RESEARCH ARTICLE

Frumkin-melik-gaykazan model in the potentiodynamic and galvanodynamic regimes of functioning

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Abstract: The main purpose of this article is to study the behavior of a metallic electrode in the electrolyte which contains a surface-active substance with the property of adsorbtion-desorbtion, in the galvanodynamic and potentiodynamic rejimes. The study of the electrochemical behavior of a metallic electrode is carried out by operational impedance method, based on the Ohms low on the interaction between the Laplace-transformed expression of current, voltage and complex resistance (impedance). It is obtained the analytical expression of interface voltage-time dependence in a solution which contains a surface-active indifferent substance with the property of adsorbtion-desorbtion; also it is obtained the analytical expression of current density-time dependence which is passing through electrochemical cell in potentiodynamic regime of functioning of the Frumkin-Melik-Gaykazan model. It is established that the relation between the interface metallic electrode-indifferent electrolyte with property of adsorbtion-desorbtion voltage in the galvanodynamic rejime has the character of second order parabola; the relation between current density which is passing through a cell and time in potentiodynamic rejime of functioning in the Frumkin-Melik-Gaykazan model has exponential character.

Keywords: Frumkin Melik Gaykazan model, indifferent electrolyte, adsorbtion-desorbtion, potentiodynamic and galvanodynamic rejimes, current density, interface voltage

1 Introduction

In the case of adsorbtion of the electrochemical indifferent substance in the electrolyte which contains the surface-active component the electrode impedance was examined by Frumkin and Melik-Gaykazan in the works.[1–3] In the considered model electrode charge depend on not only the potential but also on amount of the absorbed ions or molecules which charges are interchanges with the metallic surface.

As to as regards faraday process it should be mean that in the appointed region of potentials the surface-active substance do not electrochemically oxidize or reduction on the electrode.[3] The amount of electricity, which is communicated to electrode, it is used up (spend up) on the charging of electric double layer.[1,2] Just (namely) such model of interface electrodeorganic electrolyte solution is obtained the name Frumkin-Melic-Gaykazan model.

The investigation of adsorbtion of organic substances on the metalles of the platinum group is begin intensive in connection with the problem of using organic substances as electrochemical fuel for the combustible elements.[4]

Namely this object (task) was the one of problem of the practical (applied) electrochemistry the basic main purpose of which was the application of the fuel galvanic elements in electro motor car.[1,2]

The equivalent electric circuit of Frumkin and Melik Gaykazan model for the first time was suggestion by Grafov B.M. and Ukshe E.A..[4](see Figure 1).
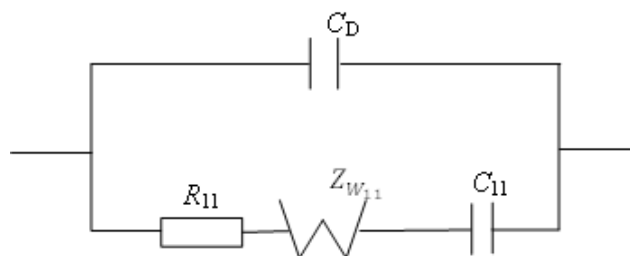

Figure 1. Equivalent electric circuit of Frumkin and Melik-Gaykazan model (scheme)

The structural elements on the Figure 1 are signified: R_{11} and C_{11} are the active resistance and supplementary capacity of the electric double layer which are connected

with the adsorption of the surface-active substances in a electrolyte; $Z_{W_{11}}$ is the diffusion impedance of Warburg; CD is the "veritable" (true) capacity of the electrode which is corresponds to constant value of adsorption.

In the works,[1,2] authors investigated the kinetic mechanism of adsorption of the organic substances on the metallic electrode in two limited cases of electrode processes: diffusion and adsorption. In the present work we make an attempt to analyze the behaviour of Frumkin and Melik Gaykazan model in the galvanodynamic and potentiodynamic rejimes of functioning of the electrochemical system.

2 Theoretical analysis

2.1 Galvanodynamic rejime

The operational impedance of the equivalent electric which is represented in Figure 1 may be exemplified in the form of relationship

$$Z\left(p\right) = R_{11} + \frac{W_{11}}{\sqrt{p}} + \frac{1}{p\left(C_A + C_{11}\right)} \qquad (1)$$

where Z_{W11} is diffusion constant of the Warburg; p is the complex variable. In the galvanodynamic rejime (in the method of linear current scan) $I(t)=I_0+\vartheta\,t$ (where I_0 is the initial current value, is the rate of linear current scan), then at $I_0 = 0$, the Laplace operator of function I(t) is $I\left(p\right) = \vartheta/p^2$.[5]

So far as $E(p) = I(p)\cdot Z(p)$, the following expression is obtained for the operator potential

$$E\left(p\right) = \frac{\vartheta}{p^2}\left[R_{11} + \frac{W_{11}}{\sqrt{p}} + \frac{1}{p\left(C_D + C_{11}\right)}\right] \qquad (2)$$

Using invers Laplace transform tables[6] we obtained the following expression for the potential

$$E\left(t\right) = \vartheta R_{11} t + \frac{\vartheta W_{11} \cdot 4 \cdot t^{3/2}}{1 \cdot 3 \cdot 5 \cdot 3\sqrt{\pi}} + \frac{\vartheta t^2}{\left(C_D + C_{11}\right) 2!} \qquad (3)$$

Potential *vs.* time dependence plotted according to equation (3) is shown in the Figure 2, which is plotted for the following parameters of equivalent circuit: $R_{11} = 5\,Ohm \cdot cm^2; W_{11} = 50\,Ohm \cdot cm^2 \cdot S^{(-1/2)}; C_D = C_{11} = 100 \cdot 10^{(-6)} F/cm^2; \vartheta = 5 \cdot 10^{(-6)} A/S.$

The basic deposit (contribution) to E t-dependence in the equation (3) introduced the third member.

As it is shown from the Figure 2 and as it is followed from the equation (3) potential-time dependence has the second order parabolic character. In that way the parabolic character of potential-time dependence may be
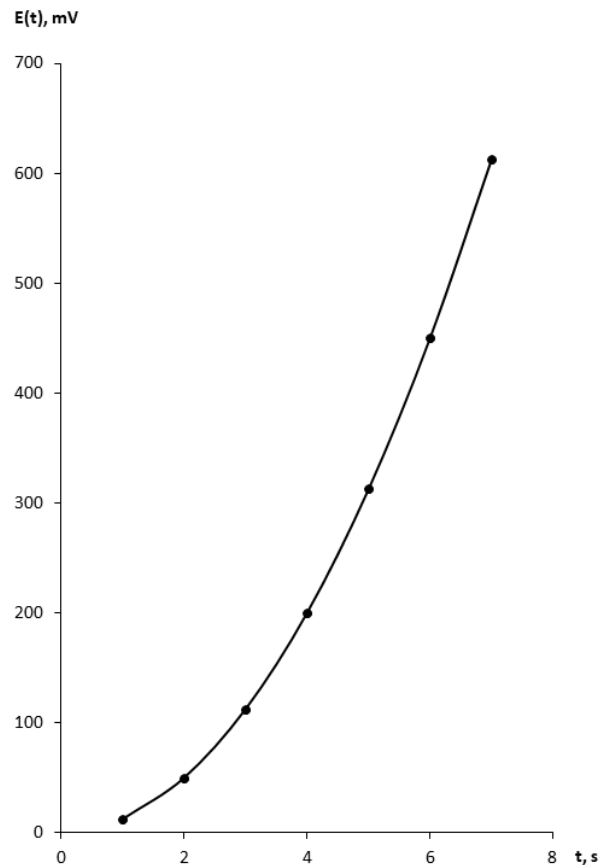

Figure 2. Potential *vs.* time dependence plotted according to equation (3) in the galvanodynamic rejime of functioning of the cell in the Frumkin and Melik-Gaykazan model

serve the evident proof of implementation of the equivalent electric scheme of Frumkin and Melik-Gaykazan model.

2.2 Potentiodynamic rejime

In the potentiodynamic rejime (in the method of linear potential scanning)$E\left(t\right) = E_0 + \vartheta t$ (where E_0 is the initial potential value and ϑ is its linear scan rate), then at $E_0 = 0$, the Laplace operator of function E(t) is $E\left(p\right) = \vartheta/p^2$. However, because $I\left(p\right) = E\left(p\right)/Z\left(p\right)$, then by substituting the values $E(p)$ and $Z(p)$ into the later expression, we obtained

$$I\left(p\right) = \frac{\vartheta a'}{p\left(p + \sqrt{p}c' + m\right)} \qquad (4)$$

The following designations are substituted into equation (4): $a = C_D + C_{11}$; $b = R_{11}\left(C_D + C_{11}\right)$; $c = W_{11}\left(C_D + C_{11}\right)$; $a' = a/b$; $c' = c/b$; $m = 1/b$.

Equation (4) can be expanded into the sum of partial

fractions

$$I\left(p\right) = \frac{\vartheta a'}{p\left(p + \sqrt{p}c' + m\right)}$$
$$= \frac{d_1}{p} + \frac{d_2}{\sqrt{p} + m_2} + \frac{d_3}{\sqrt{p} + m_1} \quad (5)$$

Where m_1 and m_2 are the roots (zero) of the characteristic square equation $p + \sqrt{p}c' + m = 0$, which are equal to m_1=-72,36; m_2=-27,64.

The values of roots of square equation are determined at the following magnitude of the parameters of the equivalent electric circuits: $W_{11} = 500\,\mathrm{Ohm}\cdot\mathrm{cm}^2\cdot\mathrm{s}^{-1/2}$; $R_{11} = 5\ \mathrm{Ohm}\cdot\mathrm{cm}^2$; $C_A = C_{11} = 50\cdot10^{-6}F/\mathrm{cm}^2$.

For the calculation of the while unknown coefficients we bring the equation (5) to the following appearance

$$I\left(p\right) = \frac{\vartheta a'}{p\left(p + \sqrt{p}c' + m\right)}$$
$$= \frac{d_1\left(\sqrt{p} + m_1\right)\left(\sqrt{p} + m_2\right) + d_2 p\left(\sqrt{p} + m_1\right) + d_3 p\left(\sqrt{p} + m_2\right)}{p\left(\sqrt{p} + m_1\right)\left(\sqrt{p} + m_2\right)} \quad (6)$$

Coefficients d_1, d_2 and d_3 can be found by equating the factor at similar p powers in the numerators on the left and on the right.[7]

$$\left.\begin{aligned} d_1 m_1 m_2 &= \vartheta a' \\ d_1 + d_2 m_2 + d_3 m_1 &= 0 \\ d_1 m_1 + d_2 m_2 &= 0 \\ d_2 + d_3 &= 0 \end{aligned}\right\} \quad (7)$$

The thus found coefficients d_1, d_2 and d_3 are $d_1 = \frac{\vartheta a'}{m_1 m_2}$; $d_2 = -\frac{d_1}{m_2 - m_1}$; $d_3 = -d_2$.

Using inverse Laplace transform tables[6] it is possible to carry out the term-by-term transformation of equation (5) into the space of original function. As a result, we obtained the following expression for the current

$$I\left(t\right) = d_1 + d_2\left[\frac{1}{\sqrt{\pi t}} - m_1 \exp(m_1^2 t)\mathrm{erfc}\left(m_1 t^{1/2}\right)\right]$$
$$+ d_3\left[\frac{1}{\sqrt{\pi t}} - m_2 \exp(m_2^2 t)\mathrm{erfc}\left(m_2 t^{1/2}\right)\right] \quad (8)$$

By taking into account the equality $d_2 + d_3 = 0$, we obtained the following expression for the current

$$I\left(t\right) = d_1 + d_2 m_1 \exp(m_1^2 t)\mathrm{erfc}\left(m_1 t^{1/2}\right)$$
$$- d_3 m_2 \exp(m_2^2 t)\mathrm{erfc}\left(m_2 t^{1/2}\right) \quad (9)$$

The numerical values of the coefficients d_1, d_2 and d_3 are equal to: $d_1 = 100\ \mu A/\mathrm{cm}^2$; $d_2 = 2,2361$; $d_3 = -2,2361$.

The final calculation of the current through the electrolytic cell can be conduct on the equation (10)

$$I\left(t\right) = 100\ \mu A/\mathrm{cm}^2 + 2,2361 \cdot 72,36 \exp(5235,96\cdot t)$$
$$\mathrm{erfc}\ \left(-72,36\times\right) - 2,2361\cdot 27,64\exp(763,96\cdot t)$$
$$\mathrm{erfc}\ \left(-27,64\cdot t^{1/2}\right) \quad (10)$$

Current-time dependence plotted based on equation (10) is represented in Figure 3, which is plotted for the indicated above equivalent circuit parameters and linear scan rate of potential $\vartheta = 1V/s$.

It is shown from Figure 3 that the current-time dependence in the case fulfilment of Frumkin and Melik-Gaykazan model has the rectilinearity character.
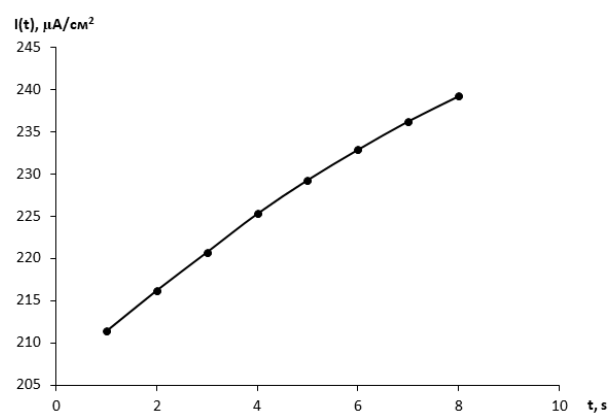

Figure 3. Dependance current *vs.* time plotted based on equation (10) in the potentiodynamic rejime de of functioning of the Frumkin and Melik-Gaykazan model

3   Conclusion

By the graphic analytical method are disclosed the two essential indications which are confirmed a presence in the electrochemical system the Frumkin and Melik-Gaykazan model (or scheme).

On the one hand this is the submission of the potential time dependence to parabola of second order in the galvanodynamic rejime ode of functioning of the electrochemical cell. On the other hand, the submission the current time dependence to linear function in the potentiodynamic rejime.

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