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Study of Metrological Properties of Voltammetric Electrodes in the Time Domain

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Additional information is available at the end of the chapter

Abstract

Metrological properties of voltammetric electrodes, in the situation where on their surface an electrochemical reaction of oxidizing/reduction takes place, were analyzed in this chapter. The properties of electrodes on which a reaction controlled by ion transport process takes place were taken into consideration. Also, it was analyzed how the electrode's shape and the voltage polarizing the electrode influence this electrode's metrological properties. The result of the analysis conducted is that in case of a reaction controlled by charge exchange process, such a voltammetric electrode functions like a converter type 0. Its metrological properties in the time domain are defined solely by sensitivity. However, if on the surface of the electrode there is a reaction controlled by ion transport process, the electrode will function like a converter type I. Its metrological properties in the time domain are defined by the sensitivity and time constant. Numeric simulations were conducted in order to determine the influence of the electrode's shape and the polarizing voltage on metrological properties of the electrode. The results show that both the sensitivity and the time constant of the electrode can be influenced by choice of an electrode's shape and the shape of the polarizing voltage.

Keywords: voltammetric electrodes, voltammetric measurements, DC voltammetry, AC voltammetry, metrologic properties, time constant

1. Introduction

Voltammetric measurements are one of the most frequently conducted measurements in order to determine ion concentration in water [1–7]. Their commonness is connected most of all to its simplicity and relatively high accuracy. There are many different types of voltammetric methods [7–15]. These methods differ from each other mainly in the voltage shape polarizing the voltammetric electrode, and in result, they also differ in accuracy of measurements conducted.

These methods are successfully applied in electrochemical measurements in stationary conditions when the marked ion concentration in the volume of analyzed solution is constant in time. At the same time, much more voltammetric measurements are conducted in situ, where the concentration of marked ions can change during the marking process [7, 10]. Some questions raise concerning the accuracy of conducted measurements, metrological properties of voltammetric electrodes, and methods of their improvement [12–15]. Hence, some work is undertaken in order to define metrological properties of voltammetric electrodes and the influence of the electrode's shape and the shape of polarizing voltage on these electrodes.

2. Metrological properties of voltammetric electrodes

Generally, metrological properties of voltammetric electrodes as measuring converters can be divided into static and dynamic ones.

Static properties are the characteristic of voltammetric electrodes which are in the steady state, i.e., in the state in which the concentration of marked ions does not change in the volume of the analyzed solution nor on the surface of the electrode. Dynamic properties are the characteristics of the electrode in the transient state, when these concentrations change while the voltammetric measurements are being conducted.

In order to simplify the analysis of the voltammetric electrode metrological properties following assumptions have been accepted:

- the input signal is the marked ion concentration $C_i^0(t)$ in the analyzed electrolyte volume,

- the output signal is the current $i_i(t)$ of the electrochemical reaction on the voltammetric electrode's surface,

- the time of charge exchange between the ions in the analyzed electrolyte and the voltammetric electrode equals 0.

Generally, the electrochemical reaction of oxidizing/reduction on the voltammetric electrode's surface is divided into several stages. The first stage is about delivery of depolarizer's ions from the volume of the electrolyte into the vicinity of the electrode's surface. The second stage of the electrochemical reaction is to transport, to or from, an electron or electrons through the depolarizer's ion. The third stage is to transport away the products from the reaction to the volume of analyzed solution. Stage four of the reaction is when the products of the electrochemical reaction can still react with other ions in the electrolyte after being transported away.

3. Electrochemical reaction controlled by a process of charge exchange on the surface of the voltammetric electrode

When on the surface of the voltammetric electrode an electrochemical reaction controlled by a process of charge exchange takes place, then the marked ion concentration in oxidizing/reduction

form on the electrode surface equals the concentration of the same ion form in the analyzed solution volume [8]:

$$C_{i,\,\mathrm{ox},\,0}(t) = C_{i,\,\mathrm{ox}}^0(t),\tag{1}$$

$$C_{i,\,\mathrm{red},\,0}(t) = C_{i,\,\mathrm{red}}^0(t).\tag{2}$$

The value of the output signal of a voltammetric electrode, which is the current on this electrode, is defined by the Butler-Volmer equation [8]:

$$i_i(t) = z_i FA[k_{i,\,\mathrm{ox}}(t)C_{i,\,\mathrm{ox},\,0}(t) - k_{i,\,\mathrm{red}}(t)C_{i,\,\mathrm{red},\,0}(t)] = i_{i,\,\mathrm{ox}}(t) - i_{i,\,\mathrm{red}}(t),\tag{3}$$

where the values of the reaction rate coefficients $k_{i,\,\mathrm{ox}}$ and $k_{i,\,\mathrm{red}}$ are defined by the following relations [8]:

$$k_{i,\,\mathrm{ox}}(t) = k^0 \exp\left\{ -\frac{\alpha z_i F}{RT}\left[E_{\mathrm{pol}}(t) - E^0\right] \right\},\tag{4}$$

$$k_{i,\,\mathrm{red}}(t) = k^0 \exp\left\{ \frac{(1-\alpha)z_i F}{RT}\left[E_{\mathrm{pol}}(t) - E^0\right] \right\}.\tag{5}$$

Keeping in mind that an oxidizing/reduction reaction may take place on the surface of the voltammetric electrode, the relation (3) may be denoted as follows:

$$i_{i,\,\mathrm{ox}}(t) = z_i FAk_{i,\,\mathrm{ox}}(t)C_{i,\,\mathrm{ox},\,0}(t),\tag{6}$$

$$i_{i,\,\mathrm{red}}(t) = z_i FAk_{i,\,\mathrm{red}}(t)C_{i,\,\mathrm{red},\,0}(t).\tag{7}$$

It is immediately clear that the voltammetric electrode functions exactly like a converter type 0. Hence, its metrological properties are defined solely by the sensitivity coefficient denoted as follows:

$$S_i(t) = \frac{\Delta i_i(t)}{\Delta C_i^0(t)} = z_i FAk_i(t),\tag{8}$$

by taking into consideration relations (6) and (7) we get:

$$S_{i,\,\mathrm{ox}}(t) = z_i FAk_{i,\,\mathrm{ox}}(t),\tag{9}$$

$$S_{i,\,\mathrm{red}}(t) = z_i FAk_{i,\,\mathrm{red}}(t).\tag{10}$$

It results from the above analysis presented that metrological properties of a voltammetric electrode are described solely by sensitivity. This parameter is characteristic to an electrode both in the steady state and in the transient state. In such electrochemical reactions, the electrode does not present any delays or dynamic errors. Its sensitivity is determined by parameters defining marked ions, area of the electrode, electrochemical reaction rate on the surface of the electrode, and the voltage polarizing the electrode.

4. Electrochemical reaction controlled by a process of ion transport to the surface of the voltammetric electrode

In the case when an electrochemical reaction controlled by a process of ion transport takes place on the surface of the electrode, its flux to the surface is defined by this relation [8]:

$$N_i(t) = D_i \nabla C_i(t) + u_i z_i F C_i(t) \nabla U(t) + V_i(t) C_i(t). \tag{11}$$

Distribution of ion concentration $\nabla D_i = 0$ in the solution volume as a function of time t is defined by the flux divergence. Hence [8]:

$$\frac{\partial C_i(t)}{\partial t} = \nabla N_i(t). \tag{12}$$

Keeping in mind the relation (11) and assuming that $\nabla D_i = 0$ we get as a result:

$$\frac{\partial C_i(t)}{\partial t} = D_i \nabla^2 C_i(t) + z_i u_i F \nabla C_i(t) \nabla U(t) + z_i u_i F C_i(t) \nabla^2 U(t) + \nabla V_i(t) C_i(t) + V_i(t) \nabla C_i(t) \tag{13}$$

In real terms, voltammetric measurements are conducted with stationary electrodes in presence of excess of concentrated basic electrolyte, which allows to simplify the relation (13) to:

$$\frac{\partial C_i(t)}{\partial t} = D_i \nabla^2 C_i(t). \tag{14}$$

It is clear that in such a case the ion transport to or from the surface of a voltammetric electrode is determined solely by the diffusion.

4.1. Metrological properties for a general case

In general cases, without making any assumptions about reversibility or irreversibility of electrochemical reactions happening on the surface of the voltammetric electrode, one may present the relation (14) using the finite difference method

$$\frac{\partial C_{i,0}(t)}{\partial t} = D_i \left[\frac{C_i^0(t) - C_{i,0}(t)}{\delta_i^2(t)} \right], \tag{15}$$

Which, after transformation, leads to:

$$\left[\frac{\delta_i^2(t)}{D_i} \right] \frac{\partial C_{i,0}(t)}{\partial t} + C_{i,0}(t) = C_i^0(t) \tag{16}$$

Keeping in mind the relation (3) and transforming it we get:

$$C_{i,0}(t) = \frac{i_i(t)}{z_i F A k_i(t)}, \tag{17}$$

$$\frac{\partial C_{i,0}(t)}{\partial t} = \frac{1}{z_i F A k_i(t)} \left[\frac{\partial i_i(t)}{\partial t} - z_i F A C_{i,0}(t) \frac{\partial i_i(t)}{\partial t} \right]. \tag{18}$$

Substituting the relation (16) with relations (17) and (18) we get:

$$\left[\frac{\delta_i^2(t)}{D_i} \right] \frac{\partial i_i(t)}{\partial t} + \left[1 - \frac{\delta_i^2(t)}{D_i} \frac{1}{k_i(t)} \frac{\partial k_i(t)}{\partial t} \right] i_i(t) = z_i F A k_i(t) C_i^0(t). \tag{19}$$

Keeping in mind all the assumptions, we can transform the above relation to:

$$\frac{\left[\frac{\delta_i^2(t)}{D_i} \right]}{\left\{ 1 - \left[\frac{\delta_i^2(t)}{D_i} \right] \frac{1}{k_i(t)} \frac{\partial k_i(t)}{\partial t} \right\}} \frac{\partial i_i(t)}{\partial t} + i_i(t) = \frac{z_i F A k_i(t)}{\left\{ 1 - \left[\frac{\delta_i^2(t)}{D_i} \right] \frac{1}{k_i(t)} \frac{\partial k_i(t)}{\partial t} \right\}} C_i^0(t). \tag{20}$$

It results from the presented analysis that in this case the voltammetric electrode functions like converter type I. Its metrological properties are defined by sensitivity and the time constant. Static properties of the electrode are defined by sensitivity, and its dynamic properties are characterized by sensitivity and the time constant. Values of these parameters define the following relations:

$$S_{i,\text{ox}}(t) = \frac{z_i F A k_{i,\text{ox}}(t)}{\left\{ 1 - \left[\frac{\delta_{i,\text{ox}}^2(t)}{D_{i,\text{ox}}} \right] \frac{1}{k_{i,\text{ox}}(t)} \frac{\partial k_{i,\text{ox}}(t)}{\partial t} \right\}}, \tag{21}$$

$$N_{T,i,\text{ox}}(t) = \frac{\left[\frac{\delta_{i,\text{ox}}^2(t)}{D_{i,\text{ox}}} \right]}{\left\{ 1 - \left[\frac{\delta_{i,\text{ox}}^2(t)}{D_{i,\text{ox}}} \right] \frac{1}{k_{i,\text{ox}}(t)} \frac{\partial k_{i,\text{ox}}(t)}{\partial t} \right\}}, \tag{22}$$

$$S_{i,\text{red}}(t) = \frac{z_i F A k_{i,\text{red}}(t)}{\left\{ 1 - \left[\frac{\delta_{i,\text{red}}^2(t)}{D_{i,\text{red}}} \right] \frac{1}{k_{i,\text{red}}(t)} \frac{\partial k_{i,\text{red}}(t)}{\partial t} \right\}}, \tag{23}$$

$$N_{T,i,\text{red}}(t) = \frac{\left[\frac{\delta_{i,\text{red}}^2(t)}{D_{i,\text{red}}} \right]}{\left\{ 1 - \left[\frac{\delta_{i,\text{red}}^2(t)}{D_{i,\text{red}}} \right] \frac{1}{k_{i,\text{red}}(t)} \frac{\partial k_{i,\text{red}}(t)}{\partial t} \right\}}. \tag{24}$$

In the case of this type of electrochemical reactions, an electrode will present a dynamic error whose values are determined above all by the time constant and the nature of changes in the marked ion concentration. One can see in the presented relations that the parameters defining metrological properties of the voltammetric electrode are determined by the parameters defining marked ions, areas of the electrodes, a thickness of the diffusion layer, a rate of the

electrochemical reaction happening on the surface of the electrode, and thereby voltage polarizing the electrode.

4.2. The influence of the voltammetric electrode's shape on its metrological properties in the time domain

Not only flat electrodes are being used in voltammetric measurements, but spherical and cylindrical as well. That is why we also analyzed the influence of the voltammetric electrode on its metrological properties.

4.2.1. Spherical voltammetric electrode

In the case of spherical voltammetric electrode, the relation of ion transport to/from the electrode's surface give in relation (14) appears as follows:

$$\frac{\partial C_{i,0}(t)}{\partial t} = D_i \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial C_{i,0}(t)}{\partial r} \right] + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left[\sin\theta \frac{\partial C_{i,0}(t)}{\partial \theta} \right] + \frac{1}{r^2 \sin^2\theta} \frac{\partial^2 C_{i,0}(t)}{\partial \varphi^2} \right\} \tag{25}$$

Assuming that the marked ion concentration on the surface of the voltammetric electrode is not determined by θ and φ, so

$$\frac{\partial C_{i,0}(t)}{\partial \theta} = 0, \tag{26}$$

$$\frac{\partial^2 C_{i,0}(t)}{\partial \theta^2} = 0, \tag{27}$$

and

$$\frac{\partial C_{i,0}(t)}{\partial \varphi} = 0, \tag{28}$$

$$\frac{\partial^2 C_{i,0}(t)}{\partial \varphi^2} = 0, \tag{29}$$

relation of the ion transport given in relation (25) is simplified as follows:

$$\frac{\partial C_{i,0}(t)}{\partial t} = D_i \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial C_{i,0}(t)}{\partial r} \right] \right\}, \tag{30}$$

and it results in:

$$\frac{\partial C_{i,0}(t)}{\partial t} = \frac{2D_i}{r} \frac{\partial C_{i,0}(t)}{\partial r} + D_i \frac{\partial^2 C_{i,0}(t)}{\partial r^2}. \tag{31}$$

We can present the relation using the finite difference method:

$$\frac{\partial C_{i,0}(t)}{\partial t} = \frac{2D_i}{r}\left[\frac{C_i^0(t) - C_{i,0}(t)}{\delta_i(t)}\right] + D_i\left[\frac{C_i^0(t) - C_{i,0}(t)}{\delta_i^2(t)}\right], \tag{32}$$

which after transformation leads to the relation:

$$\frac{\partial C_{i,0}(t)}{\partial t} + \left[\frac{2D_i\delta_i(t) + rD_i}{r\delta_i^2(t)}\right]C_{i,0}(t) = \left[\frac{2D_i\delta_i(t) + rD_i}{r\delta_i^2(t)}\right]C_i^0(t), \tag{33}$$

and it results in:

$$\frac{r\delta_i^2(t)}{2D_i\delta_i(t) + rD_i}\frac{\partial C_{i,0}(t)}{\partial t} + C_{i,0}(t) = C_i^0(t). \tag{34}$$

Substituting the relation (34) with relations (17) and (18) we get:

$$\frac{\partial i_i(t)}{\partial t} + \left[\frac{2D_i\delta_i(t) + rD_i}{r\delta_i^2(t)} - \frac{1}{k_i(t)}\frac{\partial k_i(t)}{\partial t}\right]i_i(t) = z_iFAk_i(t)\left[\frac{2D_i\delta_i(t) + rD_i}{r\delta_i^2(t)}\right]C_i^0(t), \tag{35}$$

which can be denoted as:

$$\frac{1}{\left[\frac{2D_i\delta_i(t) + rD_i}{r\delta_i^2(t)} - \frac{1}{k_i(t)}\frac{\partial k_i(t)}{\partial t}\right]}\frac{\partial i_i(t)}{\partial t} + i_i(t) = \frac{z_iFAk_i(t)\left[\frac{2D_i\delta_i(t)+rD_i}{r\delta_i^2(t)}\right]}{\left[\frac{2D_i\delta_i(t)+rD_i}{r\delta_i^2(t)} - \frac{1}{k_i(t)}\frac{\partial k_i(t)}{\partial t}\right]}C_i^0(t). \tag{36}$$

The above relation proves that the spherical voltammetric electrode functions as converter type I, both for the oxidizing reaction and for the reduction reaction. Its metrological properties are defined by sensitivity and the time constant. Static properties of the electrode are defined by sensitivity, and its dynamic properties are defined by sensitivity and the time constant. Values of these parameters are defined by the following relations:

$$S_{i,\text{ox}}(t) = \frac{z_iFAk_{i,\text{ox}}(t)\left[\frac{2D_{i,\text{ox}}\delta_{i,\text{ox}}(t)+rD_{i,\text{ox}}}{r\delta_{i,\text{ox}}^2(t)}\right]}{\left[\frac{2D_{i,\text{ox}}\delta_{i,\text{ox}}(t)+rD_{i,\text{ox}}}{r\delta_{i,\text{ox}}^2(t)} - \frac{1}{k_{i,\text{ox}}(t)}\frac{\partial k_{i,\text{ox}}(t)}{\partial t}\right]}, \tag{37}$$

$$N_{T,i,\text{ox}}(t) = \frac{1}{\left[\frac{2D_{i,\text{ox}}\delta_{i,\text{ox}}(t)+rD_{i,\text{ox}}}{r\delta_{i,\text{ox}}^2(t)} - \frac{1}{k_{i,\text{ox}}(t)}\frac{\partial k_{i,\text{ox}}(t)}{\partial t}\right]}, \tag{38}$$

$$S_{i,\text{red}}(t) = \frac{z_iFAk_{i,\text{red}}(t)\left[\frac{2D_{i,\text{red}}\delta_{i,\text{red}}(t)+rD_{i,\text{red}}}{r\delta_{i,\text{red}}^2(t)}\right]}{\left[\frac{2D_{i,\text{red}}\delta_{i,\text{red}}(t)+rD_{i,\text{red}}}{r\delta_{i,\text{red}}^2(t)} - \frac{1}{k_{i,\text{red}}(t)}\frac{\partial k_{i,\text{red}}(t)}{\partial t}\right]}, \tag{39}$$

$$N_{T,i,\text{red}}(t) = \frac{1}{\left[\dfrac{2D_{i,\text{red}}\delta_{i,\text{red}}(t) + rD_{i,\text{red}}}{r\delta_{i,\text{red}}^2(t)} - \dfrac{1}{k_{i,\text{red}}(t)}\dfrac{\partial k_{i,\text{red}}(t)}{\partial t}\right]}. \tag{40}$$

Presented relations show that a change of the shape of voltammetric electrode does not cause a change of the measuring converter's type. A spherical electrode functions as converter type I. This electrode, in this type of electrochemical reactions, will produce a dynamic error whose value is determined above all by the time constant and by the nature of changes of the marked ion concentration. The relations also show that the parameters defining metrological properties of this voltammetric electrode are determined by the parameters defining marked ions, an electrode radius, a thickness of the diffusion layer, a rate of electrochemical reaction taking place on the surface of the electrode, and thereby by the voltage polarizing the electrode.

4.2.2. Cylindrical voltammetric electrode

The relation of ion transport to/from the surface of the cylindrical voltammetric electrode shown by relation (14) is:

$$\frac{\partial C_{i,0}(t)}{\partial t} = D_i \left\{ \frac{1}{\rho}\frac{\partial}{\partial\rho}\left[\rho\frac{\partial C_{i,0}(t)}{\partial\rho}\right] + \frac{1}{\rho^2}\frac{\partial^2 C_{i,0}(t)}{\partial\varphi^2} + \frac{\partial^2 C_{i,0}(t)}{\partial z^2} \right\}. \tag{41}$$

Assuming that the concentration of marked ions on the surface of the cylindrical electrode is determined by φ, i.e.,:

$$\frac{\partial C_{i,0}(t)}{\partial\varphi} = 0, \tag{42}$$

we get:

$$\frac{\partial C_{i,0}(t)}{\partial t} = \frac{D_i}{\rho}\frac{\partial C_{i,0}(t)}{\partial\rho} + D_i\frac{\partial^2 C_{i,0}(t)}{\partial\rho^2} + D_i\frac{\partial^2 C_{i,0}(t)}{\partial z^2}. \tag{43}$$

Defining this relation with finite difference method we get:

$$\frac{\partial C_{i,0}(t)}{\partial t} = \frac{D_i}{\rho}\left[\frac{C_i^0(t) - C_{i,0}(t)}{\delta_i(t)}\right] + D_i\left[\frac{C_i^0(t) - C_{i,0}(t)}{\delta_i^2(t)}\right] + D_i\left[\frac{C_i^0(t) - C_{i,0}(t)}{\delta_i^2(t)}\right], \tag{44}$$

which finally leads to:

$$\frac{\partial C_{i,0}(t)}{\partial t} = \left[\frac{D_i}{\rho\delta_i(t)} + \frac{2D_i}{\delta_i^2(t)}\right]C_{i,0}(t) = \left[\frac{D_i}{\rho\delta_i(t)} + \frac{2D_i}{\delta_i^2(t)}\right]C_i^0(t), \tag{45}$$

and it results in:

$$\frac{\rho\delta_i^2(t)}{2\rho D_i + \delta_i(t)D_i}\frac{\partial C_{i,0}(t)}{\partial t} + C_{i,0}(t) = C_i^0(t). \tag{46}$$

Substituting relation (46) with relations (17) and (18) we get:

$$\frac{\rho\delta_i^2(t)}{2\rho D_i + \delta_i(t)D_i}\frac{\partial i_i(t)}{\partial t} + \left[\frac{2\rho D_i + \delta_i(t)D_i}{\rho\delta_i^2(t)} - \frac{1}{k_i(t)}\frac{\partial k_i(t)}{\partial t}\right]i_i(t) = z_iFAk_i(t)\left[\frac{2\rho D_i + \delta_i(t)D_i}{\rho\delta_i^2(t)}\right]C_i^0(t). \tag{47}$$

Keeping in mind the assumptions, the above relation may be transformed as follows:

$$\frac{\left[\frac{\rho\delta_i^2(t)}{2\rho D_i + \delta_i(t)D_i}\right]}{\left[\frac{2\rho D_i + \delta_i(t)D_i}{\rho\delta_i^2(t)} - \frac{1}{k_i(t)}\frac{\partial k_i(t)}{\partial t}\right]}\frac{\partial i_i(t)}{\partial t} + i_i(t) = \frac{z_iFAk_i(t)\left[\frac{2\rho D_i + \delta_i(t)D_i}{\rho\delta_i^2(t)}\right]}{\left[\frac{2\rho D_i + \delta_i(t)D_i}{\rho\delta_i^2(t)} - \frac{1}{k_i(t)}\frac{\partial k_i(t)}{\partial t}\right]}C_i^0(t). \tag{48}$$

In the above relation, it is clear that a cylindrical voltammetric electrode functions as a measuring converter type I both for the oxidizing reaction and for the reduction reaction. Its metrological properties are defined by sensititvity and the time constant. Static properties of the electrode are defined by sensitivity, and its dynamic properties are characterized by sensitivity and the time constant. Values of the parameters are described as follows:

$$S_{i,\text{ox}}(t) = \frac{z_iFAk_{i,\text{ox}}(t)\left[\frac{2\rho D_{i,\text{ox}} + \delta_{i,\text{ox}}(t)D_{i,\text{ox}}}{\rho\delta_{i,\text{ox}}^2(t)}\right]}{\left[\frac{2\rho D_{i,\text{ox}} + \delta_{i,\text{ox}}(t)D_{i,\text{ox}}}{\rho\delta_{i,\text{ox}}^2(t)} - \frac{1}{k_{i,\text{ox}}(t)}\frac{\partial k_{i,\text{ox}}(t)}{\partial t}\right]}, \tag{49}$$

$$N_{T,i,\text{ox}}(t) = \frac{\left[\frac{\rho\delta_{i,\text{ox}}^2(t)}{2\rho D_{i,\text{ox}} + \delta_{i,\text{ox}}(t)D_{i,\text{ox}}}\right]}{\left[\frac{2\rho D_{i,\text{ox}} + \delta_{i,\text{ox}}(t)D_{i,\text{ox}}}{\rho\delta_{i,\text{ox}}^2(t)} - \frac{1}{k_{i,\text{ox}}(t)}\frac{\partial k_{i,\text{ox}}(t)}{\partial t}\right]}, \tag{50}$$

$$S_{i,\text{red}}(t) = \frac{z_iFAk_{i,\text{red}}(t)\left[\frac{2\rho D_{i,\text{red}} + \delta_{i,\text{red}}(t)D_{i,\text{red}}}{\rho\delta_{i,\text{red}}^2(t)}\right]}{\left[\frac{2\rho D_{i,\text{red}} + \delta_{i,\text{red}}(t)D_{i,\text{red}}}{\rho\delta_{i,\text{red}}^2(t)} - \frac{1}{k_{i,\text{red}}(t)}\frac{\partial k_{i,\text{red}}(t)}{\partial t}\right]}, \tag{51}$$

$$N_{T,i,\text{red}}(t) = \frac{\left[\frac{\rho\delta_{i,\text{red}}^2(t)}{2\rho D_{i,\text{red}} + \delta_{i,\text{red}}(t)D_{i,\text{red}}}\right]}{\left[\frac{2\rho D_{i,\text{red}} + \delta_{i,\text{red}}(t)D_{i,\text{red}}}{\rho\delta_{i,\text{red}}^2(t)} - \frac{1}{k_{i,\text{red}}(t)}\frac{\partial k_{i,\text{red}}(t)}{\partial t}\right]}. \tag{52}$$

In presented relations, one may notice that the change of the shape of a voltammetric electrode does not change its type as a measuring converter. A cylindrical electrode functions also as a converter type I. This electrode in case of this type of electrochemical reaction will create a dynamic error whose value is determined above all by the time constant and the nature of

changes in marked ion concentration. In presented relations, one may notice that parameters defining metrological properties of the voltammetric electrode are determined by parameters of marked ions, an electrode radius, a thickness of the diffusion layer, a rate of the electrochemical reaction taking place on the surface of the electrode, and thereby by voltage polarizing the electrode.

4.3. The influence if polarizing voltage on metrological properties of a voltammetric electrode

In order to enforce a certain course of an electrochemical reaction on the surface of a voltammetric electrode, it should be polarized with a proper voltage. In measuring practice, there are different voltammetric methods applied. Most frequently used method is direct current voltammetry. In this method, an electrode used is polarized by voltage with a value changing linearly. The advantage of such a solution is the simplicity of the measuring system. At the same time, its disadvantage is relatively low accuracy. It is a solution connected with relatively great influence of capacitive current.

In order to eliminate the influence of the volume of the double layer on accuracy of voltammetric markings, there are different types of alternating currents voltammetry applied. In such cases, the voltage polarizing a voltammetric electrode has two components: variable and static. A static component is identical with one in the direct current voltammetry, and a variable component may be for example sinusoidal voltage, square wave voltage, or triangle wave voltage.

4.3.1. The influence of polarizing voltage with a value changing linearly

In the method of direct current voltammetry, a voltammetric electrode used for measuring is polarized with a voltage described as follows:

$$E_{\text{pol}}(t) = E_0 \pm S_U t. \tag{53}$$

In such a case, coefficients of the rate of an electrochemical reaction which are defined by relations (4) and (5) will take on a form:

$$k_{i,\text{ox}}(t) = k^0 \exp\left\{-\frac{\alpha z_i F}{RT}[E_0 + S_U t - E^0]\right\}, \tag{54}$$

$$k_{i,\text{red}}(t) = k^0 \exp\left\{\frac{(1-\alpha)z_i F}{RT}[E_0 - S_U t - E^0]\right\}, \tag{55}$$

and their derivatives are, respectively:

$$\frac{\partial k_{i,\text{ox}}(t)}{\partial t} = -\frac{\alpha z_i F}{RT} S_U k_{i,\text{ox}}(t), \tag{56}$$

$$\frac{\partial k_{i,\text{red}}(t)}{\partial t} = -\frac{(1-\alpha)z_i F}{RT} S_U k_{i,\text{red}}(t). \tag{57}$$

Substituting relations (21) and (22) with relations (56) and (23) and relation (24) with relation (57) we get, respectively:

$$S_{i,\text{ox}}(t) = \frac{z_i F A k_{i,\text{ox}}(t)}{\left\{1 + \left[\frac{\delta_{i,\text{ox}}^2(t)}{D_{i,\text{ox}}}\right]\frac{\alpha z_i F}{RT}S_U\right\}},\tag{58}$$

$$N_{T,i,\text{ox}}(t) = \frac{\left[\frac{\delta_{i,\text{ox}}^2(t)}{D_{i,\text{ox}}}\right]}{\left\{1 + \left[\frac{\delta_{i,\text{ox}}^2(t)}{D_{i,\text{ox}}}\right]\frac{\alpha z_i F}{RT}S_U\right\}},\tag{59}$$

and:

$$S_{i,\text{red}}(t) = \frac{z_i F A k_{i,\text{red}}(t)}{\left\{1 + \left[\frac{\delta_{i,\text{red}}^2(t)}{D_{i,\text{red}}}\right]\frac{(1-\alpha)z_i F}{RT}S_U\right\}},\tag{60}$$

$$N_{T,i,\text{red}}(t) = \frac{\left[\frac{\delta_{i,\text{red}}^2(t)}{D_{i,\text{red}}}\right]}{\left\{1 + \left[\frac{\delta_{i,\text{red}}^2(t)}{D_{i,\text{red}}}\right]\frac{(1-\alpha)z_i F}{RT}S_U\right\}}.\tag{61}$$

In relations above, one can see that a flat voltammetric electrode polarized with a voltage as in relation (53) functions as a converter type I. Parameters defining its metrological properties are determined by the rate of changes in polarizing voltage. Hence, their values can be alternated by an appropriate choice of the rate of changes in this voltage.

4.3.2. The influence of polarizing voltage with a sinusoidal variable component

In the method of alternating current sinusoidal voltammetry, the voltammetric electrode used for measuring is polarized with a voltage described this way:

$$E_{\text{pol}}(t) = E_0 \pm S_U t \pm U_m \sin \omega t.\tag{62}$$

In this case, coefficients of the rate of an electrochemical reaction described by the relations (4) and (5) are denoted:

$$k_{i,\text{ox}}(t) = k^0 \exp\left\{-\frac{\alpha z_i F}{RT}[E_0 + S_U t + U_m \sin \omega t - E^0]\right\},\tag{63}$$

$$k_{i,\text{red}}(t) = k^0 \exp\left\{\frac{(1-\alpha)z_i F}{RT}[E_0 - S_U t - U_m \sin \omega t - E^0]\right\},\tag{64}$$

and their derivatives are, respectively:

$$\frac{\partial k_{i,\text{ox}}(t)}{\partial t} = -\frac{\alpha z_i F}{RT}(S_U + \omega U_m \cos \omega t)k_{i,\text{ox}}(t),\tag{65}$$

$$\frac{\partial k_{i,\text{red}}(t)}{\partial t} = -\frac{(1-\alpha)z_i F}{RT}(S_U + \omega U_m \cos \omega t)k_{i,\text{red}}(t).\tag{66}$$

Because the variable component of polarizing voltage causes changes of ion concentration in the volume of the analyzed solution, also on the surface of the electrode, accordingly to the relation:

$$\frac{\partial[\Delta C_{i,0}(t)]}{\partial t} = \frac{\partial}{\partial t}[C_i^0(t)\sin\omega t] = \frac{\partial C_i^0(t)}{\partial t}\sin\omega t + \omega\cos\omega t C_i^0(t), \qquad (67)$$

then the relation (14) denoted on the surface of the voltammetric electrode polarized by voltage with a static and sinusoidal variable component is:

$$\frac{\partial[C_{i,0}(t) + \Delta C_{i,0}(t)]}{\partial t} = \frac{\partial C_{i,0}(t)}{\partial t} + \frac{\partial[\Delta C_{i,0}(t)]}{\partial t} = D_i\nabla^2 C_i(t) + \frac{\partial C_i^0(t)}{\partial t}\sin\omega t + \omega\cos\omega t C_i^0(t). \quad (68)$$

Denoting this relation with the use of finite difference method we have:

$$\frac{\partial C_{i,0}(t)}{\partial t} = D_i\left[\frac{C_i^0(t) - C_{i,0}(t)}{\delta_i^2(t)}\right] + \frac{\partial C_i^0(t)}{\partial t}\sin\omega t + \omega\cos\omega t C_i^0(t), \qquad (69)$$

which results in:

$$\left[\frac{\delta_i^2(t)}{D_i}\right]\frac{\partial C_{i,0}(t)}{\partial t} + C_{i,0}(t) = \left[\frac{\delta_i^2(t)}{D_i}\right]\left[\frac{D_i}{\delta_i^2(t)} + \omega\cos\omega t\right]\left\{C_i^0(t) + \frac{\frac{\partial C_i^0(t)}{\partial t}\sin\omega t}{\left[\frac{D_i}{\delta_i^2(t)} + \omega\cos\omega t\right]}\right\}. \qquad (70)$$

Substituting the relation (70) with relations (17) and (18) we get:

$$\left[\frac{\delta_i^2(t)}{D_i}\right]\frac{\partial i_i(t)}{\partial t} + \left[1 - \frac{1}{k_i(t)}\frac{\partial k_i(t)}{\partial t}\frac{\delta_i^2(t)}{D_i}\right]i_i(t) = \left\{z_i FA k_i(t)\left[1 + \frac{\delta_i^2(t)}{D_i}\omega\cos\omega t\right]\right\}$$

$$\left\{C_i^0(t) + \frac{z_i FA k_i(t)\frac{\delta_i^2(t)}{D_i}\frac{\partial C_i^0(t)}{\partial t}\sin\omega t}{z_i FA k_i(t)\left[1 + \frac{\delta_i^2(t)}{D_i}\omega\cos\omega t\right]}\right\}. \qquad (71)$$

Keeping in mind the assumptions taken, we can transform the above relation into:

$$\frac{\left[\frac{\delta_i^2(t)}{D_i}\right]}{\left[1 - \frac{1}{k_i(t)}\frac{\partial k_i(t)}{\partial t}\frac{\delta_i^2(t)}{D_i}\right]}\frac{\partial i_i(t)}{\partial t} + i_i(t) = \frac{z_i FA k_i(t)\left[1 + \frac{\delta_i^2(t)}{D_i}\omega\cos\omega t\right]}{\left[1 - \frac{1}{k_i(t)}\frac{\partial k_i(t)}{\partial t}\frac{\delta_i^2(t)}{D_i}\right]}$$

$$\left\{C_i^0(t) + \frac{z_i FA k_i(t)\frac{\delta_i^2(t)}{D_i}\frac{\partial C_i^0(t)}{\partial t}\sin\omega t}{z_i FA k_i(t)\left[1 + \frac{\delta_i^2(t)}{D_i}\omega\cos\omega t\right]}\right\}. \qquad (72)$$

It is clear from the above relation that both for the oxidizing reaction and for the reduction reaction, a flat voltammetric electrode polarized by the voltage denoted as in relation (62) functions as a converter type I with properties defined as follows:

$$S_{i,\,\mathrm{ox}}(t) = \frac{z_i F A k_{i,\,\mathrm{ox}}(t)\left[1 + \frac{\delta_{i,\,\mathrm{ox}}^2(t)}{D_{i,\,\mathrm{ox}}}\,\omega\cos\omega t\right]}{\left[1 + \frac{\alpha z_i F}{RT}\left(S_U + \omega U_m\cos\omega t\right)\frac{\delta_{i,\,\mathrm{ox}}^2(t)}{D_{i,\,\mathrm{ox}}}\right]},$$ (73)

$$N_{T,\,i,\,\mathrm{ox}}(t) = \frac{\frac{\delta_{i,\,\mathrm{ox}}^2(t)}{D_{i,\,\mathrm{ox}}}}{\left[1 + \frac{\alpha z_i F}{RT}\left(S_U + \omega U_m\cos\omega t\right)\frac{\delta_{i,\,\mathrm{ox}}^2(t)}{D_{i,\,\mathrm{ox}}}\right]},$$ (74)

$$S_{i,\,\mathrm{red}}(t) = \frac{z_i F A k_{i,\,\mathrm{red}}(t)\left[1 + \frac{\delta_{i,\,\mathrm{red}}^2(t)}{D_{i,\,\mathrm{red}}}\,\omega\cos\omega t\right]}{\left[1 + \frac{(1-\alpha)z_i F}{RT}\left(S_U + \omega U_m\cos\omega t\right)\frac{\delta_{i,\,\mathrm{red}}^2(t)}{D_{i,\,\mathrm{red}}}\right]},$$ (75)

$$N_{T,\,i,\,\mathrm{red}}(t) = \frac{\frac{\delta_{i,\,\mathrm{red}}^2(t)}{D_{i,\,\mathrm{red}}}}{\left[1 + \frac{(1-\alpha)z_i F}{RT}\left(S_U + \omega U_m\cos\omega t\right)\frac{\delta_{i,\,\mathrm{red}}^2(t)}{D_{i,\,\mathrm{red}}}\right]}.$$ (76)

It is clear that both the sensitivity of the electrode as well as its time constant are determined by the rate of changes of the static component of polarizing voltage and by the amplitude and sinusoidal frequency of the variable component. Hence, the parameters describing metrological properties of the electrode can be influenced by an appropriate choice of polarizing voltage parameters.

4.3.3. The influence of the triangle waveform variable component

In the method of triangular waveform AC voltammetry, a voltammetric electrode used for measuring is polarized by voltage denoted as follows:

$$E_{\mathrm{pol}}(t) = E_0 \pm S_U t \pm U_t(t),$$ (77)

with a variable component of the polarizing voltage which can be denoted as:

$$U_t(t) = \begin{cases} \dfrac{2At}{\pi} & -\dfrac{T}{2}\le t\le\dfrac{T}{2} \\[2ex] \dfrac{2A(\pi - t)}{\pi} & \dfrac{T}{2}\le t\le T \end{cases}.$$ (78)

Triangular bipolar waveform component $U_t(t)$ can be denoted with an expansion in the Fourier series:

$$U_t(t) = \frac{8A}{\pi^2}\sum_{n=0}^{\infty}(-1)^n\frac{\sin\left[(2n+1)\omega t\right]}{(2n+1)^2} = \frac{8A}{\pi^2}\left(\sin\omega t - \frac{1}{9}\sin 3\omega t + \frac{1}{25}\sin 5\omega t - \ldots\right).$$ (79)

In this case coefficients of the rate of electrochemical reactions denoted by the relations (4) and (5) are as follows:

$$k_{i,\,ox}(t) = k^0 \exp\left\{-\frac{\alpha z_i F}{RT}\left[E_0 + S_U t + \frac{8A}{\pi^2}\left(\sin\omega t - \frac{1}{9}\sin 3\omega t + \frac{1}{25}\sin 5\omega t - \ldots\right) - E^0\right]\right\}, \quad (80)$$

$$k_{i,\,red}(t) = k^0 \exp\left\{\frac{(1-\alpha)z_i F}{RT}\left[E_0 - S_U t - \frac{8A}{\pi^2}\left(\sin\omega t - \frac{1}{9}\sin 3\omega t + \frac{1}{25}\sin 5\omega t - \ldots\right) - E^0\right]\right\},$$
$$(81)$$

and their derivatives are, respectively:

$$\frac{\partial k_{i,\,ox}(t)}{\partial t} = -\frac{\alpha z_i F}{RT}\left[S_U + \frac{8\omega A}{\pi^2}\left(\cos\omega t - \frac{1}{3}\cos 3\omega t + \frac{1}{5}\cos 5\omega t - \ldots\right)\right]k_{i,\,ox}(t), \quad (82)$$

$$\frac{\partial k_{i,\,red}(t)}{\partial t} = -\frac{(1-\alpha)z_i F}{RT}\left[S_U + \frac{8\omega A}{\pi^2}\left(\cos\omega t - \frac{1}{3}\cos 3\omega t + \frac{1}{5}\cos 5\omega t - \ldots\right)\right]k_{i,\,red}(t). \quad (83)$$

Because the variable component of the polarizing voltage causes changes in the ion concentration of the analyzed solution, also on the surface of the electrode, accordingly to the relation:

$$\frac{\partial[\Delta C_{i,0}(t)]}{\partial t} = \frac{\partial}{\partial t}\left[\frac{8A}{\pi^2}C_i^0(t)\sum_{n=0}^{\infty}(-1)^n\frac{\sin[(2n+1)\omega t]}{(2n+1)^2}\right], \quad (84)$$

which leads to:

$$\frac{\partial[\Delta C_{i,0}(t)]}{\partial t} = \frac{8A}{\pi^2}\frac{\partial C_i^0(t)}{\partial t}\sum_{n=0}^{\infty}(-1)^n\frac{\sin[(2n+1)\omega t]}{(2n+1)^2} + \frac{8A}{\pi^2}C_i^0(t)\sum_{n=0}^{\infty}(-1)^n\frac{\omega\cos[(2n+1)\omega t]}{(2n+1)}, \quad (85)$$

then the relation (14) denoted for the surface of the voltammetric electrode polarized by the voltage with a static component and a triangular waveform variable component is:

$$\frac{\partial[C_{i,0}(t) + \Delta C_{i,0}(t)]}{\partial t} = D_i\nabla^2 C_i(t)$$
$$+ \frac{8A}{\pi^2}\left[\left(\sin\omega t - \frac{1}{9}\sin 3\omega t + \frac{1}{25}\sin 5\omega t - \ldots\right)\frac{\partial C_i^0(t)}{\partial t}\right.$$
$$\left. + \omega C_i^0(t)\left(\cos\omega t - \frac{1}{3}\cos 3\omega t + \frac{1}{5}\cos 5\omega t - \ldots\right)\right]. \quad (86)$$

Denoting this relation by using finite difference method, we get:

$$\frac{\partial C_{i,0}(t)}{\partial t} = D_i\left[\frac{C_i^0(t) - C_{i,0}(t)}{\delta_i^2(t)}\right]$$
$$+ \frac{8A}{\pi^2}\left[\left(\sin\omega t - \frac{1}{9}\sin 3\omega t + \frac{1}{25}\sin 5\omega t - \ldots\right)\frac{\partial C_i^0(t)}{\partial t}\right.$$
$$\left. + \omega C_i^0(t)\left(\cos\omega t - \frac{1}{3}\cos 3\omega t + \frac{1}{5}\cos 5\omega t - \ldots\right)\right], \quad (87)$$

which results in:

$$\left[\frac{\delta_i^2(t)}{D_i}\right]\frac{\partial C_{i,0}(t)}{\partial t} + C_{i,0}(t) = \left[\frac{\delta_i^2(t)}{D_i}\right]$$
$$\left[\frac{D_i}{\delta_i^2(t)} + \frac{8\omega A}{\pi^2}\left(\cos\omega t - \frac{1}{3}\cos 3\omega t + \frac{1}{5}\cos 5\omega t - \ldots\right)\right]$$
$$\left\{C_i^0(t) + \frac{\frac{8A}{\pi^2}\frac{\partial C_i^0(t)}{\partial t}\left(\sin\omega t - \frac{1}{9}\sin 3\omega t + \frac{1}{25}\sin 5\omega t - \ldots\right)}{\left[\frac{D_i}{\delta_i^2(t)} + \frac{8\omega A}{\pi^2}\left(\cos\omega t - \frac{1}{3}\cos 3\omega t + \frac{1}{5}\cos 5\omega t - \ldots\right)\right]}\right\}.$$

(88)

Substituting the relation (88) with relations (17) and (18), we get the relation:

$$\left[\frac{\delta_i^2(t)}{D_i}\right]\frac{\partial i_i(t)}{\partial t} + \left[1 - \frac{1}{k_i(t)}\frac{\partial k_i(t)}{\partial t}\frac{\delta_i^2(t)}{D_i}\right]i_i(t) =$$
$$\left\{z_iFAk_i(t)\left[1 + \frac{\delta_i^2(t)}{D_i}\frac{8\omega A}{\pi^2}\left(\cos\omega t - \frac{1}{3}\cos 3\omega t + \frac{1}{5}\cos 5\omega t - \ldots\right)\right]\right\}$$
$$\left\{C_i^0(t) + \frac{z_iFAk_i(t)\frac{\delta_i^2(t)}{D_i}\frac{8A}{\pi^2}\frac{\partial C_i^0(t)}{\partial t}\left(\sin\omega t - \frac{1}{9}\sin 3\omega t + \frac{1}{25}\sin 5\omega t - \ldots\right)}{z_iFAk_i(t)\left[1 + \frac{\delta_i^2(t)}{D_i}\frac{8\omega A}{\pi^2}\left(\cos\omega t - \frac{1}{3}\cos 3\omega t + \frac{1}{5}\cos 5\omega t - \ldots\right)\right]}\right\}.$$

(89)

Keeping in mind the assuptions taken, the above relation may be transformed into:

$$\frac{\left[\frac{\delta_i^2(t)}{D_i}\right]}{\left\{1 + \frac{\delta_i^2(t)}{D_i}\frac{\alpha z_iF}{RT}\left[S_U + \frac{8\omega A}{\pi^2}\left(\cos\omega t - \frac{1}{3}\cos 3\omega t + \frac{1}{5}\cos 5\omega t - \ldots\right)\right]\right\}}\frac{\partial i_i(t)}{\partial t} + i_i(t) =$$
$$\frac{z_iFAk_i(t)\left[1 + \frac{\delta_i^2(t)}{D_i}\frac{8\omega A}{\pi^2}\left(\cos\omega t + \cos 3\omega t + \cos 5\omega t + \ldots\right)\right]}{\left\{1 + \frac{\delta_i^2(t)}{D_i}\frac{\alpha z_iF}{RT}\left[S_U + \frac{8\omega A}{\pi^2}\left(\cos\omega t - \frac{1}{3}\cos 3\omega t + \frac{1}{5}\cos 5\omega t - \ldots\right)\right]\right\}}$$
$$\left\{C_i^0(t) + \frac{z_iFAk_i(t)\frac{\delta_i^2(t)}{D_i}\frac{8A}{\pi^2}\frac{\partial C_i^0(t)}{\partial t}\left(\sin\omega t - \frac{1}{9}\sin 3\omega t + \frac{1}{25}\sin 5\omega t - \ldots\right)}{z_iFAk_i(t)\left[1 + \frac{\delta_i^2(t)}{D_i}\frac{8\omega A}{\pi^2}\left(\cos\omega t - \frac{1}{3}\cos 3\omega t + \frac{1}{5}\cos 5\omega t - \ldots\right)\right]}\right\}.$$

(90)

It is clear from the above relation that both for the oxidizing reaction and for the reduction reaction, a flat voltammetric electrode polarized by voltage as in relation (77) functions as a converter type I with properties defined as follows:

$$S_{i,\,\mathrm{ox}}(t) = \frac{z_i F A k_{i,\,\mathrm{ox}}(t)\left[1 + \frac{\delta_{i,\,\mathrm{ox}}^2(t)}{D_{i,\,\mathrm{ox}}}\frac{8\omega A}{\pi^2}\left(\cos\omega t + \cos 3\omega t + \cos 5\omega t + ...\right)\right]}{\left\{1 + \frac{\delta_{i,\,\mathrm{ox}}^2(t)}{D_{i,\,\mathrm{ox}}}\frac{\alpha z_i F}{RT}\left[S_U + \frac{8\omega A}{\pi^2}\left(\cos\omega t - \frac{1}{3}\cos 3\omega t + \frac{1}{5}\cos 5\omega t - ...\right)\right]\right\}}, \tag{91}$$

$$N_{T,\,i,\,\mathrm{ox}}(t) = \frac{\left[\frac{\delta_{i,\,\mathrm{ox}}^2(t)}{D_{i,\,\mathrm{ox}}}\right]}{\left\{1 + \frac{\delta_{i,\,\mathrm{ox}}^2(t)}{D_{i,\,\mathrm{ox}}}\frac{\alpha z_i F}{RT}\left[S_U + \frac{8\omega A}{\pi^2}\left(\cos\omega t - \frac{1}{3}\cos 3\omega t + \frac{1}{5}\cos 5\omega t - ...\right)\right]\right\}}, \tag{92}$$

$$S_{i,\,\mathrm{red}}(t) = \frac{z_i F A k_{i,\,\mathrm{red}}(t)\left[1 + \frac{\delta_{i,\,\mathrm{red}}^2(t)}{D_{i,\,\mathrm{red}}}\frac{8\omega A}{\pi^2}\left(\cos\omega t + \cos 3\omega t + \cos 5\omega t + ...\right)\right]}{\left\{1 + \frac{\delta_{i,\,\mathrm{red}}^2(t)}{D_{i,\,\mathrm{red}}}\frac{(1-\alpha)z_i F}{RT}\left[S_U + \frac{8\omega A}{\pi^2}\left(\cos\omega t - \frac{1}{3}\cos 3\omega t + \frac{1}{5}\cos 5\omega t - ...\right)\right]\right\}}, \tag{93}$$

$$N_{T,\,i,\,\mathrm{red}}(t) = \frac{\left[\frac{\delta_{i,\,\mathrm{red}}^2(t)}{D_{i,\,\mathrm{red}}}\right]}{\left\{1 + \frac{\delta_{i,\,\mathrm{red}}^2(t)}{D_{i,\,\mathrm{red}}}\frac{(1-\alpha)z_i F}{RT}\left[S_U + \frac{8\omega A}{\pi^2}\left(\cos\omega t - \frac{1}{3}\cos 3\omega t + \frac{1}{5}\cos 5\omega t - ...\right)\right]\right\}}. \tag{94}$$

It is clear that the sensitivity of an electrode and its time constant are determined by the rate of changes of the static component in the polarizing voltage and by the amplitude and frequency of the fundamental component and individual harmonic components of the triangle waveform polarizing voltage.

Hence, the parameters describing metrological properties of an electrode can be influenced by an appropriate choice of polarizing voltage parameters.

5. Numerical simulations and discussion

Numeric simulations were conducted in order to determine how the electrode's shape and the shape of the voltage influencing the voltammetric electrode metrological properties.

The influence of the voltammetric electrode's shape on its metrological properties was analyzed assuming that the electrode is flat, spherical, and cylindrical and polarized only by linearly increasing voltage.

Also, the influence of the shape of the voltage polarizing the electrode on its metrological properties was analyzed assuming that the electrode is flat and polarized by the linearly increasing voltage, linearly increasing voltage with sinusoidal variable component and linearly increasing voltage with a triangular waveform variable component. It was assumed in the simulations that there is an oxidizing reaction of marked ions on the surface of the electrode and the values defining the marked ions, voltammetric electrode's shapes and polarizing voltages are: $z_i = 1$, $\alpha = 0.5$, $E_0 = 0.25...0.75$ V; $D_i = 10^{-5}...10^{-7}$ cm/s, $A = 1$ mm^2, $r = 0.1...1$ mm, $\rho = 0.1...1$ mm, $S_U = 5...100$ mV/s, $U_m = 5...100$ mV, $f = 1...100$ Hz.

Numerical simulations prove that the shape of the electrode and its geometrical dimensions influence its sensitivity. When the electrode functions like a converter type 0, the geometrical

values influence the sensitivity solely through the surface area of the electrode. However, if the electrode functions like a converter type I, the electrode's radius influences greatly the sensitivity. The sensitivity of the electrode is the highest when the electrode functions like a converter type 0, which is shown in **Figure 1**.

The highest sensitivity is the characteristic of a cylindrical electrode when there are determined: rate of changes in the voltage polarizing an electrode, a rate of oxidizing reaction, an ion diffusion coefficient, and equal geometrical dimensions. It was also proved that spherical and cylindrical electrodes sensitivity is determined by their radius. Reducing geometrical dimensions of a flat voltammetric electrode leads to reduction of its sensitivity. And reducing the radius of spherical and cylindrical electrode leads to an increase of their sensitivity.

Numeric simulation results show that the shape of the electrode influences its time constant. The lowest time constant is a characteristic of a cylindrical electrode when there are determined: rate of changes in the voltage polarizing an electrode, an ion diffusion coefficient, and equal geometrical dimensions of electrodes, which is shown in **Figure 2**.

The results of calculations show that the shape of the voltage polarizing a flat voltammetric electrode influences its metrological properties. It has been proved that a flat electrode polarized by voltage with a triangular waveform variable component has the highest sensitivity when there are determined: an ion diffusion coefficient, steady rate of the reaction, equal parameters of the polarizing voltage, which is shown in **Figure 3**.
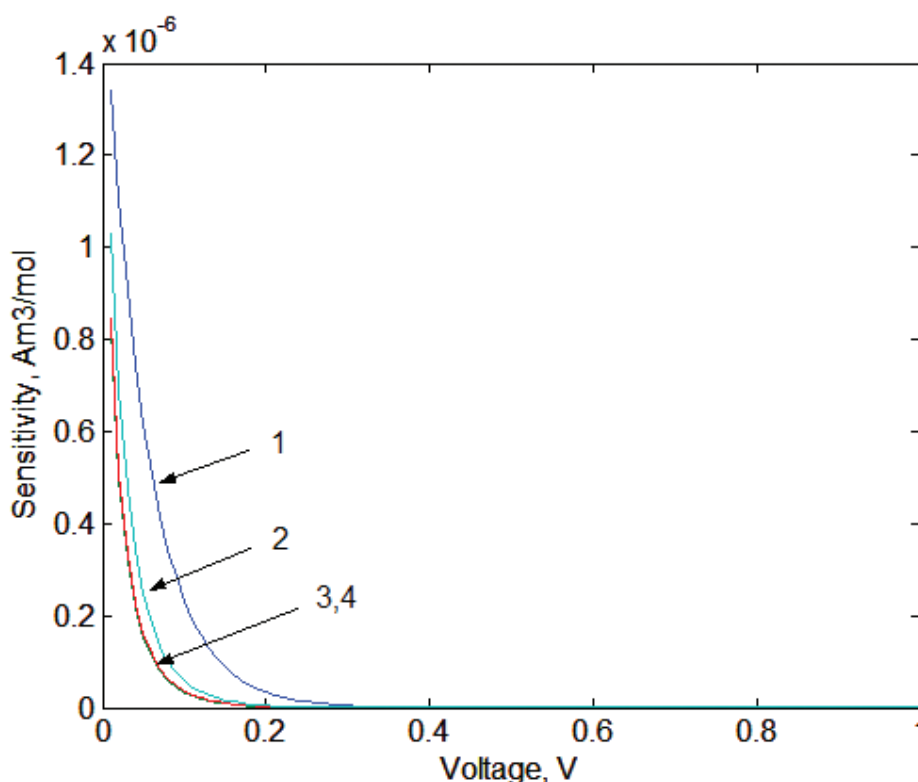

Figure 1. Influence of the shape on the sensitivity of an electrode; $E^0 = 0.50$ V; $D_i = 10^{-6}$ cm^2/s, $k_0 = 10^{-8}$ cm/s, $A = 1$ mm^2, $r = 0.5$ mm, $\rho = 0.5$ mm, $S_U = 0.025$ mV/s; The type of an electrode: (1) converter type 0; converter type I, (2) cylindrical, (3) spherical, (4) flat.
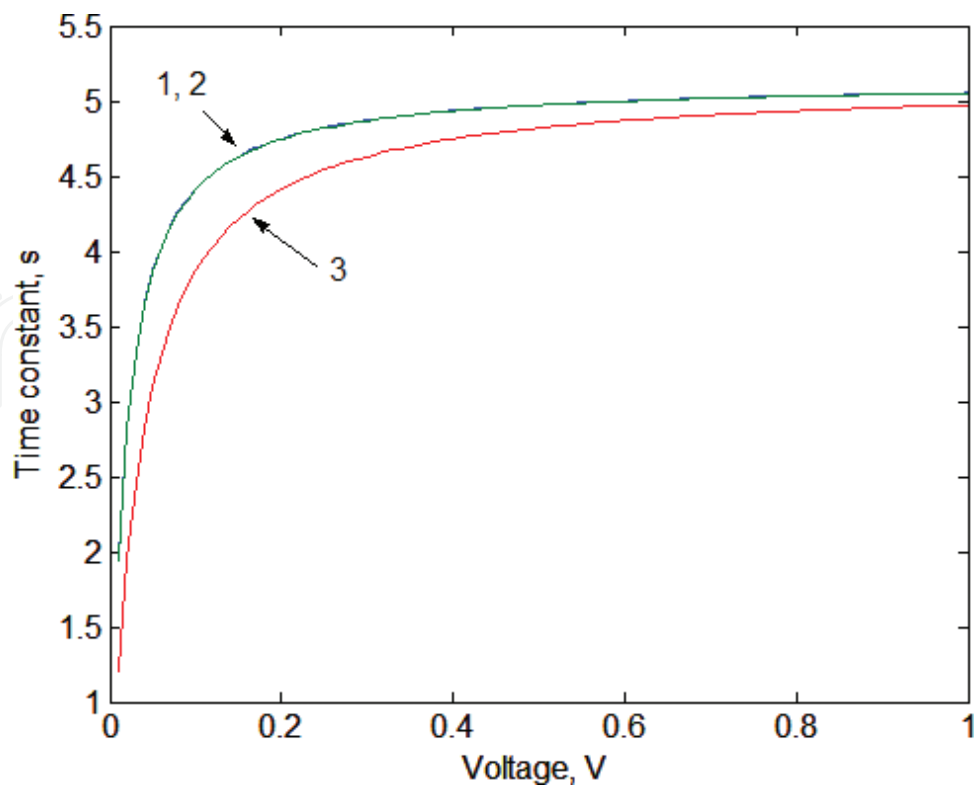
Figure 2. Influence of the shape on the time constant of an electrode; $D_i = 10^{-7} \text{cm}^2/\text{s}$, $r = 0.5$ mm, $\rho = 0.5$ mm, $S_U = 0.010$ mV/s; The type of an electrode: (1) flat, (2) spherical, (3) cylindrical.
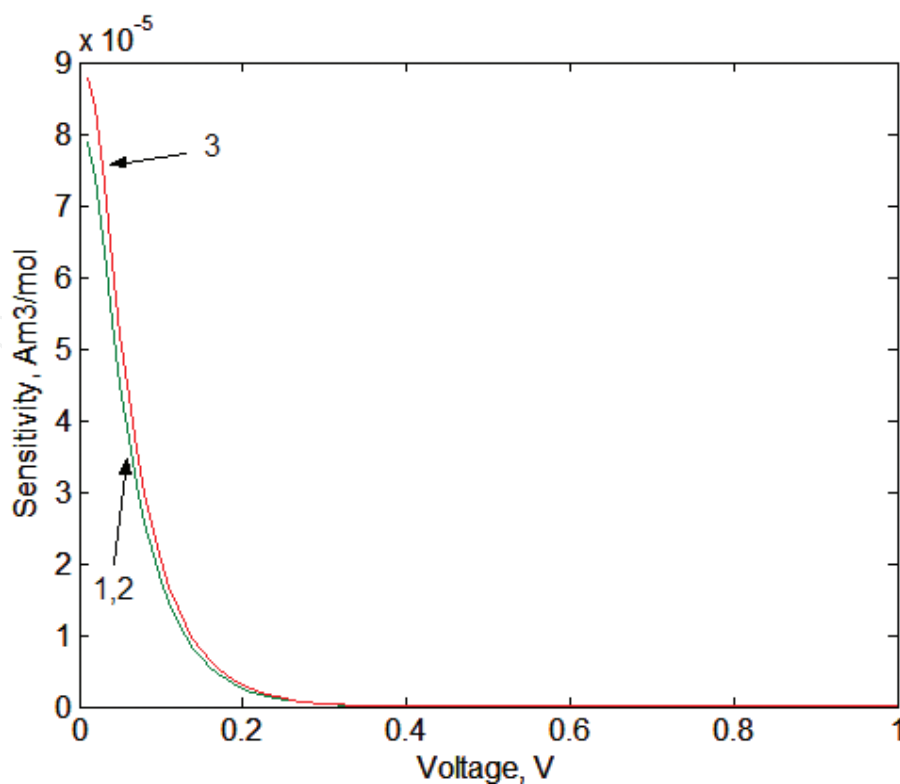

Figure 3. Influence of the shape of polarization voltage on the sensitivity of an electrode; $D_i = 10^{-7} \text{cm}^2/\text{s}$, $S_U = 0.010$ mV/s; $U_m = 5$ mV, $f = 1$ Hz; The type of polarization voltage: (1) direct voltage, (2) direct voltage with a sinusoidal component, (3) direct voltage with a triangular component.

The sensitivity of an electrode polarized with such a type of voltage is determined by the number of harmonics of the electrode's triangular waveform variable component. Including in calculations further, harmonics of this component increases the sensitivity of the electrode. The results of such calculations show that the sensitivity of a flat voltammetric electrode is also determined by the frequency of a polarizing voltage variable component. The increase of a frequency of sinusoidal and triangular waveform component voltage leads to the increase of a voltammetric electrode's sensitivity. The lower the rate of change of polarizing voltage static component the greater the increase of sensitivity. The amplitude of the polarizing voltage variable component influences the sensitivity of the electrode as well. The increase of this component's amplitude leads to the reduction of the electrode's sensitivity.

It was also proved that the time constant of a flat voltammetric electrode is determined by the shape of polarizing voltage. Results of these calculations revealed that the electrode polarized by voltage only with a static component has the highest time constant. The increase of the rate of changes in this voltage leads to the decrease of time constant of the electrode. A flat voltammetric electrode has the lowest time constant for voltage with a sinusoidal variable component when there are determined: rate of changes of the polarizing voltage static component and amplitude and frequency of the variable component, which is shown in **Figure 4**.

The increase of the variable component amplitude leads to the decrease of the voltammetric electrode time constant. Also an increase of a polarizing voltage variable component frequency leads to the decrease of the electrode's time constant. In the case when a flat electrode is polarized by voltage with a triangular waveform variable component including this electrode's individual
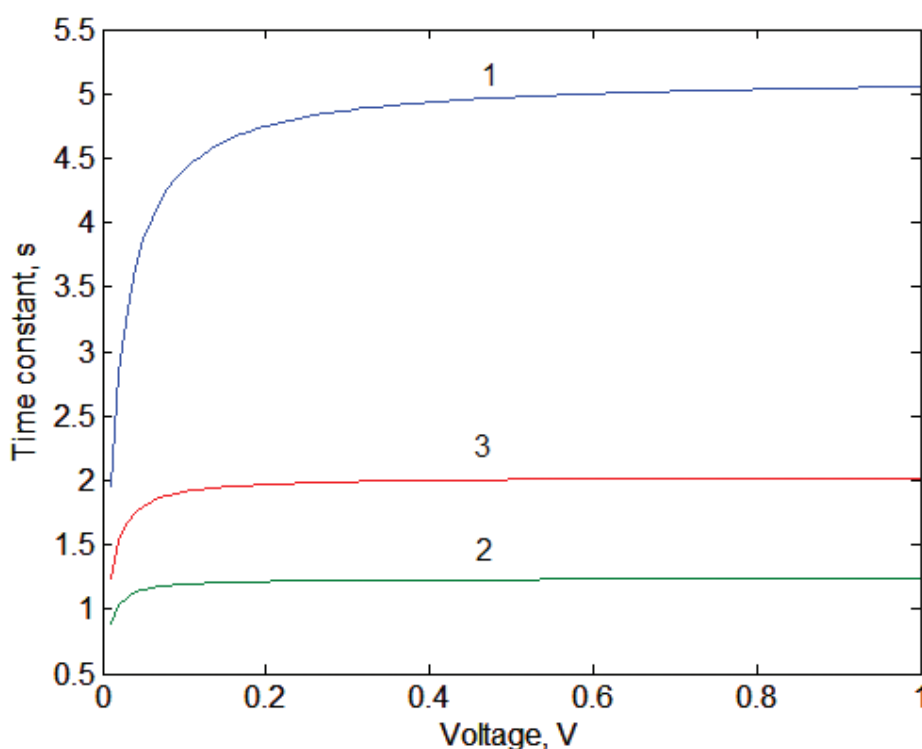

Figure 4. Influence of the shape on the time constant of a flat electrode; $D_i = 10^{-7}\,\mathrm{cm^2/s}$, $r = 0.5$ mm, $\rho = 0.5$ mm, $S_U = 0.010$ mV/s; $U_m = 5$ mV, $f = 1$ Hz. The type of polarization voltage: (1) direct voltage, (2) direct voltage with a sinusoidal component, (3) direct voltage with a triangular component.

harmonics leads to the decrease of the time constant. The electrode's time constant also decreases when the rate of gain of the electrode polarizing voltage static component increases.

6. Conclusions

Analyses conducted show that depending on the concentration of marked ion solution, the voltammetric electrode may function like a converter type 0 or type I. In the first case, its metrological properties in the time domain are determined solely by sensitivity, in the latter case by sensitivity and the time constant. Values of both parameters are determined by the type of marked ions in the analyzed solution, by the shape of the electrode and the shape of the polarizing voltage. Results of simulations conducted show that in the case of marking low ion concentrations, the cylindrical electrode has the best metrological properties. It is characterized by the highest sensitivity and the lowest time constant. It was also proved that the most beneficial metrological properties are the ones of a voltammetric electrode polarized by voltage with a static component and a sinusoidal variable component. The choice of the amplitude and the frequency of polarized voltage variable component may influence both sensitivity and the time constant of a voltammetric electrode used in markings. As a result of such activities metrological properties of a used measuring electrode may be shaped in an optional way. The ion concentration may be measured with a high sensitivity or low time constant. It will allow to match closer metrological properties of a voltammetric electrode to the expected nature of changes in marked ion concentration and as a consequence it leads to the decrease of static and dynamic errors of electrochemical markings conducted.

Major symbols

A	Surface area of electrode
$C_i^0(t)$	Bulk concentration of ions i at time t
$C_{i,0}(t)$	Surface concentration of ions i at the electrode surface at time t
$\frac{\partial C_i(x)}{\partial t}$	Gradient of concentration of ions i at time t at voltammetric electrode
$\nabla C_i(x)$	Concentration gradient of ions i at distance x
$\nabla C_i(x)$	Concentration gradient of ions i at distance x
$C_{i,\text{ox},0}(t)$	Concentration of oxidation ions i at the electrode surface at time t
$C_{i,\text{red},0}(t)$	Concentration of reduction ions i at the electrode surface at time t
D_i	Diffusion coefficient of ions i
E^0	Standard potential of an electrode
E_0	Initial potential
F	The Faraday constant
$i(t)$	Current
$i_{\text{ox}}(t)$	Anodic oxidation current
$i_{\text{red}}(t)$	Cathodic reduction current

$k_{i,\text{ox}}(t)$	Heterogeneous rate constant for oxidation
$k_{i,\text{red}}(t)$	Heterogeneous rate constant for reduction
k^0	Rate constant for a heterogeneous reaction
$\nabla N_i(t)$	Flux gradient of ions i
u_i	Mobility of ions i
z_i	Charge on ions i in signed units of electronic charge
S_U	Linear potential scan rate
t	Time
T	Absolute temperature
U_m	Amplitude of a sinusoidal component
$U_t(t)$	Amplitude of a triangle component
∇U	Potential gradient
V_i	Velocity of ions i
α	Transfer coefficient
ω	Angular frequency of rotation
$\delta_i(t)$	Diffusion layer thickness for ions i at the electrode surface at time t
$\delta_{i,\text{ox}}(t)$	Diffusion layer thickness for oxidation ions i at the electrode surface at time t
$\delta_{i,\text{red}}(t)$	Diffusion layer thickness for reduction ions i at the electrode surface at time t

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