LIMITATIONS OF A NEW POTENTIAL STEP TECHNIQUE OF IMPEDANCE MEASUREMENTS USING FOURIER TRANSFORM

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Recently, Yoo and Park introduced a new method of obtaining the impedance spectra of electrochemical systems [1]. The method is based on the Fourier transform of the *first derivative* of the current response obtained from electrochemical system after applying of the short (2 ms) potential step to the working electrode. By using DTFT (*Discrete Time Fourier Transform*) instead of FFT (*Fast Fourier Transform*) the impedance spectra might be quickly obtained for theoretically all frequencies, even very low ones. Since other methods are much more time consuming, the possibility of applying this technique would be of a great advantage. However, Lasia [2] has noticed that the spectra obtained in this way might *not* contain the full information about the impedance of the studied system, mainly in the low frequency range. In fact impedance spectra obtained by Yoo and Park [1] did not contain the Warburg impedance, the insignificance of which was attributed [1] to the fact that within 2 ms, the diffusion layer was not significantly developed and thus the diffusion processes did not show up in the impedance spectra.

In order to verify the validity of this method, and to establish the conditions for which the method may be used, digital simulations of impedance spectra for different equivalent circuits and real electrochemical systems were performed. For modeling of electrochemical processes the classical finite-difference algorithm was used. We have obtained impedance spectra in which the Warburg impedance is present. Moreover, in some cases, we have obtained two semicircles on the complex plane plots for a simple one-electron reaction. The second semicircle was simply an artifact due to unjustified truncation of transient current (or its first derivative) in the time domain. In view of the results obtained the limitations and applicability of this method will be discussed.

References

[1] J.-S. Yoo, S.-M. Park, Anal. Chem., **72**, 2035 (2000).

[2] A. Lasia, Anal. Chem., **73**, 4059 (2001).

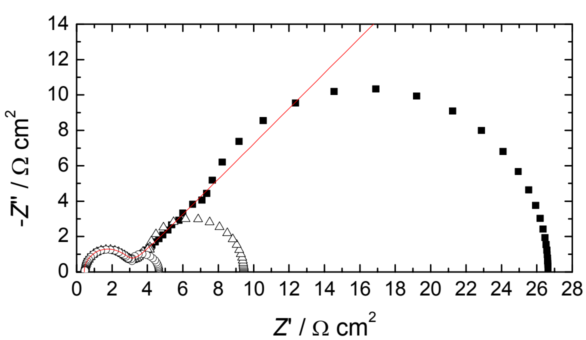

Fig. 1. Complex plane plots obtained for a simple one-electron reaction: k_s = 0.001 cm s^{-1}, η = 0.4 V, ΔE = 10 mV. Points represent numerical calculations and continuous line is the theoretical impedance spectrum for this system; truncation of the first derivative of the current response in the time domain after: 2 ms (○), 20ms (Δ), 200 ms (■).