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Sinusoidal Alternating-Current Voltammetry and Metrological Properties of a Flat Voltammetric Electrode in the Time Domain

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Krzysztof Suchocki*

Faculty of Biomedical Engineering, Technical University of Gdansk, Narutowicza 11/12, Gdansk 80-233, Poland

ABSTRACT

In this paper there were analyzed metrological properties of a flat electrode used to mark ions with the method of sinusoidal alternating-current voltammetry in the situation where on its surface an electrochemical reversible reaction of oxidizing / reduction takes place. The result of the analysis conducted is that such a voltammetric electrode functions like a converter type I.

Metrological properties of such an electrode in the time domain are defined by the sensitivity and time constant. Values of these parameters are defined by the dimensions which characterize a voltammetric electrode, polarizing voltage and marked ions. Numeric simulations were conducted in order to determine the influence of particular dimensions on the values of the parameters defining the metrological properties. Their results show that the value of the sinusoidal voltage and its frequency have the greatest influence on the values of the parameters.

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1. Introduction

Voltammetric measurements are one of the most frequently conducted measurements in order to determine ion concentration in water [1–8]. Their commonness is connected most of all to its simplicity and high accuracy. There are many different types of voltammetric methods. These methods differ from each other mainly in the voltage shape polarizing the voltammetric electrode, and as a consequence they also differ in accuracy of measurements conducted. These methods are successfully used in electrochemical measurements in stationary conditions when the marked ion concentration in the volume of analyzed solution is constant in time [9–13]. It raises a question if the methods can be used in situations when marked ion concentration alternates in the examined solution when the measurements are being conducted [14,15]. Another question is what properties characterize applied measuring electrode and how they influence the accuracy of the measurements. Also if the shape of voltage polarizing the electrode influences the metrological properties of this electrode. In order to answer above questions steps were undertaken to focus on defining the influence of the voltage polarizing voltammetric electrode parameters in the method of sinusoidal alternating-current voltammetry on the metrological properties of this electrode in the time domain.

2. Theory

In case when a reversible electrochemical reaction controlled by ion transport process takes place on the surface of the voltammetric electrode, then their flux to the electrode surface is defined by the relationship [6,16]:

$$N_i(t) = D_i \nabla C_i(t) + u_i z_i F C_i(t) \nabla U(t) + V_i(t) C_i(t) \qquad (1)$$

where: D_i is the diffusion coefficient of ions, C_i, ∇C_i is the concentration of ions, concentration gradient of ions, u_i is the mobility of ions, z_i is the valence of ions, F is the Faraday constant, V_i is velocity of the convection rate of ions, rate gradient of ions, $\nabla U(t)$ is the gradient of the electric field potential.

Distribution of ion concentration C_i in the solution volume in the function of time t, with no chemical reaction, is defined by the flux divergence, hence [11,16]:

$$\frac{\partial C_i(t)}{\partial t} = -\nabla N_i(t), \qquad (2)$$

where: $\nabla N_i(t)$ is the gradient of marked ions flux.

Taking into consideration the relationship (1) and assuming that $\nabla D_i = 0(t)$, the following is a result:

$$\frac{\partial C_i(t)}{\partial t} = D_i \nabla^2 C_i(t) + z_i u_i F \nabla C_i(t) \nabla U(t) + z_i u_i F C_i(t) \nabla^2 U(t) \\ - \nabla V_i(t) C_i(t) - V_i(t) \nabla C_i(t). \qquad (3)$$

* Corresponding author.
  E-mail address: krzsucho@pg.gda.pl (K. Suchocki).

As one can see the ion i concentration distribution depends upon their diffusion coefficient D_i, mobility u_i, ion valence z_i and their concentration $C_i(t)$, their concentration gradient $\triangledown C_i(t)$, electric potential $U(t)$ and its gradient $\triangledown U(t)$, their convection rate $V_i(t)$ and its gradient $\triangledown V_i(t)$ on the surface of the voltammetric electrode.

In reality voltammetric measurements are taken with immobile static electrodes in presence of the excess of concentrated bulk electrolyte in order to eliminate the phenomenon of marked ions migration. Hence, the Eq. (3) takes on the following form [16]:

$$\frac{\partial C_i(t)}{\partial t} = D_i \nabla^2 C_i(t). \tag{4}$$

A variable component of the voltage polarizing a voltammetric electrode causes local changes in the marked ions concentration in the area around the electrode. Characteristics of local changes in the marked ions concentration on the surface of the electrode are consistent with the changes in alternating polarizing voltage, which can be described as follows:

$$\partial \frac{[\Delta C_{i,0}(t)]}{\partial t} = \frac{\partial}{\partial t}\left[C_i^0(t)\sin\omega t\right] = \frac{\partial C_i^0(t)}{\partial t}\sin\omega t + \omega\cos\omega t C_i^0(t), \tag{5}$$

where: $\triangledown C_{i,0}(t)$ is concentration increase on the surface of the electrode, C_i^0 is ion concentration in the volume of analyzed solution, ω is sinusoidal component pulse of the voltage polarizing an electrode.

As a consequence the Eq. (4) noted for the surface of the voltammetric electrode polarized with voltage with one variable component and one static component takes on the form:

$$\partial \frac{[C_{i,0}(t) + \Delta C_{i,0}(t)]}{\partial t} = \frac{\partial C_{i,0}(t)}{\partial t} + \partial \frac{[\Delta C_{i,0}(t)]}{\partial t}$$
$$= D_i \nabla^2 C_i(t) + \frac{\partial C_i^0(t)}{\partial t}\sin\omega t + \omega\cos\omega t C_i^0(t). \tag{6}$$

If we assume that a reversible electrochemical reaction takes place on the surface of the voltammetric electrode and there are ions of both forms in the volume of the analyzed solution, then the above equation may be defined as follows:

$$\frac{\partial C_{i,red,0}(t)}{\partial t} + \frac{D_{i,red}}{\delta_{i,red}^2(t)}C_{i,red,0}(t) = \frac{D_{i,red}}{\delta_{i,red}^2(t)}C_{i,red}^0(t) + \frac{\partial C_{i,red}^0}{\partial t}\sin\omega t$$
$$+ \omega\cos\omega t C_{i,red}^0, \tag{7}$$

$$\frac{\partial C_{i,ox,0}(t)}{\partial t} + \frac{D_{i,ox}}{\delta_{i,ox}^2(t)}C_{i,ox,0}(t) = \frac{D_{i,ox}}{\delta_{i,ox}^2(t)}C_{i,ox}^0(t) + \frac{\partial C_{i,ox}^0}{\partial t}\sin\omega t$$
$$+ \omega\cos\omega t C_{i,ox}^0, \tag{8}$$

where: $D_{i,red}$ is a diffusion coefficient of reduced form ions, $C_{i,red,0}(t)$ is concentration of reduced form ions on the surface of the voltammetric electrode, $C_{i,red}^0(t)$ is concentration of reduced form ions in the volume of the analyzed solution, $\partial C_{i,red}^0(t)/\partial t$ is a derivative of reduced form ion concentration in the volume of the analyzed solution, $\delta_{i,red}(t)$ is a thickness of the diffusion layer of reduced form ions, $D_{i,ox}$ is a diffusion coefficient of oxidised form ions, $D_{i,ox,0}(t)$ is concentration of oxidised form ions on the surface of the voltammetric electrode, $C_{i,ox}^0(t)$ is concentration of oxidised form ions in the volume of the analzyed solution, $\partial C_{i,ox}^0(t)/\partial t$ is a derivative of oxidised form ions in the volume of the analzyed solution, $\delta_{i,ox}(t)$ is a thickness of the diffusion layer of oxidised form ions.

Taking into consideration the fact that a reversible electrochemical reaction takes place on the surface of a flat voltammetric electrode, there also appears a relationship as follows [16]:

$$N_{i,ox,0}(t) = N_{i,red,0}(t). \tag{9}$$

Keeping in mind the relationship (6) the ion flux on the surface of an electrode may be defined this way:

$$N_{i,0}(t) = \delta_i(t)\frac{\partial C_{i,0}(t)}{\partial t}$$
$$= \delta_i(t)\left[D_i\nabla^2 C_i(t)|)_{x=0} + \frac{\partial C_i^0(t)}{\partial t}\sin\omega t + \omega\cos\omega t C_i^0(t)\right]. \tag{10}$$

In that case the relationship (9) determining the equality of fluxes takes on the form:

$$\delta_{i,ox}(t)\left[D_{i,ox}\nabla^2 C_{i,ox,0}(t) + \frac{\partial C_{i,ox}^0(t)}{\partial t}\sin\omega t + \omega\cos\omega t C_{i,ox}^0(t)\right]$$
$$= \delta_{i,red}(t)\left[D_{i,red}\nabla^2 C_{i,red,0}(t) + \frac{\partial C_{i,red}^0(t)}{\partial t}\sin\omega t + \omega\cos\omega t C_{i,red}^0(t)\right], \tag{11}$$

where: $\triangledown C_{i,ox,0}(t)$ is a gradient of oxidised form concentration on the surface of the flat voltammetric electrode,

$\triangledown C_{i,red,0}(t)$ is a gradient of reduced form concentration on the surface of the flat voltammetric electrode.

Moreover, in the case of a reversible voltammetric reaction there is also a relationship [16]:

$$\frac{C_{i,ox,0}(t)}{C_{i,red,0}(t)} = \exp\left\{\frac{z_iF}{RT}\left[E_{pol}(t) - E^0\right]\right\} = \theta(t), \tag{12}$$

where: $E_{pol}(t)$ is a voltage polarizing the voltammetric electrode,

E^0 is a standard potential of an electrochemical reaction on the surface of the voltammetric electrode.

When applying the sinusoidal alternating-current voltammetric method to mark ion concentration, a flat electrode is polarized with a voltage defined as:

$$E_{pol}(t) = \pm E_0 \pm S_U t + U_m\sin\omega t, \tag{13}$$

where: E_0 is an initial voltage of voltammetric electrode polarization, S_U is a rate of static voltage increase, U_m is an amplitude of sinusoidal voltage, ω is sinusoidal voltage pulse, t is time.

Bearing in mind the relationship (12) we get:

$$\frac{\partial C_{i,red,0}(t)}{\partial t} = \frac{1}{\theta(t)}\frac{\partial C_{i,ox,0}(t)}{\partial t} - \frac{1}{\theta^2(t)}C_{i,ox,0}(t)\frac{\partial\theta(t)}{\partial t}, \tag{14}$$

$$\frac{\partial C_{i,ox,0}(t)}{\partial t} = \frac{\partial C_{i,red,0}(t)}{\partial t}\theta(t) + C_{i,red,0}(t)\frac{\partial\theta(t)}{\partial t}. \tag{15}$$

Substituting the relationship (7) with (14) and (8) with (15) we obtain:

$$\frac{1}{\theta(t)}\frac{\partial C_{i,ox,0}(t)}{\partial t} - \frac{1}{\theta^2(t)}C_{i,ox,0}(t)\frac{\partial\theta(t)}{\partial t} =$$
$$= D_{i,red}\frac{C_{i,red}^0(t)}{\delta_{i,red}^2(t)} - D_{i,red}\frac{C_{i,red,0}(t)}{\delta_{i,red}^2(t)} + \frac{\partial C_{i,red}^0(t)}{\partial t}\sin\omega t + \omega\cos\omega t C_{i,red}^0(t), \tag{16}$$

$$\frac{\partial C_{i,red,0}(t)}{\partial t}\theta(t) + C_{i,red,0}(t)\frac{\partial\theta(t)}{\partial t} =$$
$$= \frac{D_{i,ox}}{\delta_{i,ox}^2(t)}C_{i,ox}^0(t) - \frac{D_{i,ox}}{\delta_{i,ox}^2(t)}C_{i,ox,0}(t) + \frac{\partial C_{i,ox}^0(t)}{\partial t}\sin\omega t + \omega\cos\omega t C_{i,ox}^0(t). \tag{17}$$