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Voltamperometry of a Kinetically Irreversible Electrochemical Process on a Rough Electrode

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Abstract

We investigated the role of the effect of morphological inhomogeneity of the electrode surface in the voltammetric response of the irreversible electrochemical process in the mixed-kinetic mode. An algorithm was developed using the Comsol Multiphysics computer package for the numerical simulation of the electrode reaction, including successive stages of irreversible charge transfer and diffusion mass-transfer, using the finite element method. By numerical solution of the diffusion-kinetic problem, polarization curves of the irreversible electrochemical process on electrodes with a rough surface formed by the irregularities of various geometric types (sinusoidal surface, surface with protrusions, trapezoidal surface, sawtooth surface, and “random” surface) were obtained. We established the usage conditions for the voltammetric method of studying the kinetics of electrochemical processes under which the roughness of the electrode should be considered. It was found that at relatively high potential scan rates, the voltammetric maximum on the polarization curve was formed under conditions of a very small thickness of the diffusion layer, repeating the profile of the rough surface, therefore the peak current strength was proportional to the roughness factor. If the scanning rate was relatively low, then by the time the peak on the voltammogram was reached, the diffusion front was completely smoothed out, and the surface roughness of the electrode no longer affected the maximum current. At the same time, the shape of the irregularities responsible for the roughness did not significantly affect the voltammetric response of the irreversible electrochemical process.

Keywords: voltammetry, irreversible process, diffusion, roughness.

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1. Introduction

Voltammetry is one of the most informative transient methods for studying the kinetics and mechanism of electrochemical processes [1–5]. At the same time, the theoretical basis of this method was developed mainly for perfectly smooth flat electrodes, while the vast majority of electrochemical processes occur on the surface of solid electrodes, which are characterized by a noticeable geometric heterogeneity. The roughness effect in the voltammetric response was previously studied

for a diffusion-controlled electrode process [6–10], while the stage of charge transfer was considered reversible or quasi-reversible. At the same time, the electrochemical process, which is complicated by non-stationary diffusion mass-transfer, is often irreversible [1, 11–17]. The solution to the corresponding diffusion-kinetic problem can be obtained by computer simulation of the electrode process on the surface of a solid electrode with varying degree of geometric heterogeneity.

The purpose of this study was the quantitative description of the effect of morphological heterogeneity of the electrode surface in

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the voltammetric response to an irreversible electrochemical process.

The objectives of the study were as follows:

1. The calculation of voltammograms of an irreversible electrochemical process on electrodes with a rough surface formed by irregularities of various harmonic types (sinusoidal surface, surface with protrusions, trapezoidal surface, sawtooth surface and “random” surface).

2. The establishment of the roles of potential scan rate, roughness factor, and geometric shape of roughness in the value of the criterion parameters of the voltammetric signal of an irreversible electrochemical process - current and overpotential maximum.

2. Formulation of the Problem

Consider the process of electrochemical transformation, described by the first-order reaction equation:



in which n – the number of electrons, \vec{k} and \bar{k} – heterogeneous rate constants of the anodic and cathodic reactions, respectively, depending on the electrode potential E (overpotential η) [20]. Assuming that $\vec{k} \gg \bar{k}$, i.e. reverse transformation Ox in Red is neglected. This assumption is valid for sufficiently high overpotentials, several times higher than $RT/F \approx 25$ mV (R – universal gas constant, T – temperature, F – Faraday constant), or in cases where the oxidized form of a substance Ox is insoluble or has a very high diffusion mobility in the solution.

We suppose that the electrochemically active substance Red is delivered to the electrode by semi-infinite diffusion, and the spatio-temporal profile of its concentration c is described by the equation of Fick's second law [4]. For a perfectly smooth flat surface, the diffusion problem will be one-dimensional:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2}. \quad (2)$$

Where D – volume diffusion coefficient, t – time; coordinate axis z directed deep into the solution perpendicular to the plane of the electrode. As model surfaces, we will consider corrugated profiles (Fig. 1) with the distance between adjacent irregularities λ , the height of

the irregularities ε and roughness factor $f_r = S/S_g$, equal to the ratio of real S and geometric S_g electrode area. In this case, for the calculation of the concentration profile, it is necessary to solve a two-dimensional differential equation:

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial z^2} \right). \quad (3)$$

Coordinate axis x directed perpendicular to the axis z .

The moment the polarization is turned on ($t = 0$) the concentration of substance Red in all points of the solution is the same and equal to its volumetric value (the initial condition of the diffusion-kinetic problem):

$$c|_{t=0} = c^0. \quad (4)$$

According to the first boundary condition, the concentration of the substance Red approaches the value c^0 the further from the surface of the electrode.

$$c|_{z \rightarrow \infty} = c^0. \quad (5)$$

The second boundary condition connects the diffusion flux of the substance to the electrode surface along the normal vector \vec{n} and its consumption rate during the electrode reaction:

$$D \frac{\partial c}{\partial \vec{n}} \Big|_s = \vec{k}c. \quad (6)$$

The rate constant \vec{k} exponentially depends on the overpotential $\eta = Vt$ which in the potentiodynamic polarization mode varies linearly with time at a rate equal to the potential scan rate $V = dE/dt$:

$$\vec{k} = \frac{i^0}{nFc^0} \exp\left(\frac{\alpha nF}{RT} Vt\right). \quad (7)$$

Here i^0 – exchange current density, α – charge transfer coefficient.

The voltammogram of the process was calculated as a dependence of the current density i on overpotential η , taking into account the following ratio:

$$I = nFD \frac{\partial c}{\partial \vec{n}} \Big|_s. \quad (8)$$

Graphically, the potentiodynamic curves were presented in dimensionless H, Y coordinates where $H = nF\eta/RT$ (dimensionless overpotential) and $Y = I/nFc^0DS_g$ (dimensionless current).

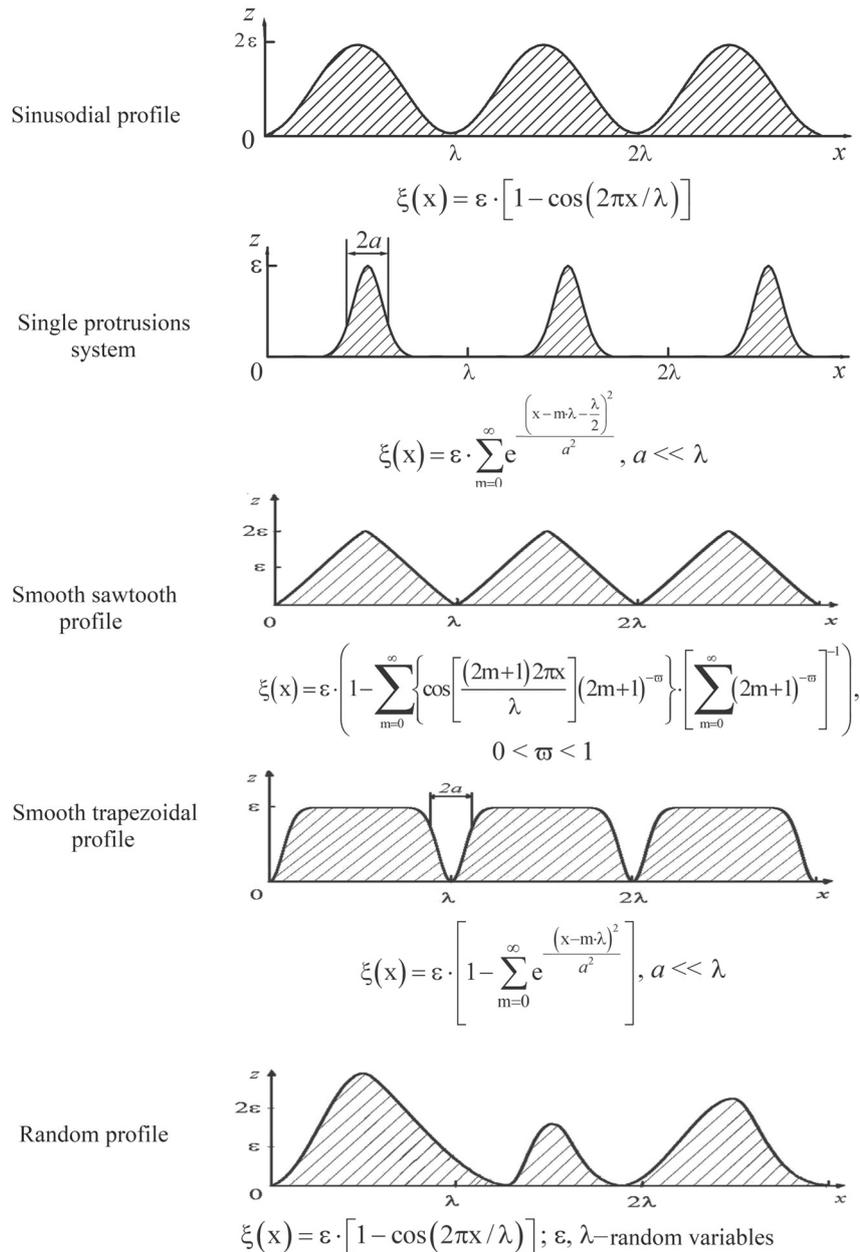


Fig. 1. Geometric profiles simulating the rough surface of the electrode

The system of equations (1)–(8) was solved numerically by the finite element method in the Comsol Multiphysics program [18, 19] for different values of the dimensionless potential scan rate $\nu = \frac{nF\lambda^2}{RTD} V$. The values of the estimated input parameters in Table 1 were selected so that they corresponded to the irreversible charge transfer stage on the electrode complicated by the non-stationary diffusion mass-transfer of *Red* in an electrolyte solution.

For checking the adequacy of the choice of input parameter values and the numerical solution

as a whole, during the first stage we compared the results obtained in Comsol Multiphysics for a perfectly smooth electrode with a flat surface (Fig. 2a) with an analytical solution known from the literature [19]. It turned out that the peak height Y_{\max} on the calculated curves was proportional to the square root of the dimensionless scan rate $\nu^{1/2}$ (Fig. 2b). In the logarithmic $H, \lg \nu$ -coordinates the maximum overpotential $H_{\max} = nF\eta_{\max}/RT$ linearly increased. At the same time, the results of the numerical and analytical solutions completely coincided, which allowed using the developed algorithm for the rough surface of the electrode.

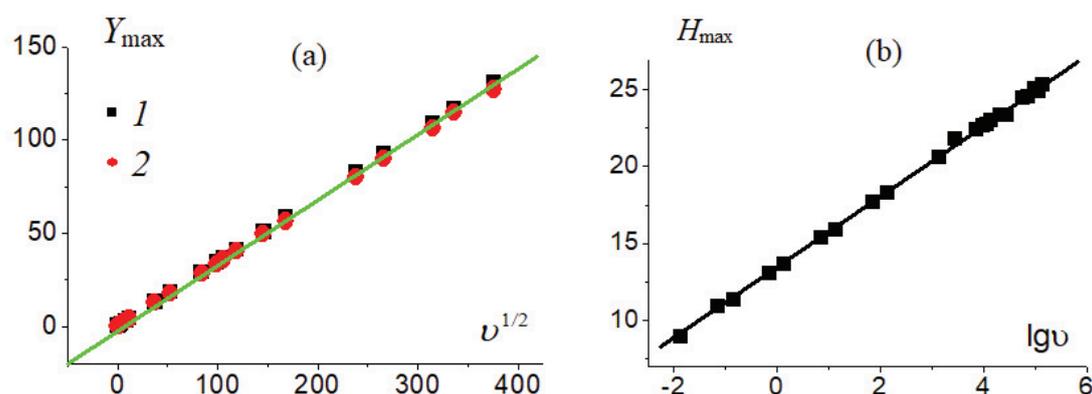


Fig. 2. Criterion dependences of current density (a) and overpotential (b) of the voltammogram maximum of an irreversible electrochemical process, obtained based the results of analytical (1) and numerical (2) solutions to the diffusion-kinetic problem and presented in dimensionless coordinates

Table 1. The values of the parameters of numerical calculation

Parameter	Value
Volume concentration of diffusant c^0	1 mol/m ³
Exchange current density i^0	10 ⁻³ A/m ²
The number of electrons n	1
Charge transfer coefficient α	0.5
Faraday constant F	96485 C/mol
Universal gas constant R	8.314 J/K·mol
Temperature T	298 K
Diffusion coefficient D	10 ⁻⁹ m ² /s
Roughness factor f_r	1 ÷ 5
The distance between adjacent irregularities λ	0.5 μ m
Potential scan rate V	10 ⁻⁴ ÷ 10 ³ V/s

3. Results and discussion

Voltammograms of a kinetically irreversible electrochemical process calculated for two values of dimensionless potential scan rates ν , which differ by 10⁷ times, are shown in Fig. 3. As on a perfectly smooth electrode, the presented curves had a characteristic maximum of dimensionless current density Y . At the same time, if the scan rate was relatively low, then the maximum height did not depend on the roughness factor (Fig. 3a). With a high scan rate, on the contrary, a clear dependence of the peak height on f_r was revealed (Fig. 3b).

The observed difference in the potentiodynamic behaviour of the considered system can be explained by analysing the concentration field of the diffusant near the electrode (Fig. 4).

When the potential is scanned slowly, by the time the current peak is reached, the diffusion front propagates deep enough into the solution, acquiring a flat shape. The height of the electrode irregularities is much less than the thickness of the formed diffusion layer. As a result, the surface roughness factor does not affect the current strength (Fig. 4a). If the scan rate is high, then upon reaching the peak value of the current, the diffusion front propagates deep into the solution to a very small distance. In this case, the diffusion front repeats the profile of the rough surface, and the height of the irregularities is much higher than the thickness of the diffusion layer (Fig. 4b). That is why the diffusion flux of the electrochemically active substance, the electrochemical reaction rate, and the current strength are proportional to the roughness factor.

Consider the dependences of the maximum current strength and the maximum overpotential of the voltammogram on the scan rate, plotted in coordinates, criterion for voltammetry $Y_{\max}, \nu^{1/2}$ - and $H_{\max}, \lg \nu$ (Fig. 5). It can be seen that with $\nu < 1$, the calculated curves coincide, while for $\nu > 2$ their divergence is observed. The analysis shows that for $\nu \gg 1$ criterion $Y_{\max}, \nu^{1/2}$ -dependencies are linearized and extrapolated to the origin of the coordinates. In turn, the maximum overpotential H_{\max} is linearly dependent on the logarithm of the scan rate over the entire range of values ν only in the case of a perfectly smooth flat electrode surface. If the process occurs on a rough surface, then the dependence of H_{\max} on $\lg \nu$ is linear only for $\lg \nu < 0$ and $\lg \nu > 3$, i.e. in the region of very

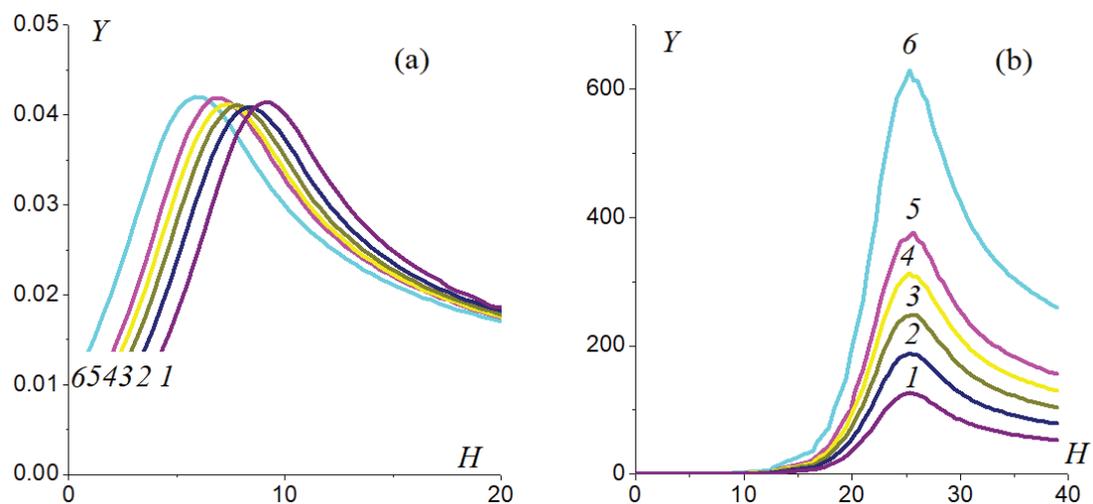


Fig. 3. Voltammograms of a kinetically irreversible electrochemical process occurring on the surface of an electrode with a roughness factor $f_r = 1$ (1), 1.5 (2), 2 (3), 2.5 (4), 3 (5), 5 (6), calculated for a corrugated electrode with a sinusoidal microroughness at the dimensionless potential scan rate $\nu = 0.0141$ (a) and 141000 (b)

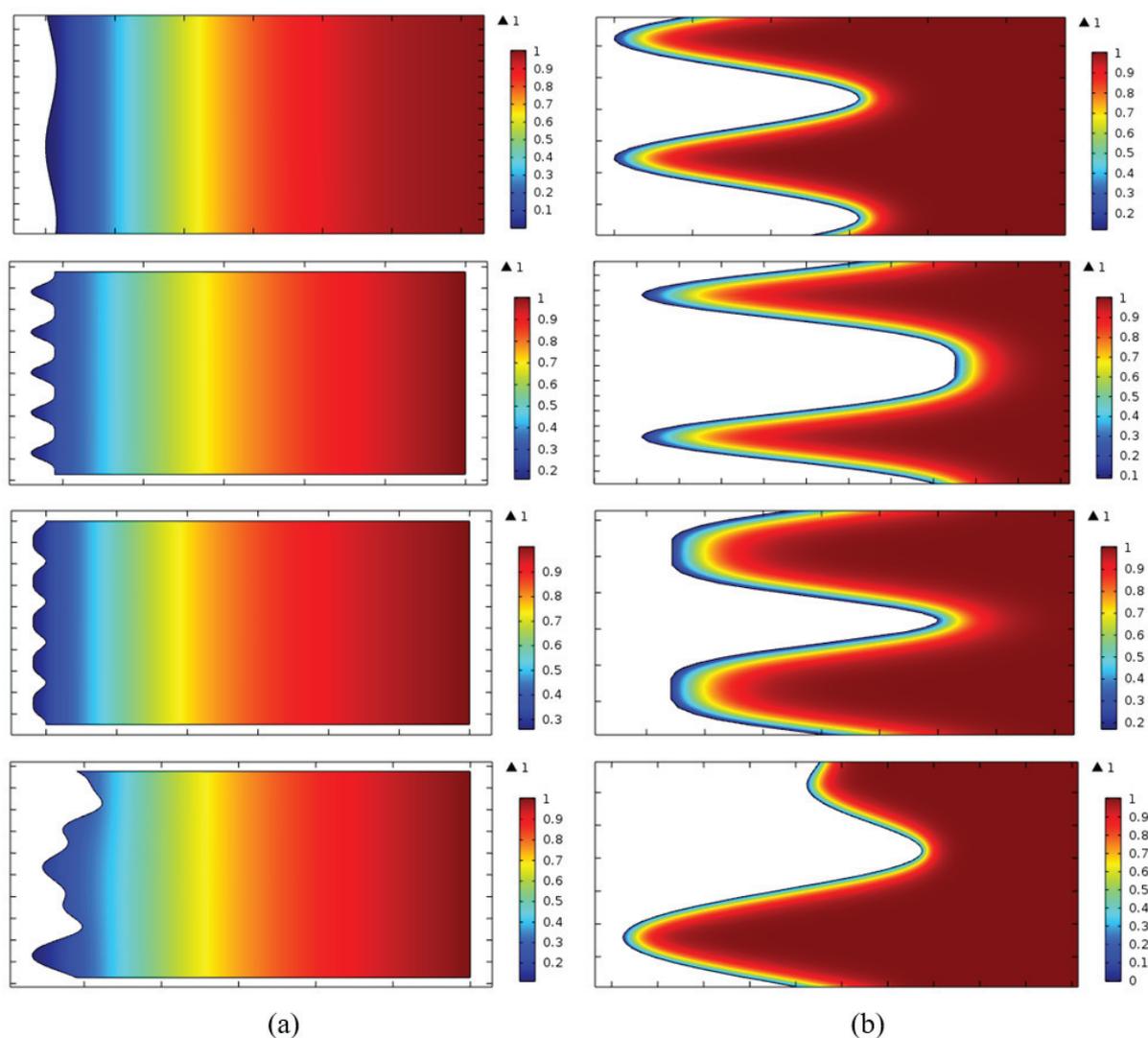


Fig. 4. The concentration field of the diffusant (in dimensionless c/c^0 units) in a solution near a rough surface of various harmonic types by the time the current maximum was reached at $f_r = 2$ and $\nu = 0.0141$ (a) and 141000 (b)

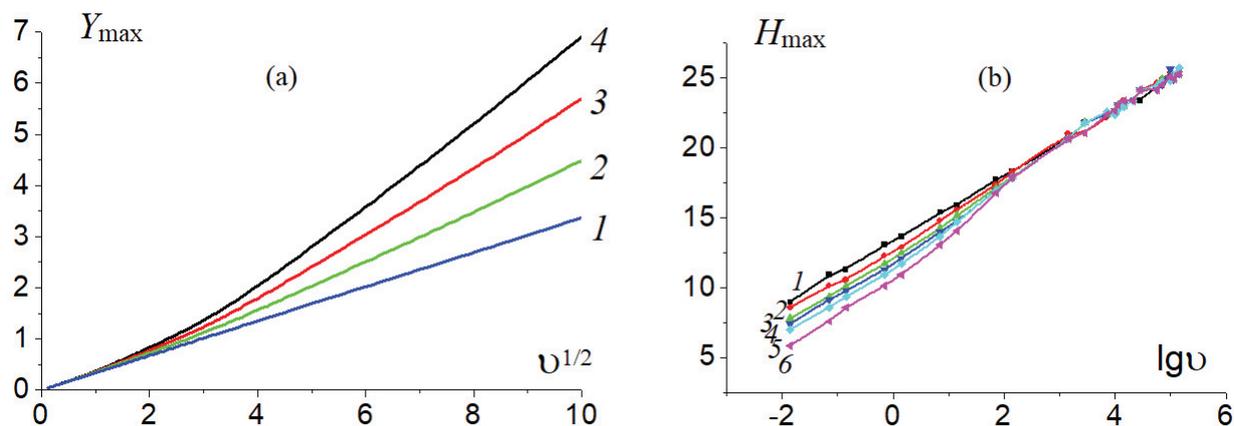


Fig. 5. Criterion dependences of the voltammetric maximum parameters - peak current (a) and peak overpotential (b), calculated for a perfectly smooth plane (1) and sinusoidal (2) - (6) electrode surface at different values of the roughness factor $f_r = 1.5$ (2), 2 (3), 2.5 (4), 3 (5), 5 (6)

low or very high values of the potential scan rate. Moreover, if v is low, then the maximum overpotential decreases with an increase in the roughness factor.

For electrodes with irregularities of various shapes the dependence of the ratio of currents on rough and flat electrodes ϕ , which we will call the “roughness function” is shown in Fig. 5. In the case where the time to reach the maximum of the voltammogram was very short (i.e., at high potential scan rates), the roughness function is simply equal to the roughness factor $\phi = f_r$. Under such conditions of the voltammetric experiment, taking into account the roughness of the electrode surface is mandatory and is reduced to dividing the current strength by f_r . If the potential scan rate is low, then the roughness function is equal to one, and the correction of current at the maximum of the voltammogram for the electrode roughness is not required.

We come to the same conclusion, taking into account the behaviour of the roughness function ϕ calculated over a wide range of dimensionless time to reach maximum current $\tau_{\max} = Dt_{\max}/\lambda^2$. The independence of the ϕ function from the roughness factor f_r and from time is observed only over relatively large times $\tau_{\max} > 50$ (Fig. 6), i.e. for the slow potential scan rate. If the maximum current is reached quickly, which corresponds to high scan rates and values $\tau_{\max} < 10^{-2}$ then $\phi = f_r$ since the diffusion front replicates the surface profile.

A comparison of the calculation results for rough surfaces of various harmonic types showed

that the geometric shape of the irregularities does not affect the shape of voltammograms irrespective of the potential scan rate value (Fig. 7).

It should be noted that under real conditions, the fact that at high scan potential rates electrochemical measurements can be complicated by the flow of a non-faradic capacitive current through the electrode should be also taken into account. The occurrence of non-faradic capacitive current is caused by the charging of a double electric layer, the electric capacity of which (especially with a highly developed surface) can reach very high values. The consideration of this effect was not included in the objectives of this study and requires additional research within the framework of the corresponding diffusion-kinetic problem.

4. Conclusions

The numerical solution to the non-stationary diffusion-kinetic problem demonstrated that taking into account the roughness of the electrode surface in voltammetry of an irreversible electrochemical process, which is complicated by the non-stationary diffusion transfer of an electroactive substance, is mandatory if the potential scan rate is relatively high. Under these conditions, upon reaching the peak value of the current, the diffusion front propagates deep into the solution to a very small distance, and the diffusion layer completely replicates the profile of the rough surface, therefore, the diffusion flux density and current density should be normalized to the electrode roughness factor.

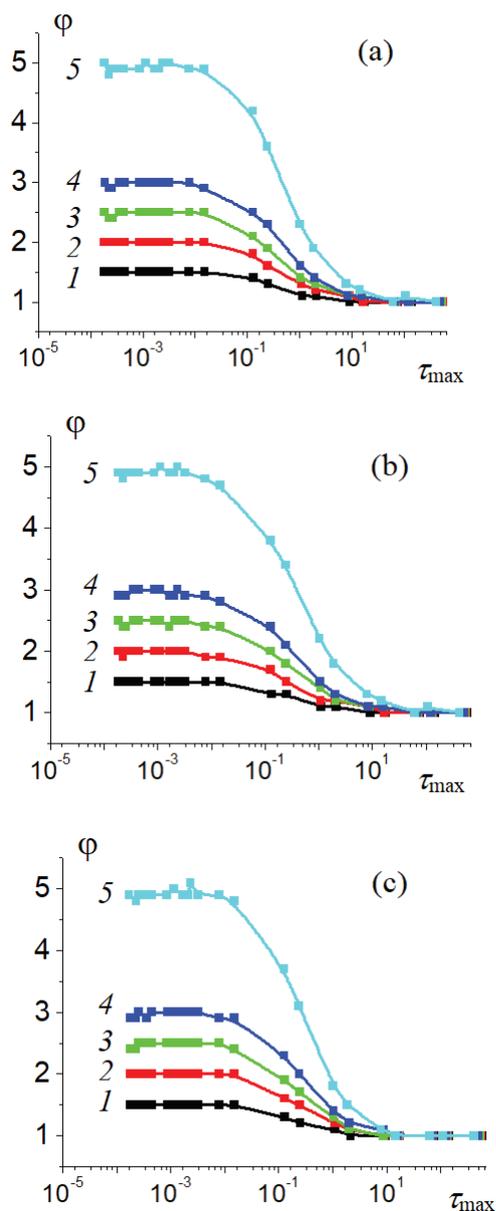


Fig. 6. Transients of roughness function calculated for sinusoidal (a), sawtooth (b), and consisting of single protrusion (c) surfaces with roughness factor $f_r = 1.5$ (1), 2 (2), 2.5 (3), 3 (4), 5 (5)

If the potential scan rate is relatively low, then by the time the current peak is reached, the diffusion front propagates deep into the solution and is completely smoothed, therefore, the diffusion flux density and the current density are proportional not to the real, but to the geometric area of the electrode.

Conflict of interests

The authors declare that they have no known competing financial interests or personal

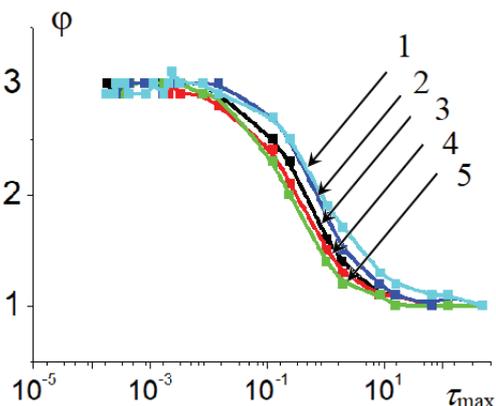


Рис. 7. Транзиенты функции шероховатости, рассчитанные для случайной (1), трапецидальной (2), синусоидальной (3), пилообразной (4), состоящей из одиночных выступов (5) поверхностей при значении фактора шероховатости $f_r = 3$

relationships that could have influenced the work reported in this paper.

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