

# Quasi Reversible Electrochemical Reaction and Metrological Properties in the Time Domain of Flat Voltammetric Electrodes

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## -----ABSTRACT-----

Metrological properties of a flat voltammetric electrode on whose surface a quasi-reversible electrochemical reaction takes place were being analyzed in this paper. The conducted analysis showed that such an electrode functions like a measuring converter type I. Its metrological properties in the time domain are defined by sensitivity and a time constant. Results of the simulations proved that these parameters depend on values of indicated ions, a voltammetric electrode construction and parameters of the polarizing voltage.

**KEYWORDS** - voltammetric electrodes, voltammetric measurements, quasi-reversible electrochemical reaction, metrological properties of voltammetric electrodes

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## I. INTRODUCTION

Voltammetric measurements are some of the most frequently conducted measurements that are to determine the condition of the environment [1-4]. The condition is often determined by the level of heavy-metal pollution of an aquatic environment [5-11]. A series of measurements of the ion concentration in water reservoirs is conducted. Not always these measurements are based on liquid samples collected earlier. Due to their growing popularity measuring systems Lab-on chip are conducted in situ [12-14]. During the measurements the metal concentration is being determined in the examined reservoir. It is quite frequent that the measurements are being conducted while the examined liquid is flowing or when the indicated ion concentration is changing. That is when questions appear about the metrological properties of the voltammetric electrode used in these measurements and about the influence of the quasi reversibility of the electrochemical reaction taking place on the surface of the voltammetric electrode used [15-16].

## II. THEORY

Usually voltammetric measurements are conducted when the indicated ion concentration is not high. Then the electrochemical reaction is controlled by the process of the ion transport and their flux to the surface is defined by the relationship [17]:

(1)

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

where:  $D_i$  is a diffusion coefficient of ions,

$C_i, \nabla C_i$ , is a concentration of ions, a concentration gradient of ions,

$u_i$  is a mobility of ions,

$z_i$  is a valence of ions,

$F$  is the Faraday constant,

$V_i$  is a velocity of the convection rate of ions,

$\nabla U$  is a gradient of the electric field potential.

Distribution of ion concentration  $C_i$  in the solution volume in the function of time  $t$ , is defined by the flux divergence  $N_i(t)$  hence [17]:

(2)

$$\frac{\partial C_i(t)}{\partial t} = -\nabla N_i(t) + R_i,$$

where:  $R_i$  is a rate of a chemical reaction taking place in the volume of examined solution, what in the case of concentrated bulk electrolyte presence, measurements with a steady voltammetric electrode and ions not taking part in the sequential chemical reaction,  $R_i = 0$ , leads us to the relationship [17]:

$$(3) \quad \frac{\partial C_i(t)}{\partial t} = D_i \nabla^2 C_i(t).$$

The analysis of metrological properties of a voltammetric electrode was conducted with the assumption that input signal is the concentration  $C_i^0(t)$  of indicated ions in the volume of the examined electrolyte and the output signal is the current  $i_i(t)$  of the electrochemical reaction taking place on the surface of the voltammetric electrode.

## II. I QUASI-REVERSIBLE ELECTROCHEMICAL REACTION

In the case when on the surface of the flat voltammetric electrode a quasi-reversible electrochemical reaction takes place, ion transport to the surface of the electrode is defined by the relationship (3), and their flux can be presented as [17]:

$$(4) \quad D_{i,ox} \frac{\partial C_{i,ox,0}(t)}{\partial x} = k_{i,ox}(t) C_{i,ox,0}(t) - k_{i,red}(t) C_{i,red,0}(t),$$

$$(5) \quad D_{i,red} \frac{\partial C_{i,red,0}(t)}{\partial x} = k_{i,ox}(t) C_{i,ox,0}(t) - k_{i,red}(t) C_{i,red,0}(t),$$

where:  $D_{i,ox}$  is a diffusion coefficient of oxidized ions,

$D_{i,red}$  is a diffusion coefficient of reduced ions,

$C_{i,ox,0}(t)$  is a concentration of oxidized ions on the electrode surface,

$C_{i,red,0}(t)$  is a concentration of reduced ions on the electrode surface,

$k_{i,ox}(t)$  is a heterogeneous rate constant for oxidation,

$k_{i,red}(t)$  is a heterogeneous rate constant for reduction.

Keeping in mind the expanding of the derivative of the concentration on the surface of the electrode in a Taylor series [18]:

$$(6) \quad \frac{\partial C_{i,0}(t)}{\partial x} = \frac{C_i^0(t) - C_0(t)}{\delta_i(t)} - \frac{\delta_i(t)}{2} \frac{\partial^2 C_{i,0}(t)}{\partial x^2} - \frac{\delta_i^2(t)}{6} \frac{\partial^3 C_{i,0}(t)}{\partial x^3},$$

where:  $\delta_i(t)$  is a diffusion layer thickness,

$C_{i,0}(t)$  is a concentration of ions on the electrode surface,

$C_i^0(t)$  is a concentration of ions in the volume of the solution,

relationships (4) and (5) can be presented as:

$$(7)$$

$$D_{i,ox} \left[ \frac{C_{i,ox}^0(t) - C_{i,ox,0}(t)}{\delta_{i,ox}(t)} - \frac{\delta_{i,ox}(t)}{2} \frac{\partial^2 C_{i,ox,0}(t)}{\partial x^2} - \frac{\delta_{i,ox}^2(t)}{6} \frac{\partial^3 C_{i,ox,0}(t)}{\partial x^3} \right] = k_{i,ox}(t) C_{i,ox,0}(t) - k_{i,red}(t) C_{i,red,0}(t), \quad (8)$$

$$D_{i,red} \left[ \frac{C_{i,red}^0(t) - C_{i,red,0}(t)}{\delta_{i,red}(t)} - \frac{\delta_{i,red}(t)}{2} \frac{\partial^2 C_{i,red,0}(t)}{\partial x^2} - \frac{\delta_{i,red}^2(t)}{6} \frac{\partial^3 C_{i,red,0}(t)}{\partial x^3} \right] = k_{i,ox}(t) C_{i,ox,0}(t) - k_{i,red}(t) C_{i,red,0}(t).$$

Transforming the ion transport equation (3) to this form:

$$\frac{\partial^2 C_{i,0}(t)}{\partial x^2} = \frac{1}{D_i} \frac{\partial C_{i,0}(t)}{\partial t}, \quad (9)$$

and noting:

$$\frac{\partial^3 C_{i,0}(t)}{\partial x^3} = \frac{\partial}{\partial x} \left[ \frac{\partial^2 C_{i,0}(t)}{\partial x^2} \right] = \frac{\partial}{\partial x} \left[ \frac{1}{D_i} \frac{\partial C_{i,0}(t)}{\partial t} \right] = \frac{1}{\delta_i(t) D_i} \frac{\partial C_{i,0}(t)}{\partial t}, \quad (10)$$

and substituting with it relationships (7) and (8) we obtain:

$$D_{i,ox} \left[ \frac{C_{i,ox}^0(t) - C_{i,ox,0}(t)}{\delta_{i,ox}(t)} - \frac{\delta_{i,ox}(t)}{2} \frac{\partial^2 C_{i,ox,0}(t)}{\partial x^2} - \frac{\delta_{i,ox}^2(t)}{6} \frac{\partial^3 C_{i,ox,0}(t)}{\partial x^3} \right] = k_{i,ox}(t) C_{i,ox,0}(t) - k_{i,red}(t) C_{i,red,0}(t), \quad (11)$$

$$D_{i,red} \left[ \frac{C_{i,red}^0(t) - C_{i,red,0}(t)}{\delta_{i,red}(t)} - \frac{\delta_{i,red}(t)}{2} \frac{\partial^2 C_{i,red,0}(t)}{\partial x^2} - \frac{\delta_{i,red}^2(t)}{6} \frac{\partial^3 C_{i,red,0}(t)}{\partial x^3} \right] = k_{i,ox}(t) C_{i,ox,0}(t) - k_{i,red}(t) C_{i,red,0}(t), \quad (12)$$

which after rearranging results in:

$$-\frac{2\delta_{i,ox}(t)}{3} \frac{\partial C_{i,ox,0}(t)}{\partial t} - \frac{D_{i,ox} C_{i,ox,0}(t)}{\delta_{i,ox}(t)} - k_{i,ox}(t) C_{i,ox,0}(t) = -\frac{D_{i,ox} C_{i,ox}^0(t)}{\delta_{i,ox}(t)} - k_{i,red}(t) C_{i,red,0}(t), \quad (13)$$

$$-\frac{2\delta_{i,red}(t)}{3} \frac{\partial C_{i,red,0}(t)}{\partial t} - \frac{D_{i,red} C_{i,red,0}(t)}{\delta_{i,red}(t)} + k_{i,red}(t) C_{i,red,0}(t) = -\frac{D_{i,red} C_{i,red}^0(t)}{\delta_{i,red}(t)} + k_{i,ox}(t) C_{i,ox,0}(t). \quad (14)$$

The current in the electrochemical reaction on the surface of the voltammetric electrode is its output signal. A value of this current is defined by the Butler-Volmer equation [17]:

$$i_i(t) = z_i F A [k_{i,ox}(t) C_{i,ox,0}(t) - k_{i,red}(t) C_{i,red,0}(t)] = i_{i,ox}(t) - i_{i,red}(t), \quad (15)$$

where:  $z_i$  is a valence of ions,

$F$  is the Faraday constant,

$A$  is a surface area of voltammetric electrode,

$i_{i,ox}(t)$  is a oxidized current component,

$i_{i,red}(t)$  is a reduced current component.

The coefficients of the reaction rate  $k_{i,ox}(t)$  and  $k_{i,red}(t)$  are defined by following relationships [17]:

(16)

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

(17)

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

where:  $k^0$  is a standard heterogeneous rate constant,

$\alpha$  is a transfer coefficient,

$R$  is the gas constant,

$T$  is an absolute temperature,

$E_{pol}(t)$  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 linear sweep voltammetry to mark ion concentration, a flat electrode is polarized with a voltage defined as:

(18)

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

where:  $E_0$  is an initial voltage of voltammetric electrode polarization,

$S_U$  is a rate of static voltage increase,

$t$  is time.

In the case of the oxidizing reaction the voltage polarizing the voltammetric electrode has the value:

(19)

$$E_{pol}(t) = E_0 + S_U t,$$

which leads to:

(20)

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

And in the case of the reduction reaction the voltammetric electrode is polarized by this voltage:

(21)

$$E_{pol}(t) = E_k - S_U t,$$

where:  $E_k$  is a cut-off voltage of the voltammetric electrode polarization, hence one obtains:

(22)

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

Assuming that on the surface of the voltammetric electrode there is running only reduction or oxidation reaction, relationship (15) can be presented in the general form as:

(23)

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

we get from here:

(24)

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

and

$$(25) \quad \frac{\partial i_i(t)}{\partial t} = z_i F A C_{i,0}(t) \frac{\partial k_i(t)}{\partial t} + z_i F A k_i(t) \frac{\partial C_{i,0}(t)}{\partial t},$$

which, as a consequence, results in:

$$(26) \quad \frac{\partial C_{i,0}(t)}{\partial t} = \frac{1}{z_i F A k_i(t)} \left[ \frac{\partial i_i(t)}{\partial t} - z_i F A C_{i,0}(t) \frac{\partial k_i(t)}{\partial t} \right],$$

where:  $k_i(t)$  is a heterogeneous rate constant,

$i_i(t)$  is an electrochemical reaction current.

Keeping in mind relationships (24) we obtain:

$$(27) \quad C_{i,ox,0}(t) = \frac{i_{i,ox}(t)}{z_i F A k_{i,ox}(t)},$$

(28)

$$C_{i,red,0}(t) = \frac{i_{i,red}(t)}{z_i F A k_{i,red}(t)},$$

and as a consequence:

$$(29) \quad \frac{\partial C_{i,ox,0}(t)}{\partial t} = \frac{1}{z_i F A k_{i,ox}(t)} \frac{\partial i_{i,ox}(t)}{\partial t} + \frac{\alpha z_i F}{RT} S_U C_{i,ox,0}(t),$$

(30)

$$\frac{\partial C_{i,red,0}(t)}{\partial t} = \frac{1}{z_i F A k_{i,red}(t)} \frac{\partial i_{i,red}(t)}{\partial t} + \frac{(1-\alpha) z_i F}{RT} S_U C_{i,red,0}(t).$$

In such a case we can present the relationship (3) for the quasi-reversible electrochemical reaction taking place on the surface of the flat voltammetric electrode in the following form:

$$(31) \quad \frac{2\delta_{i,ox}(t)}{3} \frac{\partial i_{i,ox}(t)}{\partial t} + \left[ \frac{D_{i,ox}}{\delta_{i,ox}(t)} + k_{i,ox}(t) + \frac{2\delta_{i,ox}(t)\alpha z_i F S_U}{3RT} \right] i_{i,ox}(t) = \frac{z_i F A k_{i,ox}(t) D_{i,ox}}{\delta_{i,ox}(t)} \left[ C_{i,ox}^0(t) + \frac{k_{i,red}(t)\delta_{i,ox}(t)C_{i,red,0}(t)}{z_i F A k_{i,ox}(t) D_{i,ox}} \right],$$

(32)

$$\frac{2\delta_{i,red}(t)}{3} \frac{\partial i_{i,red}(t)}{\partial t} + \left[ \frac{D_{i,red}}{\delta_{i,red}(t)} - k_{i,red}(t) + \frac{2\delta_{i,red}(t)(1-\alpha) z_i F S_U}{3RT} \right] i_{i,red}(t) = \frac{z_i F A k_{i,red}(t) D_{i,red}}{\delta_{i,red}(t)} \left[ C_{i,red}^0(t) - \frac{k_{i,ox}(t)\delta_{i,red}(t)C_{i,ox,0}(t)}{z_i F A k_{i,red}(t) D_{i,red}} \right].$$

Relationships (31) and (32) defining the behaviour of a flat voltammetric electrode in the transient state, that is in the moment of a concentration change in the volume of analyzed solution, can be presented also in the following form:

(33)

$$A_{1,i}(t) \frac{\partial y_i(t)}{\partial t} + A_{0,i}(t) y_i(t) = B_{0,i}(t) x_i'(t),$$

where:  $y_i(t)$  is an output signal,

$x_i'(t)$  is a modified input signal,

$A_{1,i}(t), A_{0,i}(t), B_{0,i}(t)$  are equation coefficients defined by the converter construction and depending on time.

From the above equation one can see that a flat voltammetric electrode with a quasi-reversible electrochemical reaction on its surface functions like a converter type I, where the concentration of indicated ions in the analyzed solution volume is the input signal  $x_i(t)$  and the concentration of these ions on the surface of the voltammetric electrode is the output signal  $y_i(t)$ . Their metrological properties in the time domain are defined by: sensitivity

$S_i(t)$  and the time constant  $N_{T,i}(t)$ . The values of these parameters are defined as follows:

(34)

$$S_i(t) = \frac{B_{0,i}(t)}{A_{0,i}(t)},$$

(35)

$$N_{T,i}(t) = \frac{A_{1,i}(t)}{A_{0,i}(t)}.$$

The coefficients of the relationship (33) are different for oxidation and reduction reactions and are respectively:

(36)

$$A_{1,i,ox}(t) = \frac{2}{3} \delta_{i,ox}(t),$$

(37)

$$A_{0,i,ox}(t) = \frac{D_{i,ox}}{\delta_{i,ox}(t)} + k_{i,ox}(t) + \frac{2\delta_{i,ox}(t)\alpha z_i F S_U}{3RT},$$

(38)

$$B_{0,i,ox}(t) = \frac{z_i F A k_{i,ox}(t) D_{i,ox}}{\delta_{i,ox}(t)},$$

(39)

$$x_{i,ox}'(t) = \left[ C_{i,ox}^0(t) + \frac{k_{i,red}(t)\delta_{i,ox}(t)C_{i,red,0}(t)}{z_i F A k_{i,ox}(t) D_{i,ox}} \right],$$

(40)

$$x_{i,ox}(t) = C_{i,ox}^0(t),$$

(41)

$$y_{i,ox}(t) = i_{i,ox}(t),$$

(42)

$$A_{1,i,red}(t) = \frac{2}{3} \delta_{i,red}(t),$$

(43)

$$A_{0,i,red}(t) = \frac{D_{i,red}}{\delta_{i,red}(t)} - k_{i,red}(t) + \frac{2\delta_{i,red}(t)(1-\alpha)z_i F S_U}{3RT},$$

(44)

$$B_{0,i,red}(t) = \frac{z_i F A k_{i,red}(t) D_{i,red}}{\delta_{i,red}(t)},$$

(45)

$$x'_{i,red}(t) = \left[ C_{i,red}^0(t) - \frac{k_{i,ox}(t)\delta_{i,red}(t)C_{i,ox,0}(t)}{z_i F A k_{i,red}(t) D_{i,red}} \right],$$

(46)

$$x_{i,red}(t) = C_{i,red}^0(t),$$

(47)

$$y_{i,red}(t) = i_{i,red}(t).$$

Keeping in mind the relationships (34)-(47) we can determine the values of the metrological properties of the voltamperometric electrode, which are respectively:

(48)

$$S_{i,ox}(t) = \frac{B_{0,i,ox}(t)}{A_{0,i,ox}(t)} = \frac{3z_i F A k_{i,ox}(t) D_{i,ox} RT}{3D_{i,ox} RT + 3k_{i,ox}(t)\delta_{i,ox}(t) RT + 2\delta_{i,ox}^2(t)\alpha z_i F S_U},$$

(49)

$$S_{i,red}(t) = \frac{B_{0,i,red}(t)}{A_{0,i,red}(t)} = \frac{3z_i F A k_{i,red}(t) D_{i,red} RT}{3D_{i,red} RT - 3k_{i,red}(t)\delta_{i,red}(t) RT + 2\delta_{i,red}^2(t)(1-\alpha)z_i F S_U},$$

(50)

$$N_{T,i,ox}(t) = \frac{A_{1,i,ox}(t)}{A_{0,i,ox}(t)} = \frac{2\delta_{i,ox}^2(t) RT}{3D_{i,ox} RT + 3k_{i,ox}(t)\delta_{i,ox}(t) RT + 2\delta_{i,ox}^2(t)\alpha z_i F S_U},$$

(51)

$$N_{T,i,red}(t) = \frac{A_{1,i,red}(t)}{A_{0,i,red}(t)} = \frac{2\delta_{i,red}^2(t) RT}{3D_{i,red} RT - 3k_{i,red}(t)\delta_{i,red}(t) RT + 2\delta_{i,red}^2(t)(1-\alpha)z_i F S_U}.$$

From all presented relationships it can be seen that in the case of a quasi-reversible electrochemical reaction, the parameters that define metrological properties of a voltammetric electrode are determined by the values describing indicated ions – their valence, diffusion coefficient and parameters defining this electrode construction – they are also determined by the area, the thickness of the diffusion layer and as well by the rate of the electrochemical reaction taking place on the surface of the electrode, and that is indirectly by the voltage polarizing the electrode.

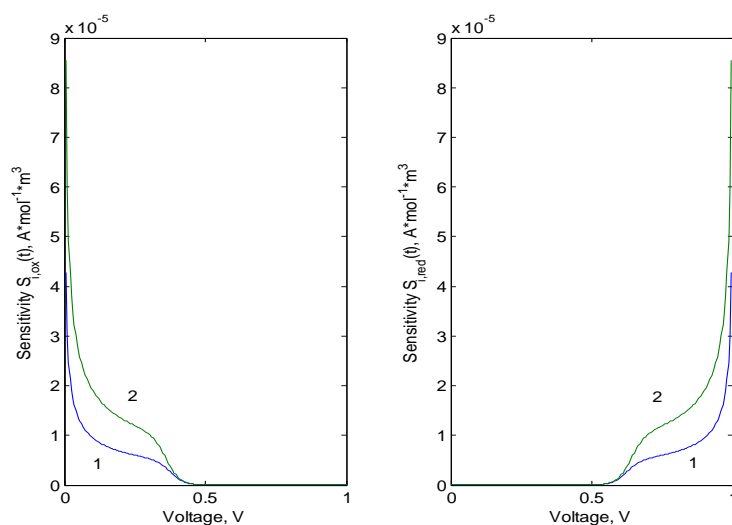
### III. RESULTS AND DISCUSSION

Numeric simulations were conducted in order to determine the influence of quasi-reversible electrochemical reaction taking place on the surface of a flat voltammetric electrode on its sensitivity  $S_i(t)$  and on the time constant  $N_{T,i}(t)$ . The influence of the valence and the indicated ion diffusion coefficient, the standard heterogeneous rate constant  $k^0$ , the layer thickness around the electrode  $\delta_i(t)$ , standard potential  $E^0$ , increase rate  $S_U$  of the polarizing voltage  $E_{pol}(t)$  on sensitivity  $S_i(t)$  and the time constant  $N_{T,i}(t)$  of the electrode was analyzed.

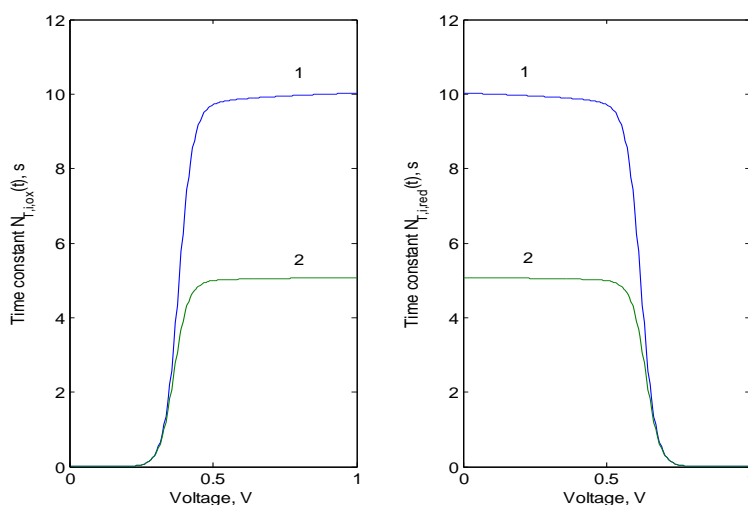
It has been assumed that a flat voltammetric electrode of 1 mm diameter is polarized with direct current with a value increasing linearly within the range from 0 V to 1 V and from 1 V to 0 V with the rate  $S_U$  changing within the range from 1 to 100 mV/s. It has also been assumed that the standard potential  $E^0$  has values within the

range from 0.25 V to 1.0 V, and the value of the indicated ion diffusion coefficient  $D_i$  is  $D_i = 10^{-5}, 10^{-6}, 10^{-7} \text{ cm}^2/s$ , and the standard heterogeneous rate constant is  $k^0 = 10^{-5}, 10^{-6}, 10^{-7} \text{ cm/s}$

The results of conducted simulations showed that the indicated ion valence has a great influence on the sensitivity  $S_i(t)$  and the time constant  $N_{T,i}(t)$  of a flat voltammetric electrode. With other set values characterizing ions and with the set polarizing voltage of the electrode  $E_{pol}(t)$ , the increase of the indicated ion valence  $z_i$  leads to the increase of the electrode sensitivity  $S_i(t)$  and to the decrease of its time constant  $N_{T,i}(t)$ , which is presented in figures 1 and 2.



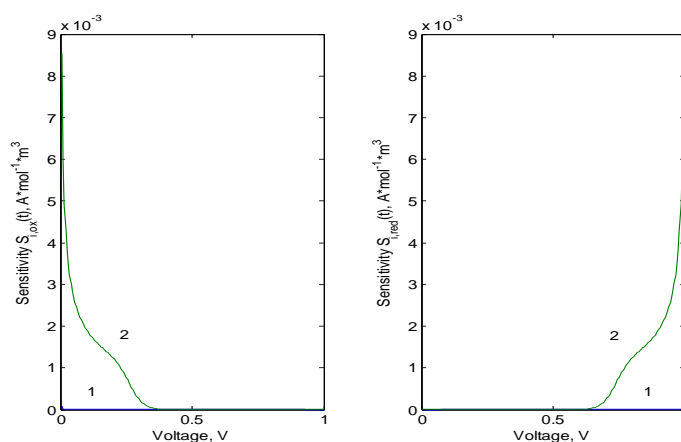
**Figure 1.** Influence of the valence  $z_i$  of ions on the sensitivity  $S_i(t)$  of flat voltammetric electrodes by a quasi-reversible reaction; the valence of ions: 1.  $z_i = 1$ ;  $z_i = 2$ ; the transfer coefficient  $\alpha = 0.5$ ; the diffusion coefficient of ions  $D_i = 10^{-6} \text{ cm}^2/s$ ; the standard heterogeneous rate constant  $k^0 = 10^{-6} \text{ cm/s}$ ; the rate of change of the polarization voltage  $S_U = 5 \text{ mV/s}$ ; the standard potential  $E^0 = 0.5 \text{ V}$ ;



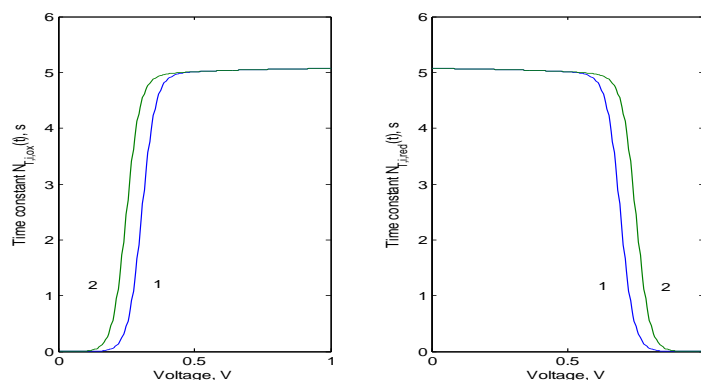


**Figure 2.** Influence of the valence  $z_i$  of ions on the time constant  $N_{T,i}(t)$  of flat voltammetric electrodes by a quasi-reversible reaction; the valence of ions: 1.  $z_i = 1$ ;  $z_i = 2$ ; the transfer coefficient  $\alpha = 0.5$ ; the diffusion coefficient of ions  $D_i = 10^{-6} \text{ cm}^2/\text{s}$ ; the standard heterogeneous rate constant  $k^0 = 10^{-6} \text{ cm/s}$ ; the rate of change of the polarization voltage  $S_U = 5 \text{ mV/s}$ ; the standard potential  $E^0 = 0.5 \text{ V}$ ;

Simulations conducted also prove that the indicated ion diffusion coefficient  $D_i$  has an influence on metrological properties of a flat voltammetric electrode. With other set values characterizing indicated ions and with the set polarizing voltage of the electrode  $E_{pol}(t)$  the increase of the indicated ion diffusion coefficient  $D_i$  leads to the increase of its sensitivity  $S_i(t)$  and to the decrease of the time constant  $N_{T,i}(t)$ , which is showed in figures 3 and 4.



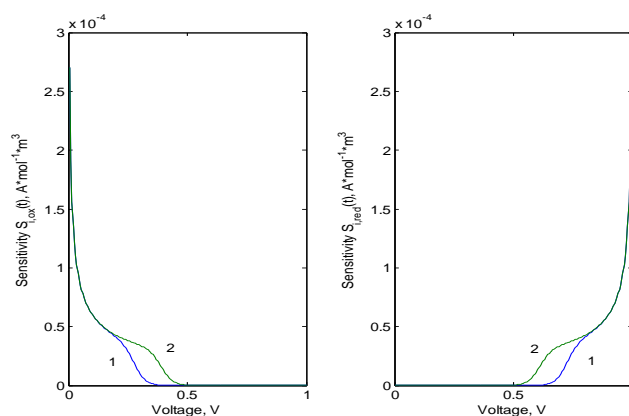
**Figure 3.** Influence of the diffusion coefficient  $D_i$  of ions on the sensitivity  $S_i(t)$  of flat voltammetric electrodes by a quasi-reversible reaction; the diffusion coefficient of ions: 1.  $D_i = 10^{-7} \text{ cm}^2/\text{s}$ ; 2.  $D_i = 10^{-5} \text{ cm}^2/\text{s}$ ; the transfer coefficient  $\alpha = 0.5$ ; the valence of ions  $z_i = 1$ ; the standard heterogeneous rate constant  $k^0 = 10^{-7} \text{ cm/s}$ ; the rate of change of the polarization voltage  $S_U = 5 \text{ mV/s}$ ; the standard potential  $E^0 = 0.5 \text{ V}$ ;



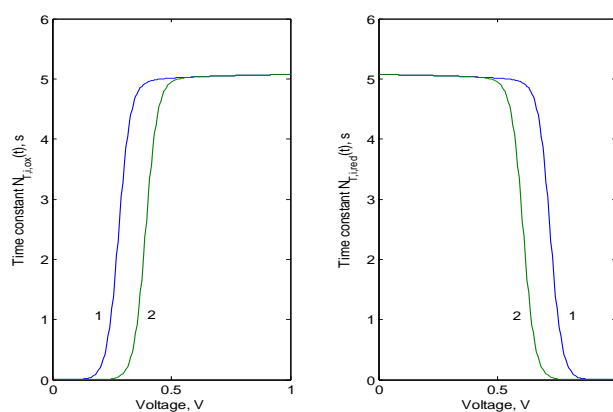
**Figure 4.** Influence of the diffusion coefficient  $D_i$  of ions on the time constant  $N_{T,i}(t)$  of flat voltammetric electrodes by a quasi-reversible reaction; the diffusion coefficient of ions: 1.  $D_i = 10^{-7} \text{ cm}^2/\text{s}$ ; 2.

$D_i = 10^{-5} \text{ cm}^2/\text{s}$ ; the transfer coefficient  $\alpha = 0.5$ ; the valence of ions  $z_i = 1$ ; the standard heterogeneous rate constant  $k^0 = 10^{-7} \text{ cm/s}$ ; the rate of change of the polarization voltage  $S_U = 5 \text{ mV/s}$ ; the standard potential  $E^0 = 0.5 \text{ V}$ ;

Moreover, it appeared that the standard heterogeneous rate constant  $k^0$  of the electrochemical reaction taking place on the surface of the voltammetric electrode has an influence on parameters defining metrological properties of this electrode. With set values characterizing indicated ions and with the set polarizing voltage of the electrode  $E_{pol}(t)$ , the increase of the standard heterogeneous rate constant  $k^0$  causes the increase of the sensitivity  $S_i(t)$  and the decrease of the time constant  $N_{T,i}(t)$ , which is presented in figures 5 and 6.



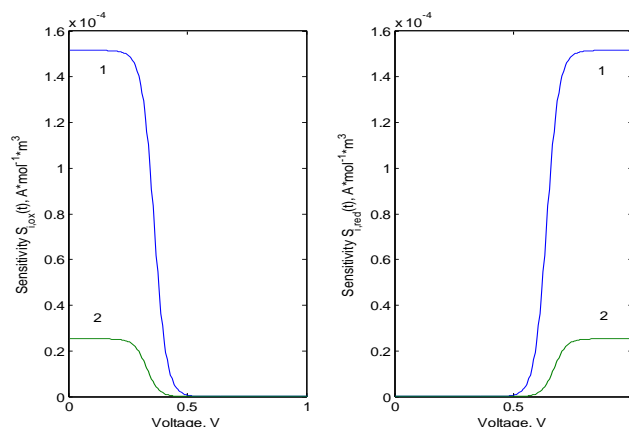
**Figure 5.** Influence of the standard heterogeneous rate constant  $k^0$  on the sensitivity  $S_i(t)$  of flat voltammetric electrodes by a quasi-reversible reaction; the standard heterogeneous rate constant: 1.  $k^0 = 10^{-7} \text{ cm/s}$ ; 2.  $k^0 = 10^{-5} \text{ cm/s}$ ; the diffusion coefficient of ions  $D_i = 10^{-5} \text{ cm}^2/\text{s}$ ; the transfer coefficient  $\alpha = 0.5$ ; the valence of ions  $z_i = 1$ ; the rate of change of the polarization voltage  $S_U = 5 \text{ mV/s}$ ; the standard potential  $E^0 = 0.5 \text{ V}$ ;



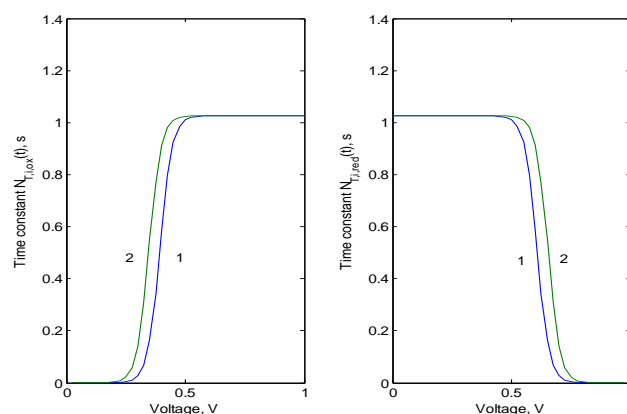
**Figure 6.** Influence of the standard heterogeneous rate constant  $k^0$  on the time constant  $N_{T,i}(t)$  of flat voltammetric electrodes by a quasi-reversible reaction; the standard heterogeneous rate constant: 1.  $k^0 = 10^{-7} \text{ cm/s}$ ; 2.  $k^0 = 10^{-5} \text{ cm/s}$ ; the diffusion coefficient of ions  $D_i = 10^{-5} \text{ cm}^2/\text{s}$ ; the transfer

coefficient  $\alpha = 0.5$ ; the valence of ions  $z_i = 1$ ; the rate of change of the polarization voltage  $S_U = 5 \text{ mV} / \text{s}$ ; the standard potential  $E^0 = 0.5 \text{ V}$ ;

Conducted simulations showed that metrological properties of a flat voltammetric electrode depend greatly on the diffusion layer thickness  $\delta_i(t)$  which appears near the surface of this electrode while the measurements are being made. With set values characterizing indicated ions and with the set voltage polarizing the electrode  $E_{pol}(t)$ , the increase of this layer thickness  $\delta_i(t)$  leads to the decrease of the electrode sensitivity  $S_i(t)$  and to the increase of its time constant  $N_{T,i}(t)$ , which is presented in figures 7 and 8.



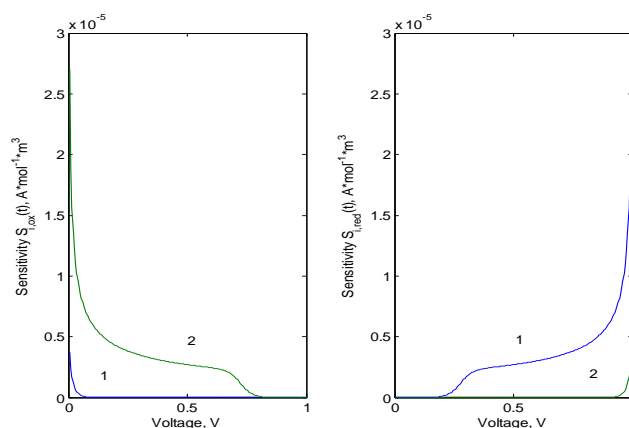
**Figure 7.** Influence of the thickness of diffusion layer  $\delta_i(t)$  on the sensitivity  $S_i(t)$  of flat voltammetric electrodes by a quasi-reversible reaction; the thickness of diffusion layer: 1.  $\delta_i(t) = 0.01 \text{ cm}$ , 2.  $\delta_i(t) = 0.06 \text{ cm}$ ; the transfer coefficient  $\alpha = 0.5$ ; diffusion coefficient of ions  $D_i = 10^{-7} \text{ cm}^2 / \text{s}$ ; the standard heterogeneous rate constant  $k^0 = 10^{-5} \text{ cm} / \text{s}$ ; the standard potential  $E^0 = 0.5 \text{ V}$ ; the rate of change of the polarization voltage  $S_U = 25 \text{ mV} / \text{s}$ ;



**Figure 8.** Influence of the thickness of diffusion layer  $\delta_i(t)$  on the time constant  $N_{T,i}(t)$  of flat voltammetric electrodes by a quasi-reversible reaction; the thickness of diffusion layer: 1.  $\delta_i(t) = 0.01 \text{ cm}$ , 2.  $\delta_i(t) = 0.06 \text{ cm}$ ; the transfer coefficient  $\alpha = 0.5$ ; diffusion coefficient of ions  $D_i = 10^{-7} \text{ cm}^2 / \text{s}$ ; the

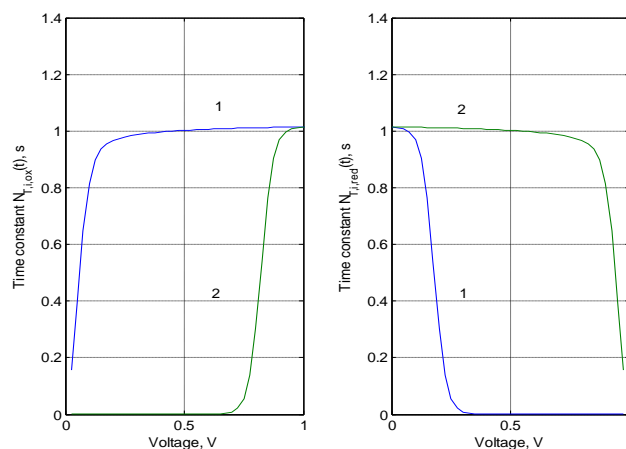
standard heterogeneous rate constant  $k^0 = 10^{-5} \text{ cm/s}$ ; the standard potential  $E^0 = 0.5 \text{ V}$ ; the rate of change of the polarization voltage  $S_U = 25 \text{ mV/s}$ ;

It also appeared that the flat voltammetric electrode sensitivity  $S_i(t)$  and its time constant  $N_{T,i}(t)$  depend on the standard potential  $E^0$ . With set values characterizing indicated ions and with the set polarizing voltage of the electrode  $E_{pol}(t)$ , the increase of the standard potential  $E^0$  causes the increase of this electrode sensitivity  $S_{i,ox}(t)$  for the oxidized form of indicated ions and the decrease of the sensitivity  $S_{i,red}(t)$  for the reduced form of ions. Examples of these simulations' results are presented in the figure 9.



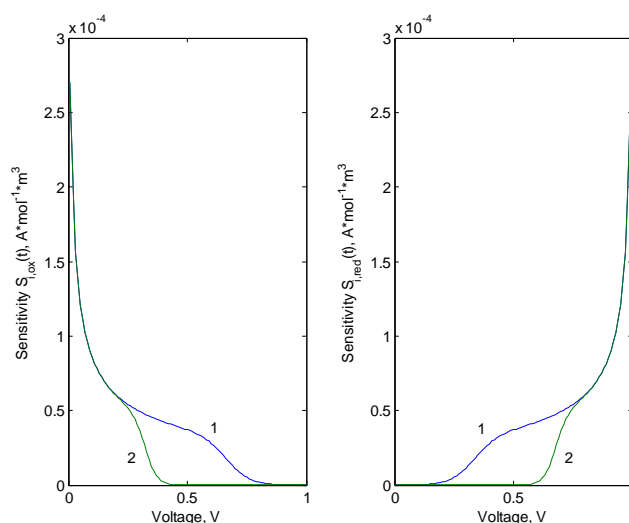
**Figure 9.** Influence of the standard potential  $E^0$  on the sensitivity  $S_i(t)$  of flat voltammetric electrodes by a quasi-reversible reaction; standard potential: 1.  $E^0 = 0.1 \text{ V}$ , 2.  $E^0 = 0.9 \text{ V}$ ; the transfer coefficient  $\alpha = 0.5$ ; diffusion coefficient of ions  $D_i = 10^{-7} \text{ cm}^2/\text{s}$ ; the standard heterogeneous rate constant  $k^0 = 10^{-7} \text{ cm/s}$ ; the rate of change of the polarization voltage:  $S_U = 5 \text{ mV/s}$ ;

The increase of the standard potential  $E^0$  causes the decrease of the time constant  $N_{T,i,ox}(t)$  of this electrode for the oxidized form of indicated ions and the increase of the time constant  $N_{T,i,red}(t)$  for the reduced form. Examples of these simulations results are presented in the figure 10.



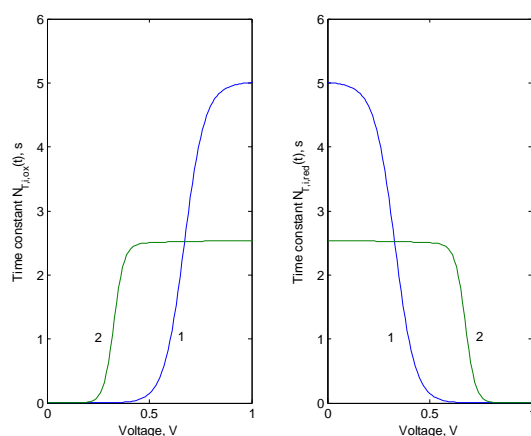
**Figure 10.** Influence of the standard potential  $E^0$  on the time constant  $N_{T,i}(t)$  of flat voltammetric electrodes by a quasi-reversible reaction; standard potential: 1.  $E^0 = 0.1 \text{ V}$ , 2.  $E^0 = 0.9 \text{ V}$ ; the transfer coefficient  $\alpha = 0.5$ ; diffusion coefficient of ions  $D_i = 10^{-7} \text{ cm}^2/\text{s}$ ; the standard heterogeneous rate constant  $k^0 = 10^{-7} \text{ cm/s}$ ; the rate of change of the polarization voltage:  $S_U = 5 \text{ mV/s}$ ;

Results of conducted measurements showed that the rate  $S_U$  of changes of the voltage  $E_{pol}(t)$  polarizing a flat voltammetric electrode also influences metrological properties of this electrode. The increase of the rate  $S_U$  of the polarizing voltage change, with set values characterizing indicated ions, cause a significant decrease of the electrode sensitivity  $S_i(t)$ , and that is presented in the figure 11.



**Figure 11.** Influence of the rate of change  $S_U$  of the polarization voltage  $E_{pol}(t)$  on the sensitivity  $S_i(t)$  of flat voltammetric electrodes by a quasi-reversible reaction; the rate of change of the polarization voltage: 1.  $S_U = 5 \text{ mV/s}$ , 2.  $S_U = 25 \text{ mV/s}$ ; the transfer coefficient  $\alpha = 0.5$ ; diffusion coefficient of ions  $D_i = 10^{-7} \text{ cm}^2/\text{s}$ ; the standard heterogeneous rate constant  $k^0 = 10^{-5} \text{ cm/s}$ ; the standard potential  $E^0 = 0.5 \text{ V}$ ;

The increase of the rate  $S_U$  causes the increase of the time constant  $N_{T,i}$  of the electrode in the range of lower polarizing voltages, however, the maximum value of the time constant decreases, and that is shown in the figure 12.



**Figure 12.** Influence of the rate of change  $S_U$  of the polarization voltage  $E_{pol}(t)$  on the time constant  $N_{T,i}(t)$  of flat voltammetric electrodes by a quasi-reversible reaction; the rate of change of the polarization voltage: 1.  $S_U = 5 \text{ mV/s}$ , 2.  $S_U = 25 \text{ mV/s}$ ; the transfer coefficient  $\alpha = 0.5$ ; diffusion coefficient of ions  $D_i = 10^{-7} \text{ cm}^2/\text{s}$ ; the standard heterogeneous rate constant  $k^0 = 10^{-5} \text{ cm/s}$ ; the standard potential  $E^0 = 0.5 \text{ V}$ ;

#### IV. CONCLUSION

Mathematical analyses and numerical simulations that were conducted proved that the flat voltammetric electrode, on whose surface a quasi-reversible electrochemical reaction controlled by a process of indicated ions diffusion transport takes place, functions like a measuring converter type I. Its metrological properties are defined by the sensitivity  $S_i(t)$  and the time constant  $N_{T,i}(t)$ .

Simulations' results showed that metrological properties of a flat voltammetric electrode depend on values characterizing indicated ions, values defining the quasi-reversible electrochemical reaction taking place on the surface of the electrode and they also depend on the voltage polarizing the electrode. It has been also observed that metrological properties of the voltammetric electrode can be improved by a choice of a proper construction, so it would provide the smallest width of the diffusion layer and as well by a selection of change rates of voltage polarizing the electrode.

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