Electrochimica Acta 130 (2014) 286–289

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Theory of square wave voltammetry of amalgam forming ions at spherical electrodes

Šebojka Komorsky-Lovrić, Dijana Jadreško, Milivoj Lovrić*

Department of marine and environmental research, "Ruđer Bošković" Institute, 10000 Zagreb, Hrvatska (Croatia)

ARTICLE INFO

Article history:
Received 4 February 2014
Received in revised form 4 March 2014
Accepted 4 March 2014
Available online 15 March 2014

Keywords:
Square wave voltammetry
Spherical electrodes
Theory
Microelectrode.

ABSTRACT

A theoretical model of reversible reduction of amalgam forming ion on stationary mercury drop electrode is developed for square wave voltammetry. The dependence of dimensionless net peak current on the dimensionless inverse electrode radius is investigated. This relationship is not linear, but it is a curve with two asymptotes. These results apply to electroanalytical measurements at spherical microelectrodes.

1. Introduction

A square wave voltammetry is electrochemical technique that is used for both kinetic and analytic measurements [1–5]. It can be applied either to the mercury drop electrode, or to solid electrodes [6,7]. If electrode reaction is fast and reversible and both the reactant and product are soluble in the electrolyte, the shape of the net response and its peak potential are independent of electrode geometry and size [8]. Under these conditions dimensionless net peak current on spherical electrode depends linearly on the inverse value of the product of electrode radius and square-root of frequency [9]. If this product is increased the linear diffusion prevails and the transient response is observed, but if the electrode radius and frequency are small the radial diffusion is the dominant mode of mass transport and the system tends to the steady-state [10,11]. As the consequence of latter the maximum and minimum of forward and backward components of the net response gradually vanish as the sphericity is increased and both components acquire the form of polarographic wave. If the frequency is high and hanging mercury drop electrode is used, the spherical effect is usually negligible, but the influence of the sphericity must be taken into consideration under most other conditions and generally at microelectrodes. At the inlaid micro disk electrode the described relationship is linear only if the radius is moderately small [12].

In this paper the dependence of net peak current and peak potential on the electrode radius and frequency is investigated for the reversible reduction of amalgam forming ions. In this reaction the diffusion within the mercury drop has to be considered [13,14].

2. The model

A reversible electrode reaction on mercury drop electrode is considered:

$$OX^{n+} + ne^- \rightleftarrows Red(Hg) \quad (1)$$

$$t = 0; \quad r \geq r_m: \quad C_{Ox} = C_{Ox}^*, \quad C_{Red} = 0 \quad (2)$$

$$0 \leq r < r_m: \quad C_{Ox} = 0, \quad C_{Red} = 0 \quad (3)$$

$$t > 0; \quad r \to \infty: \quad C_{Ox} \to C_{Ox}^* \quad (4)$$

$$r = r_m: \quad (C_{Ox})_{r=r_m} = (C_{Red})_{r=r_m} \exp(\varphi) \quad (5)$$

$$\varphi = \frac{nF}{RT}(E - E^0) \quad (6)$$

$$D\left(\frac{\partial c_{Ox}}{\partial r}\right)_{r=r_m} = -\frac{I}{nFS} \quad (7)$$

$$D\left(\frac{\partial c_{Red}}{\partial r}\right)_{r=r_m} = -\frac{I}{nFS} \quad (8)$$

$$r = 0: \quad \left(\frac{\partial c_{Red}}{\partial r}\right)_{r=0} = 0 \quad (9)$$

* Corresponding author.
E-mail address: mlovric@irb.hr (M. Lovrić).

http://dx.doi.org/10.1016/j.electacta.2014.03.023
0013-4686/

The meanings of symbols are the following: C_{Ox} and C_{Red} are concentrations of ions in the electrolyte and atoms in the mercury, respectively, C^*_{Ox} is the bulk concentration of ions, E is electrode potential, E^0 is standard potential of electrode reaction (1), D is a common diffusion coefficient, I is a current, n is a number of electrons, F is Faraday constant, S is the electrode surface area and r_m is the radius of mercury electrode.

The mass transport is calculated by the Feldberg approximation [15]:

$$\frac{\Delta c}{\Delta t} = D\left[\frac{A_i}{V_i}\left(\frac{\Delta c}{\Delta r}\right)_{i+1,i} - \frac{A_{i-1}}{V_i}\left(\frac{\Delta c}{\Delta r}\right)_{i,i-1}\right] \tag{10}$$

Where: $A_i = 4\pi r_i^2$, $A_{i-1} = 4\pi r_{i-1}^2$, $V_i = \frac{4}{3}\pi\left(r_i^3 - r_{i-1}^3\right)$, $r_i = i\Delta r$ and $r_m = m\Delta r$. Dimensionless concentrations are defined as $cox(k,i) = (C_{Ox})_{k,r_i}/C^*_{Ox}$ and $cred(k,i) = (C_{Red})_{k,r_i}/C^*_{Ox}$. Dimensionless current $w = I\Delta t\left(nFSc^*_{Ox}\Delta r\right)^{-1}$ is calculated by the following formulae:

$$w_k = 2d\left[cred(k,m)\exp(\varphi_k) - cox(k,m+1)\right]\left[1+\exp(\varphi_k)\right]^{-1} \tag{11}$$

$$cox(k+1,m+1) = cox(k,m+1)(1-3df_{m+1}) + 3df_{m+1}cox(k,m+2) + 3f_m w_k \tag{12}$$

$$\begin{matrix} i \geq m+2 \\ cox(k+1,i) = cox(k,i)[1-3d(f_i+f_{i-1})] + 3d[f_i cox(k,i+1) + f_{i-1}cox(k,i-1)] \end{matrix} \tag{13}$$

$$cred(k+1,1) = cred(k,1)(1-3d) + 3dcred(k,2) \tag{14}$$

$$\begin{matrix} 2 \leq i \leq m-1 \\ cred(k+1,i) = cred(k,i)[1-3d(f_i+f_{i-1})] \\ \quad +3d[f_i cred(k,i+1) + f_{i-1}cred(k,i-1)] \end{matrix} \tag{15}$$

$$cred(k+1,m) = cred(k,m)(1-3df_{m-1}) + 3df_{m-1}cred(k,m-1) - 3f_m w_k \tag{16}$$

$$d = D\Delta t\Delta r^{-2} \tag{17}$$

$$f_i = \left(i-(i-1)^3 i^{-2}\right)^{-1} \tag{18}$$

$$f_{i-1} = \left(i^3(i-1)^{-2} - i + 1\right)^{-1} \tag{19}$$

The results are reported as new dimensionless current $\Phi = I\left(nFSc^*_{Ox}\right)^{-1}(Df)^{-1/2}$. In square wave voltammetry the current is sampled at the end of each pulse and the difference between two subsequent samples is called the net response: $\Delta\Phi = \Phi_f - \Phi_b$. The forward, reductive (Φ_f) and the backward, oxidative (Φ_b) components of the net response are also reported as a function of the potential of staircase ramp.

The response depends on the pulse amplitude E_{sw}, the potential step dE and the inverse value of dimensionless electrode radius $\rho = r_m^{-1}\left(D/f\right)^{1/2}$. In the simulation each pulse is divided into 25 time increments and the dimensionless diffusion coefficient $d = 0.4$ was used. So, the parameter ρ depends on the number of space increments into which the electrode radius is divided: $\rho = \sqrt{20}/m$. In this paper only the parameter ρ is changed. Under its influence are both the dimensionless net current ($-\Delta\Phi = \Phi_{Ox} - \Phi_{Red}$) and the peak potential.

3. Results and discussion

Square wave voltammogram of electrode reaction (1) is shown in Fig. 1, for the inverse value of dimensionless electrode radius

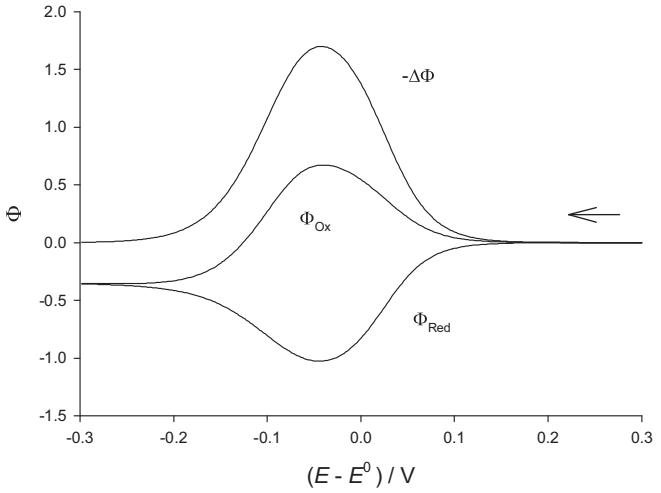

Fig. 1. A theoretical dimensionless square wave voltammogram of electrode reaction (1). A negative net response ($-\Delta\Phi$) and its forward (Φ_{Red}) and backward (Φ_{Ox}) components are shown. E_{st} = 0.3 V *vs.* E^0, E_{sw} = 0.050 V, dE = −0.002 V and ρ = 0.3.

ρ = 0.3. The net peak current is 1.6979 and the peak potential is -0.042 V *vs.* E^0. The minimum and maximum of the reductive and oxidative components of the response and the potentials of these extremes are the following: $\Phi_{Red,\min} = -1.0264$, $E_{p,Red}$ = −0.044 V, $\Phi_{Ox,\max}$ = 0.6723 and $E_{p,Ox}$ = −0.040 V. The limiting currents of both components tend to −ρ if $E \ll E^0$. The value of ρ may correspond to the following real parameters: $D = 9\times10^{-6}$ cm²/s, f = 100 Hz and r_m = 10 μm.

Fig. 2A shows the relationship between dimensionless net peak current and the parameter ρ. It is a curve with two asymptotes: $-\Delta\Phi_p$ = 4.4 ρ + 0.7383, for ρ < 0.1, and $-\Delta\Phi_p$ = 1.59 ρ + 1.21 for ρ > 0.2. The surface area of small spherical electrode is $S = 4r_m^2\pi$ and under the condition that ρ < 0.1 the real net peak currents depend on electrode radius and frequency as follows:

$$-\Delta I_p = 4\pi nFc^*_{Ox}r_m\sqrt{D}\left(0.7383r_m\sqrt{f} + 4.4\sqrt{D}\right) \tag{20}$$

If r_m = 0.05 cm and $D = 9\times10^{-6}$ cm²/s the second term in the brackets of Eq. (20) contributes less than 2% to the current if the frequency is higher than 320 Hz. Generally, the graphical representation of the relationship between $-\Delta I_p$ and $\sqrt{f}$ does not pass through the origin. This is particularly emphasized on hemispherical microelectrode with the surface area $S = 2r_m^2\pi$. At this electrode and for ρ > 0.2 the relationship between the real net peak current and the electrode radius and frequency is the following one:

$$-\Delta I_p = 2\pi nFc^*_{Ox}r_m\sqrt{D}\left(1.21r_m\sqrt{f} + 1.59\sqrt{D}\right) \tag{21}$$

If r_m = 10 μm and $D = 9\times10^{-6}$ cm²/s the terms in the brackets of Eq. (21) are mutually equal if f = 16 Hz. This means that in square-wave voltammetry the theoretical steady-state net peak current $-\Delta I_{p,ss} = 3.18\pi nFs^*_{Ox}r_m D$ cannot be achieved because of the semi-infinite diffusion in the solution and finite diffusion within the drop. The minima and maxima of the components of dimensionless theoretical response are also non-linear functions of the parameter ρ. These relationships can be approximated by the following asymptotes: $\Phi_{Red,\min} = -2.59\,\rho - 0.4397$, for ρ < 0.1, $\Phi_{Red,\min} = -1.16\,\rho - 0.69$, for ρ > 0.2, $\Phi_{Ox,\max} = 1.95\,\rho + 0.2993$, for ρ < 0.1, and $\Phi_{Ox,\max} = 0.43\,\rho + 0.54$ for ρ > 0.2.

The dependence of peak potential of the net response on the parameter ρ is shown in Fig. 2B. The straight lines in this figure are defined by the following equations: $E_p - E^0 = -0.2\rho$ (V), for ρ < 0.1, and $E_p - E^0 = -0.1\,\rho - 0.013$ (V) for ρ > 0.1. The potentials of minima and maxima of the components can be described by the