analysis method, originally proposed by Stoynov, can not only be used for the correction of existing (experimentally measured) impedance data, but it also opens up the possibility of the estimation of impedance spectra outside the time interval of the measurements. As an illustrative example the method has been applied for the determination of the charge transfer resistance (R_{ct}) of poly(3,4-ethylenedioxytiophene) (PEDOT) modified electrode as a function of time, including the R_{ct} value corresponding to the time instant just after overoxidation of the polymer film. After the overoxidation the charge transfer resistance decreased continuously with experiment time to a value somewhat higher than the R_{ct} of the pristine electrode. The results imply that a “healing process” may occur at the film/substrate interface. A better understanding of this effect may have an impact on practical applications.

1. Introduction

There are several impedance measurement methods used in electrochemistry which mainly differ in the type of the excitation signal (e.g. sinusoidal, multi-sinusoidal, white noise, etc.). Nevertheless, the single sine excitation method is by far the most popular. When this method is employed the system under investigation is sequentially excited by applying small sinusoidal waves of a quantity, such as current or voltage. This is done within a given frequency range (e.g. from some mHz to some MHz). The response of the system is an alternating voltage or current signal with the same frequency as that of the input signal. The frequency dependence of the response can be attributed to specific processes occurring either at the interfaces or inside the phases in contact.

The impedance at a given frequency is the complex ratio of the Fourier transforms of the voltage and the current signals (sinusoids of the same frequency) for a two-terminal circuit, which fulfill the criteria of stationarity, linearity and causality under investigated conditions. A frequency spectrum can be obtained by sweeping the excitation frequency. Unfortunately, single sine impedance spectroscopy measurements suffer from increasing time consumption if the frequency range is extended toward lower frequencies. When data recording occurs at low frequencies a complete measurement sequence can take significant time (at least several minutes). However, many electrochemical systems are intrinsically nonstationary and are affected by time-dependent phenomena. So, the requirement of stationarity in the classical version of impedance spectroscopy appears to be in conflict with the essential properties of the object. Strictly speaking, in such cases the obtained results are not “impedances” and cannot be used directly in any analysis.

According to Stoynov [1] there are two general cases in the impedance measurements related to the non-stationary errors:

☆ This paper is dedicated to Professor Zdravko Stoynov on the occasion of his 80th birthday in recognition of his great contribution to electrochemistry.

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(i) measurements in a stationary system under non-steady state conditions;
(ii) investigation of non-stationary systems.

The error of the first type increases sharply with decrease of the frequency (see ref. [2]). In the second case, an additional error appears, related to the measurement delay due to the classical "frequency by frequency" mode of impedance measurements.

Different methods to deal with a non-stationary behavior can be found in literature. Stoynov proposed a method of determining instantaneous impedance diagrams for non-stationary systems based on a four-dimensional approach [1,3]. (The instantaneous impedance is defined as an instantaneous projection of the non-stationary state of the system into the frequency domain [1].) Darowicki et al. developed a dynamic EIS method to trace the dynamics of the degradation process by the calculation of an instantaneous impedance [4]. In [5] a procedure was proposed to quantify and correct for the time-evolution by means of the calculation of an instantaneous impedance.

The method of Stoynov (the 4-dimensional analysis) provides for correction of the systematic errors, arising during the measurements of time-evolving impedance, i.e. when the consecutive impedance measurements are performed at different system states, but each of the measured impedance values can be accepted as "valid" in the classical sense. Of course, in this case the individual values (especially those measured at the lower frequencies) may be still corrupted by typical errors caused by the system evolution during the experiment [6]. (If the problem is related to the mathematical basis of the transfer function analysis [2,7], the so called rotating Fourier transform can be used to overcome this limitation [6,8].)

As discussed before, the four-dimensional analysis method is based on the assumption for the continuum of the object's state and parameters space. It requires a number of impedance spectra recorded subsequently at the same set of frequencies. Every measured data at a given frequency should additionally contain the time of measurement. Thus, the experimental data form a set of 4-dimensional arrays, containing frequency, real and imaginary components of the impedance and the time of measurement. The post-experimental analytical procedure previews the reconstruction of calculated instantaneous impedances. For every measured frequency two one dimensional functions of "iso-frequency dependencies" (e.g. for the real and for the imaginary components or for the magnitude and phase angle of the complex immittance) are constructed. Then, each iso-frequency dependence is modeled by an approximating formal model. On the basis of the continuity of the evolution, interpolation (and/or extrapolation) is performed resulting in instantaneous projections of the full impedance-time space and "reconstructed" instantaneous impedances related to a selected instant of the time (e.g. the beginning of each frequency scan, but the procedure can be applied to any time instants). Thus a set of impedance diagrams is obtained, containing "instantaneous" (virtually simultaneously recorded) impedances. Each of these diagrams can be regarded as a stationary one, free of non-steady-state errors. On the basis of the above, one could conclude that the four-dimensional analysis method can be most effective in the correction of low-frequency impedance data. However, as it will be shown in the present study, this technique can also be used for solving other problems.

For instance, it is known that the impedance spectra of overoxidized poly(3,4-ethylenedioxythiophene) (PEDOT) films on gold recorded in aqueous sulphuric acid solutions differ from those measured for freshly prepared films [9]. The most interesting feature is the appearance of an arc (or a "depressed semicircle") at high frequencies in the complex plane impedance plot. The published results support the mechanistic picture, according to which the originally compact and strongly adherent polymer films undergo structural changes during the overoxidation (degradation) process [10–15]. Overoxidation may result in the partial delamination of the polymer layer and may lead to the exposure of some parts of the underlying metal substrate to the electrolyte solution [12]. It should be emphasized here that the polymer film still present on the substrate after (partial) overoxidation remains electroactive, and its internal structure may be an interesting subject for further studies, since according to literature reports conducting polymers in different overoxidation states show unique features useful for analytical, sensing and biomedical applications [16–20].

The time evolution of the impedance spectra is another remarkable feature of the electrodes with overoxidized PEDOT films. To our knowledge, this phenomenon was first reported in ref. [21]. According to this observation, the impedance spectra change continuously over several hours when the electrode potential is held in the "stability region" after overoxidation of the film. This means that the impedance spectra recorded using the consecutive frequency sweep mode (typical of EIS) are corrupted by typical errors caused by the system evolution during the experiment. On the other hand, for reasons of measuring technology, we are not able to record an impedance spectrum immediately after the overoxidation process. But even if we would be able to do so it wouldn't solve the problems related to the nonstationarity of the system. Nevertheless, it is beyond doubt that the knowledge of the "initial" impedance parameters like charge transfer resistances, high and low frequency capacitances, etc., may be essential for a better understanding of the degradation/overoxidation process and it may also have an impact on practical applications.

In the present study, an attempt is made to solve these problems simultaneously by using a method similar to that proposed by Stoynov (4-dimensional analysis). The most important assumption is that although the consecutive impedance measurements were performed at different system states, each of the measured impedance values can be accepted as "valid" in the classical sense.

2. Experimental

2.1. Electrodeposition of PEDOT

Poly(3,4-ethylenedioxytiophene) films were prepared by galvanostatic deposition on both sides of thin gold plates from 0.01 mol dm^{-3} ethylenedioxytiophene (EDOT) solution containing 0.1 mol dm^{-3} Na_2SO_4 supporting electrolyte (all the plates were practically identical and were cut from the same gold sheet). Analytical grade 3,4-ethylenedioxythiophene (Aldrich), p.a. Na_2SO_4 (Fluka), and ultra-pure water (specific resistance 18.3 MΩ cm) were used for solution preparation. All solutions were purged with oxygen-free argon (Linde 5.0) before use and an inert gas blanket was maintained throughout the experiments.

The deposition was performed in a standard three electrode cell in which the gold plate in contact with the solution served as the working electrode (WE). A spiral shaped gold wire immersed in the same solution served as the counter electrode (CE), and a KCl-saturated calomel electrode (SCE) as the reference electrode (RE). A constant current density of $j = 0.2$ mA cm^{-2} ($I = 0.2$ mA) was applied for 1000 s (the geometric surface area of the working electrode was $A = 1.0$ cm^2). The film thickness was estimated from the polymerization charge by using the charge/film volume ratio determined earlier by direct thickness measurements [22–24]. The average thickness of the PEDOT film was about 0.8 μm, the structure of the PEDOT film was globular, cauliflower-like [9,12,14], i.e. the thickness of the film was non-uniform.