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Validity of Impedance Spectra Obtained by Dynamic Electrochemical Impedance Spectroscopy Verified by Kramers-Kronig Transformation[*]

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The paper presents the verification of the validity of impedance spectra obtained by recently developed experimental technique – Dynamic Electrochemical Impedance Spectroscopy (DEIS). The technique assumes, that the investigated system is pseudo-stationary if the measurement time is suitably short. The time necessary to calculate single spectrum depends on the window length used during Short Time Fourier Transform (STFT) application. The verification of the validity of impedance spectra was performed using Kramers-Kronig transform. The verification confirmed, that the obtained spectra are valid in respect to KK transform.

Key words: impedance spectroscopy, short time Fourier transformation, Kramers-Kronig transformation

Electrochemical Impedance Spectroscopy (EIS) is a powerful tool providing a lot of information about the electrochemical characteristics of the system being examined, like the double layer capacitance, charge transfer resistance, diffusion impedance, solution resistance [1]. Because of the nature of impedance measurements, there is major requirement, which is the stationarity and stability of the system for the whole measurement duration. That is major limitation of the classical electrochemical impedance measurement technique – Frequency Response Analysis (FRA) [2]. In this technique the impedance is being measured frequency-by-frequency and the whole measurement time may excess one hour. Because of this limitation the FRA technique is useless in the analysis of dynamic processes [3].

There are several proposals concerning the reduction of measurement time. Popkirov *et al.* tried to overcome the problem of very long measurement time by using Fast Fourier Transform (FFT) analysers [4–5] and thus reduce the time necessary to obtain a single spectrum to a few seconds. The stability and stationarity during measurements are still required, but are much easier to achieve. There are several recent developments in the field of instantaneous impedance measurements. Hazi *et al.* proposed to use frequency compositions as the perturbation signals with various frequency components applied one by other [6]. Park *et al.* proposed to use

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[*] Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

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potential step as the perturbation signal followed by dedicated postprocessing [7–8]. Barsoukov *et al.* proposed to use simple excitations like current pulse or interrupt and the Laplace transform to process the response [9]. Ragoisha and Bondarenko use the stream of wavelets in a limited frequency range and self-developed virtual instruments dedicated to the analysis of system responses [10].

Here we present the Kramers-Kronig transformations of the results obtained by the technique of impedance measurements developed by our team, which may be called the Dynamic Electrochemical Impedance Spectroscopy (DEIS). This technique utilizes the constant perturbation signal, being the sum of selected sine waves, and the Short Time Fourier Transform (STFT) analysis to obtain impedance spectra of potentiodynamic electrochemical processes. The fundamentals of this method are described elsewhere [11]. This technique has been widely applied in the examination of various processes [12–13] and is still being developed by our team.

Kramers-Kronig (KK) transform is the mathematical formula connecting the real and imaginary parts of any complex quantities (1).

$$\begin{aligned} Z''(\omega) &= -\left(\frac{2\omega}{\pi}\right)\int_0^\infty \frac{Z'(x)-Z'(\omega)}{x^2-\omega^2}dx \\ Z'(\omega) &= Z'(\infty)+\left(\frac{2}{\pi}\right)\int_0^\infty \frac{xZ''(x)-\omega Z''(\omega)}{x^2-\omega^2}dx \end{aligned} \tag{1}$$

As impedance is a complex value, KK relations may be applied to the electrochemical impedance as well. MacDonald and Urquidi-MacDonald proposed to use KK transform to verify the validity of experimental impedance data [14]. There many papers on the application of KK relations in the field of electrochemical impedance. Mansfeld and Shih suggested, that KK transforms are not suitable for results not covering the whole variability of the system [15]. MacDonald *et al.* emphasized the need to obtain the results in suitably wide frequency range, covering all time constants of the system [16]. Although MacDonald and Urquidi-MacDonald presented the procedure of KK transformation of any impedance data [17], it is difficult to apply these relations for systems with mixed or diffusion control. The problem is the integration along frequency between 0 and infinity. If real or imaginary part of the impedance for frequencies approaching 0 is not finite, the calculation of such an integral may be difficult. Esteban and Orazem presented the procedure of the application of KK transform as an evaluation of the consistency of EIS data [18].

The aim of this work is to present the results of KK transform as a test of validity of impedance spectra. We selected a nonlinear electrical model to verify the technique. It was a electrical circuit composed of resistor, capacitor and diode.

EXPERIMENTAL

The measurements of the impedance of model electrical circuit were performed for the circuit presented in Fig. 1. The potential was linearly swept between 0.5 and 0.75 V with 3 mV/s scan rate.

The perturbation signal used for analysis was the sum of 20 selected sine waves of various amplitudes with optimized phase shifts and was generated by the DAQ card (PCI 6110E, National Instruments). Frequencies were in the range between 7 and 7001 Hz for window length of 1 s. This signal was supplied to a potentiostat (Home-made fast potentiostat). Sweep signal was generated by analog Linear Sweep Generator (EG-20, Elpan). Potential and current responses were measured with DAQ cards (2×PCI 6052E, National Instruments). Sampling frequency was 20 kS/s. The system was supervised by the PC computer with LabVIEW (National Instruments) software.

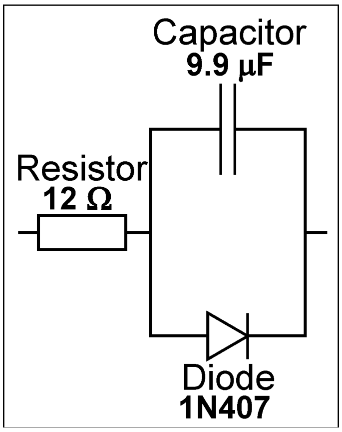

Figure 1. Investigated non-linear electrical circuit.

DEIS is based on the assumption, that even if the system is nonstationary on the whole, it may be assumed to be pseudo-stationary in short time interval. Thus if we apply constant perturbation signal to the sweep d.c. potential and then we process the resulting potential and current registers using STFT with properly chosen window length, we will be able to measure impedance for potentiodynamic processes. The window length must be short enough to sustain the assumption of pseudo-stationarity for window duration. This technique allows one to trace the changes of the impedance for both potential- and time-dependent systems. In present case the system was potential-variant, but as the potential was linearly swept, it may be also acknowledged as time-variant.

The major limitation of this technique is the frequency range of measurements. The window length determines the lowest frequency in the composition. There must be at least a few periods of the lowest frequency component in the data used for single spectrum calculation. The highest frequency component is limited by the sampling frequency. According to Nyquist's theorem, the highest frequency must not be higher than the half of sampling frequency. More information about the use of STFT and its applications can be found elsewhere [19–20].

Validity of obtained impedance spectra was verified using the procedure described by Esteban and Orazem [18] included in Electrochemical Impedance Spectroscopy analysis software ZSimpWin by Princeton Applied Research.

RESULTS AND DISCUSSION

To check the validity of the spectra obtained by DEIS we selected a model process. Fig. 2 presents the current *versus* potential plot obtained for the investigated non-linear electrical circuit in the potential range between 0.5 and 0.75 V for scan rate of 3 mV/s.

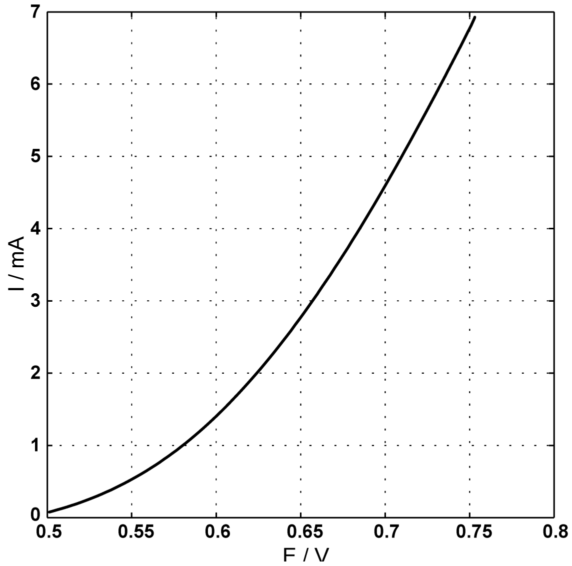

Figure 2. Polarization dependence of the current *versus* potential obtained for electrical non-linear circuit.

For present case of potential-variant system, we obtained the bunch of impedance spectra along varied potential. Fig. 3 presents the impedance diagram obtained in the range of 7–7001 Hz and potential scan rate 3 mV/s. The numbered spectra were used in the validation procedure as described below.

The procedure of impedance spectra validation used here assumes, that if we extrapolate the data down three decades with respect to the lowest frequency used in real measurement, we should obtain smooth curves of real and imaginary data. If there is some discontinuity between measurement data and KK calculated values, it is the indication of inconsistency of impedance obtained in experiment. The algorithm is very sensitive for any nonstationarity, but allows the existence of some small deviations resulting from apparatus or surrounding noise. To make the plots more clear we present every fifth spectrum from the set presented in Fig. 3. Fig. 4 shows the results of KK transformations of the spectra obtained for electrical circuit for frequency range 7–7001 Hz for 3 mV/s sweep rate. The numbers correspond to the numbers in Fig. 3.

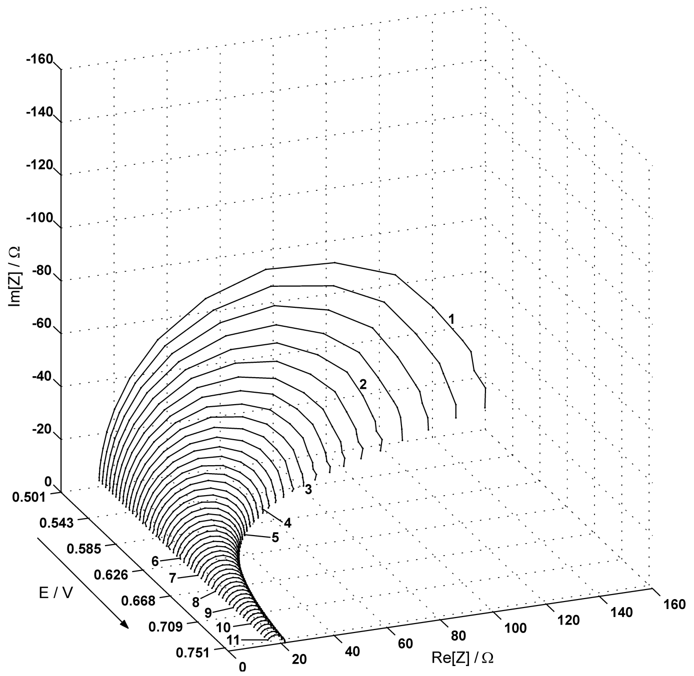

Figure 3. The impedance spectra obtained in the range of 7–7001 Hz. Length of analysing window 3 mV (or 1 s), potential scan rate 3 mV/s, sampling frequency f_S = 20 kS/s.

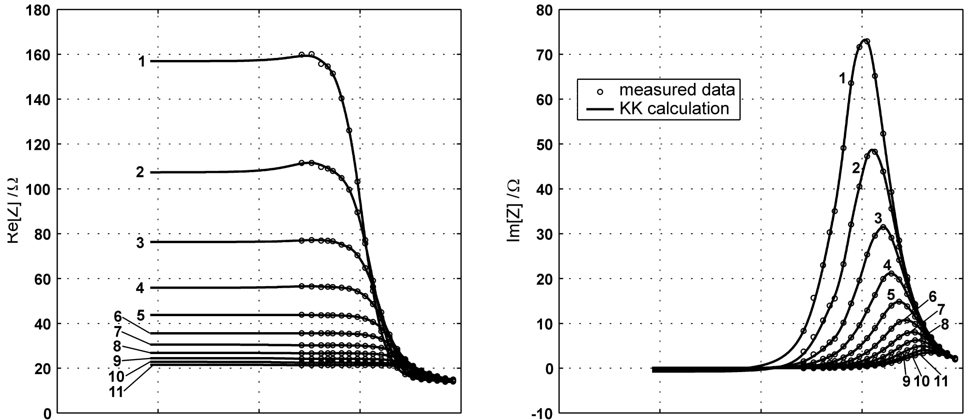

Figure 4. Kramers-Kronig transformations of impedance spectra. Frequency range 7–7001 Hz, potential scan rate 3 mV/s.

As seen in these plots, the data obtained by DEIS and transformed by KK relations show no discontinuity at the boundary between experimental and extrapolated data. It is clear evidence, that the spectra are valid and there are no signs of nonstationarity for single spectrum calculation times, while whole process was potentiodynamic and nonstationary by definition. More strictly for the potential range (length of analysing window) of 3 mV the investigated process is quasi-stationary.

CONCLUSIONS

The presented results prove, that the spectra obtained by DEIS show no nonstationarity and are valid in respect to KK transform. The investigated system was nonstationary on the whole, because the experiment was potentiodynamic. The STFT transformation of the current and potential registers, using the proper window length provides a quasi-stationarity and allows us to trace the changes of the electrochemical impedance for time- or potential-variant systems. In this case the more general problem is a validity of low frequency limit of measurements.

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