

Full Paper

A Model of Irreversible Electro-Oxidation Inhibited by Either Adsorption or Surface Complexation of the Product

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Abstract- Theoretical models of irreversible electro-oxidation of dissolved reactant giving dissolved product on the stationary planar electrode are developed for the conditions of staircase cyclic voltammetry. In the first model it is assumed that the product is adsorbed on the electrode surface and that the adsorbate prevents the transfer of electrons. In the second model it is assumed that the electrode surface is reversibly covered by the oxide monolayer and that the product of electro-oxidation forms the inhibiting complex with the oxide. The calculations were performed by the transformation of transport defining differential equations into integral equations and by the numerical solution of the latter. The described mechanisms are investigated in order to analyse the relationship between the second anodic peak in cyclic voltammetry and the type of inhibition. It is shown that anomalous responses appear only if the electro-oxidation is inhibited by the surface complex of its product and the electrode oxide. The condition is that the electrode oxidation is reversible and that the complex disappears when the oxide is reduced.

Keywords- Cyclic voltammetry; Inhibition of electron transfer; Surface complexation; Numerical integration; Theoretical model

1. INTRODUCTION

Several electrode reactions may be hindered by the products [1-4]. This phenomenon is called autoinhibition to be distinguished from the inhibition by the adsorption of an

electroinactive foreign substance [1]. Some of examples are reductions of o-hydroxyphenil mercury chloride [5] and CO₂ [6] and oxidations of furan [7] and phenol [8]. The first reaction is inhibited by the precipitation of insoluble product of the first electron transfer, while in the second reaction the inhibition is caused by the adsorption of carbon monoxide. The other two reactions are obstructed by the adsorbed opening ring products and the polymeric film, respectively. The best known is electro-oxidation of methanol that is important for the development of direct methanol fuel cells [9-15]. The experiments are performed on electrodes of platinum [11,12,14] and its alloys with ruthenium [13] and molybdenum [15]. This reaction is reversibly inhibited by either the oxide layer on the electrode surface [16-19] or the adsorption of intermediates of the reaction [20-22]. The surface platinum oxide is inert for methanol oxidation. In the return cathodic cycle the oxide film is reduced and the oxidation of methanol starts again [16]. However, it is also shown that the catalytic activity of platinum may be diminished by the carbon monoxide poisoning [20]. The effect depends on the adsorption and desorption of methanol and methanol-derived surface carbon monoxide [22]. On majority of electrodes the oxidation of methanol is faster after the reactivation than before the deactivation of catalyst. In cyclic voltammetry the response consists of anodic peaks in both anodic and cathodic branches. This can be explained by the potential dependent deactivation and reactivation of electrode [23]. However, the physical meanings of these processes depend on the particular electrode reaction. In this paper it is shown that the surface complexation may be the mechanism in which the potential dependent inhibition is physically justified. Two theoretical models are developed with the purpose to compare the simple adsorption of product with the formation of complex between the product and the surface oxide. It is demonstrated that the effects of these two mechanisms in cyclic voltammetry are essentially different. These calculations suggest new explanation of experimental observations.

2. MODEL

An irreversible electro-oxidation of dissolved reactant giving dissolved product on the stationary planar electrode is considered:



In the first model it is assumed that the product is adsorbed on the electrode surface and that the adsorbate prevents the transfer of electrons. This mechanism is described by the following systems of equations:

$$\partial c_R / \partial t = D \partial^2 c_R / \partial x^2 \quad (2)$$

$$\partial c_O / \partial t = D \partial^2 c_O / \partial x^2 \quad (3)$$

$$t = 0, x \geq 0: \quad c_R = c_R^*, \quad c_O = 0, \quad \Gamma_O = 0 \quad (4)$$

$$t > 0, x \rightarrow \infty: \quad c_R \rightarrow c_R^*, \quad c_O \rightarrow 0 \quad (5)$$

$$x = 0: \quad D(\partial c_R / \partial x)_{x=0} = I / FS \quad (6)$$

$$I / FS = k_s \exp((1 - \alpha)F(E - E^0) / RT) c_{R,x=0} \quad (7)$$

$$D(\partial c_O / \partial x)_{x=0} = -I / FS + d\Gamma_O / dt \quad (8)$$

$$\beta c_{O,x=0} = \Gamma_O / (\Gamma_{O,max} - \Gamma_O) \quad (9)$$

The meanings of all symbols are reported in Table 1. Differential equations (2) and (3) are transformed into integral equations and solved numerically for the staircase cyclic voltammetry [24]. The solutions are systems of recursive formulae for the dimensionless current density $\Psi = I(FSc_R^*)^{-1}(DvF/RT)^{-1/2}$ and the surface coverage $\theta = \Gamma_O/\Gamma_{O,max}$:

$$\Psi_m = \kappa \exp((1 - \alpha)\varphi_m) [1 - f \sum_{j=1}^{m-1} \Psi_j Z_{m-j+1}] / [1 + \kappa f \exp((1 - \alpha)\varphi_m)] \quad (10)$$

$$\varphi_m = F(E_m - E^0) / RT \quad (m = 1, 2, 3 \dots) \quad (11)$$

$$\kappa = k_s / \sqrt{DvF/RT} \quad (12)$$

$$f = 2\sqrt{dEF/RT\pi}/5 \quad (13)$$

$$v = dE/\tau \quad (14)$$

$$p = 10\beta\Gamma_{O,max}\sqrt{v/D\pi dE} \quad (15)$$

$$\theta_m = (-B + \sqrt{B^2 - 4AC})/2A \quad (16)$$

$$A = -p \quad (17)$$

$$B = 1 + \beta c_R^* f \sum_{j=1}^m \Psi_j Z_{m-j+1} + p - p \sum_{j=1}^{m-1} \theta_j (Z_{m-j+1} - Z_{m-j}) \quad (18)$$

$$C = -\beta c_R^* f \sum_{j=1}^m \Psi_j Z_{m-j+1} + p \sum_{j=1}^{m-1} \theta_j (Z_{m-j+1} - Z_{m-j}) \quad (19)$$

$$Z_k = \sqrt{k} - \sqrt{k-1} \quad (20)$$

The calculations were performed with the time increment $d = \tau/25$. The results are presented as a relationship between the average dimensionless current density $\Phi = I(FS_0c_R^*)^{-1}(DvF/RT)^{-1/2}$ and the electrode potential. The average density depends on the surface coverage because $S_m = S_0(1 - \theta_m)$:

$$\Phi_m = (1 - \theta_m)\Psi_m \quad (21)$$

In the second model it is assumed that the electrode surface is covered by the monolayer of oxide and that the product of reaction (1) forms a complex with this oxide:



The reaction (22) is defined by the following electro-kinetic equations:

$$I_{MO}/2FS = -k_{s,MO} \exp(-2\alpha_{MO}F(E - E_2^0)/RT) *$$

$$[\Gamma_{MO} - \exp(2F(E - E_2^0)/RT)(\Gamma_{MO,max} - \Gamma_{MO})] \quad (24)$$

$$d\Gamma_{MO}/dt = I_{MO}/2FS \quad (25)$$

The solutions are recursive formulae for the dimensionless current density $\Psi_{MO} = I_{MO}(2FS\Gamma_{MO,max}vF/RT)^{-1}$ and the surface coverage $\theta_{MO} = \Gamma_{MO}/\Gamma_{MO,max}$:

$$\Psi_{MO,m} = \kappa_{MO} \exp(-\alpha_{MO}\varphi_{2,m}) \left[\exp(\varphi_{2,m}) - (1 + \exp(\varphi_{2,m})) \omega \sum_{j=1}^{m-1} \Psi_j \right] * \left[1 + \kappa_{MO}(-\alpha_{MO}\varphi_{2,m}) (1 + \exp(\varphi_{2,m})) \omega \right]^{-1} \quad (26)$$

$$\varphi_{2,m} = 2F(E_m - E_2^0)/RT \quad (27)$$

$$\omega = (dE/25)(F/RT) \quad (28)$$

$$\kappa_{MO} = k_{s,MO} RT/Fv \quad (29)$$

$$\theta_{MO,m} = \omega \sum_{j=1}^m \Psi_{MO,j} \quad (30)$$

The surface complexation (23) is defined by the equilibrium:

$$K = \Gamma_{MO-ox}(\Gamma_{MO} - \Gamma_{MO-ox})^{-1} c_{O,x=0}^{-1} \quad (31)$$

The concentration of the product of electrode reaction (1) is calculated by equations (3) and (8) and the surface concentration of oxide is defined by equation (30). It is further assumed that $\Gamma_{MO-ox,max} = \Gamma_{MO,max}$. Under this condition the surface coverage of inhibiting complex $\theta_{MO-ox} = \Gamma_{MO-ox}/\Gamma_{MO-ox,max}$ is given by the equation (16) with the parameters:

$$A = -q \quad (32)$$

$$B = 1 + Kc_R^* f \sum_{j=1}^m \Psi_j Z_{m-j+1} + q\theta_{MO,m} - \sum_{j=1}^{m-1} \theta_{MO-ox,j} (Z_{m-j+1} - Z_{m-j}) \quad (33)$$

$$C = q\theta_{MO,m} \sum_{j=1}^{m-1} \theta_{MO-ox,j} (Z_{m-j+1} - Z_{m-j}) - Kc_R^* \theta_{MO,m} f \sum_{j=1}^m \Psi_j Z_{m-j+1} \quad (34)$$

$$q = 10K\Gamma_{MO-ox,max} \sqrt{v/D\pi dE} \quad (35)$$

The currents of electrode reactions (1) and (22) must be added. Considering the definitions of Ψ and Ψ_{MO} , the following relationship exists:

$$\Psi_{MO}R = \Psi \quad (36)$$

$$R = 2\Gamma_{MO,max} \sqrt{vF/RTD}/c_R^* \quad (37)$$

In this paper the value $R = 0.1$ was used. The current of electrode reaction (1) is inhibited by the surface complex:

$$\Phi = (1 - \theta_{MO-ox})\Psi \quad (38)$$

3. RESULTS AND DISCUSSION

Cyclic staircase voltammogram of electrode reaction (1) in the absence of inhibition is

shown as curve (1) in Figure 1. It is characterized by the maximum $\Phi_p = 0.338$ appearing at 0.140 V vs. E^0 . In the reverse branch no minimum can be observed. Under the influence of inhibition by the adsorbed product, the peak current is diminished to $\Phi_p = 0.197$ and the peak potential decreases to 0.120 V vs. E^0 , as can be seen in the curve (2) in Fig. 1. However, the form of response does not change and the current monotonously decreases in the cathodic branch.

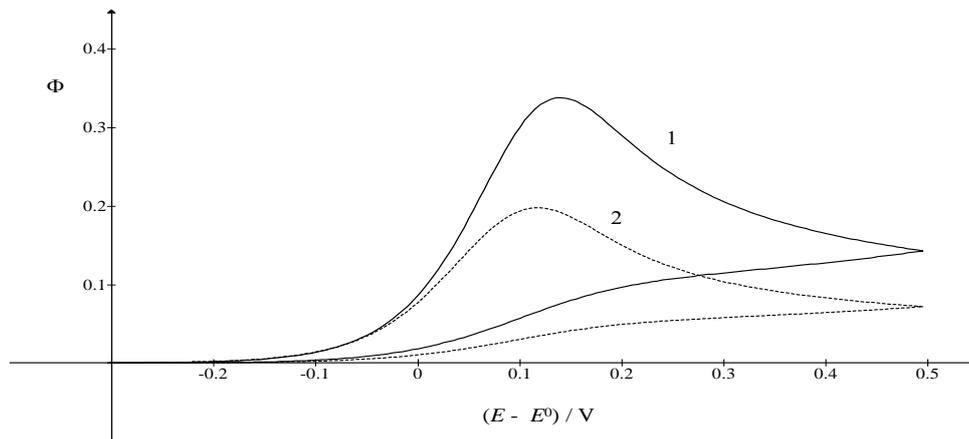


Fig. 1. Staircase cyclic voltammograms of electrode reaction (1) in the absence (1) and the presence of inhibition by the adsorbed product (2); $\kappa = 0.1$, $\alpha = 0.5$ and $dE = 5$ mV. For the curve (2) only: $\beta c_R^* = 1$ and $p = 1$

The peak currents of inhibited voltammograms depend sigmoidally on the logarithm of the product βc_R^* . If $p = 1$, the peak current decreases to one half of the limiting value if $\beta c_R^* = 1.42$. So, this relationship can be described by the simple equation:

$$\Phi_p = 0.48 / (1.42 + \beta c_R^*) \quad (39)$$

If $\beta c_R^* > 1$, the peak potentials depend linearly on the logarithm of this product, with the slope -0.055 V.

Figure 2 shows the dependence of surface coverage by the adsorbed product on the electrode potential. For the given parameters βc_R^* and p , the coverage increases sigmoidally between -0.2 V and 0.3 V vs. E^0 , with the maximum $\theta_{0.5V} = 0.5$. A half-wave potential of this relationship, at which the coverage is one half of the limiting value, is equal to 0.060 V vs. E^0 . In the reverse, cathodic branch of cyclic voltammogram the coverage decreases moderately and remains as high as 0.38 at the starting potential.

The maximum coverage depends sigmoidally on the logarithm of the product βc_R^* . If $p = 1$, this relationship satisfies simple equation:

$$\theta_{0.5V} = \beta c_R^* / (1 + \beta c_R^*) \quad (40)$$

The half-wave potentials decrease with the increasing values of this product, with the

slope $\Delta E_{1/2}/\Delta \log(\beta c_R^*) = -0.11$ V. This relationship is satisfied if $\beta c_R^* > 1$.

The parameter p depends on the maximum surface concentration of adsorbed product. If the product βc_R^* is kept constant, the variation of p may influence the surface coverage if $p > 10$. Under these conditions the amount of adsorbed product provided by the flux of reactant makes a smaller fraction of maximum coverage than at smaller p values. Considering Fig. 2, the value $\theta_{0.5V}$ decreases to 0.486 if $p = 10$, then to 0.421 if $p = 50$ and to 0.336 if $p = 100$. For the same p values the half-wave potentials increase to 0.075 V, 0.125 V and 0.150 V vs. E^0 , respectively. For these reasons, the variation of parameter p may diminish the inhibiting effect of adsorbed product. Considering the curve (2) in Fig. 1, the maximum current increases to 0.212 for $p = 10$ and to 0.290 for $p = 100$.

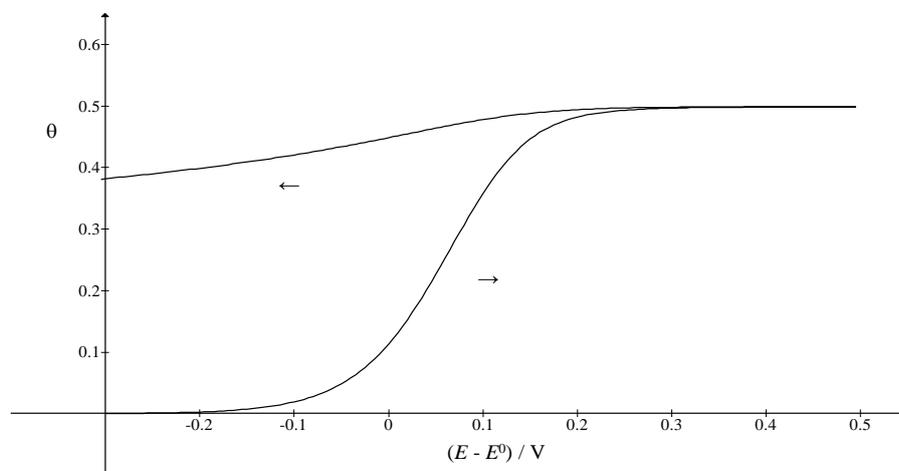


Fig. 2. Relative surface concentration of adsorbed product of the electrode reaction (1); as a function of potential in the staircase cyclic voltammetry, all parameters are as in Fig. 1

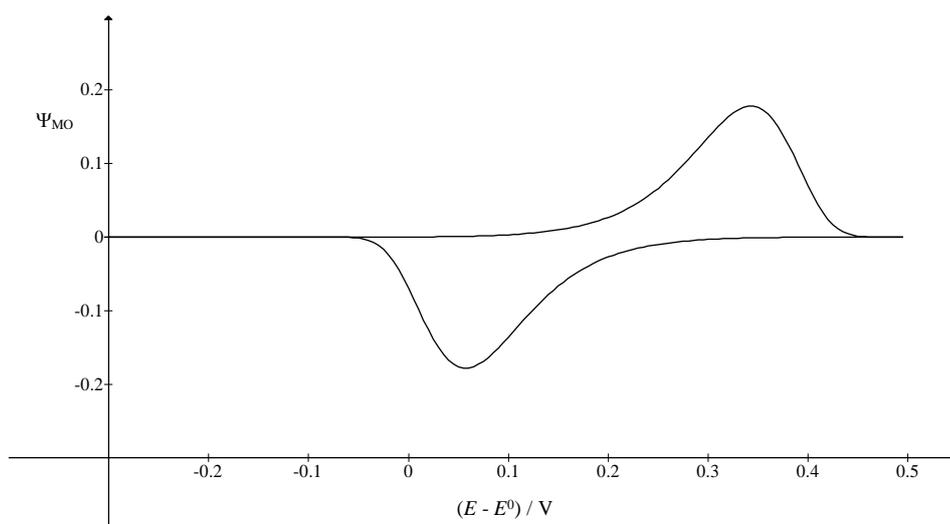


Fig. 3. Cyclic voltammogram of electrode reaction (22), $E_2^0 - E^0 = 0.2$ V, $\kappa_{MO} = 0.03$ and $\alpha_{MO} = 0.5$

The second model is based on the assumption that the electrode surface is reversibly oxidized. Figure 3 shows cyclic voltammogram of the formation and dissolution of the surface oxide. For the chosen parameters the peak currents and potentials are as follows: $\Psi_{p,a} = 0.18$, $E_{p,a} = 0.345$ V, $\Psi_{p,c} = -0.18$ and $E_{p,c} = 0.055$ V vs. E^0 . The corresponding relationship between the relative surface concentration of oxide and the electrode potential is shown by the curve (1) in Figure 4.

In the anodic branch the potential at which the one half of the surface is covered by oxide is equal to 0.325 V and in the reverse, cathodic branch this potential is 0.075 V vs. E^0 . The curve (2) in this figure shows the surface coverage by the complex $MO-Ox^+$. The curves (1) and (2) are similar and they share half-wave potentials, but the latter is smaller because it depends on the product Kc_R^* and the parameter q . If $q < 100$ this dependence is the simple one:

$$\theta_{MO-Ox,0.5V} = Kc_R^*/(1 + Kc_R^*) \quad (41)$$

Hence, for $Kc_R^* = 10$, as in Fig. 4, $\theta_{MO-Ox,0.5V} = 0.909$. The most important information in the Fig. 4 is the decreasing of the concentration of the inhibiting surface complex in the reverse, cathodic branch of cyclic voltammogram. This is essentially different from the result that is shown in Fig. 2. For this reason the inhibition disappears in the reverse branch and the second anodic peak may appear in the cyclic voltammetry.

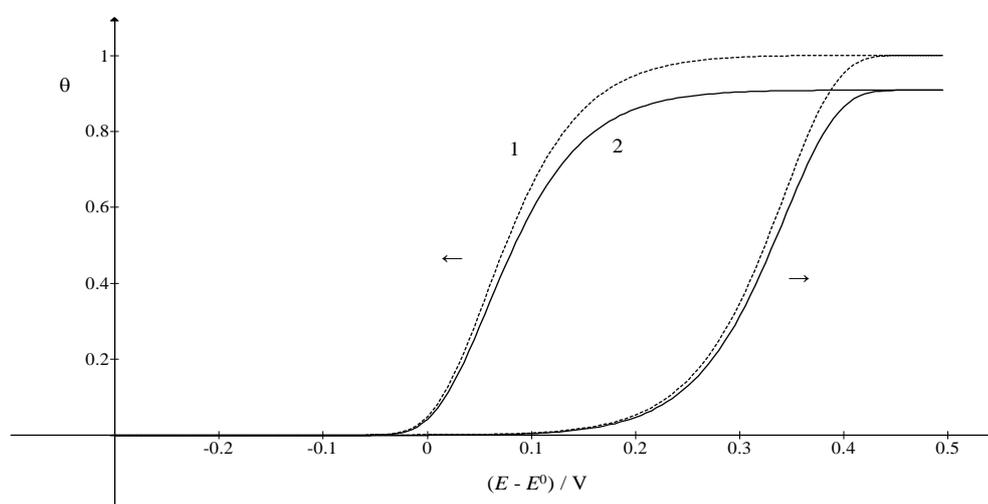


Fig. 4. Relative surface concentrations of oxide (1) and the surface complex of the product (2); for the curve (2) only: $Kc_R^* = 10$ and $q = 1$. All other data are as in Fig. 3

This can be seen in Figure 5. The curve (2) in this figure consists of the main peak at 0.140 V and the small; second one at 0.065 V in the cathodic branch. This curve represents a pure oxidation current, while the curve (3) shows the sum of oxidations of the reactant and

the electrode surface: $\Phi = (1 - \theta_{MO-ox})\Psi + 0.1\Psi_{MO}$. The latter curve exhibits both the minimum at 0.050 V and the second maximum at -0.015 V vs. E^0 . After the minimum the inhibiting complex is mostly removed from the surface and the inhibition vanishes. Figure 6 shows the influence of the second standard potential on the voltammograms influenced by the electrode deactivation and reactivation. If $E_2^0 - E^0 = 0.1$ V the surface complex inhibits oxidation in the anodic branch and the first peak is diminished to 0.312.

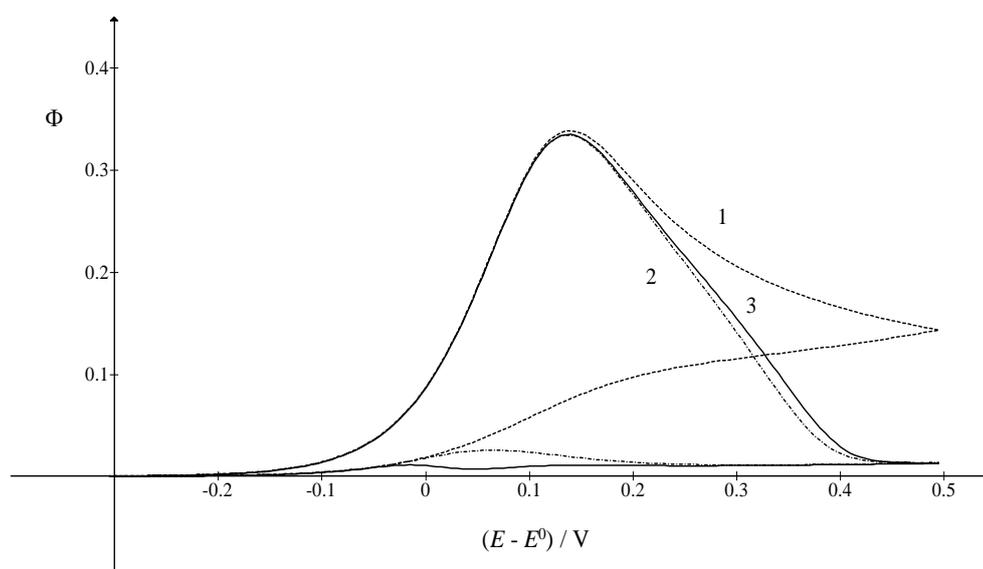


Fig. 5. Cyclic voltammograms of electrode reaction (1) inhibited by the surface complex of the product. Curve (1) is calculated for the absence of inhibition. Curve (2) is calculated by equation (38) and curve (3) is a sum of oxidation current and the oxide formation current. All parameters are as in Figs. 3 and 4

The reverse branch is dominated by the reduction of oxide with the minimum at -0.050 V vs. E^0 . However, if the difference $E_2^0 - E^0$ is as high as 0.3 V, the first peak does not change and the second anodic peak is well developed at 0.105 V vs. E^0 . These two standard potentials are independent and the form of response is coincidental.

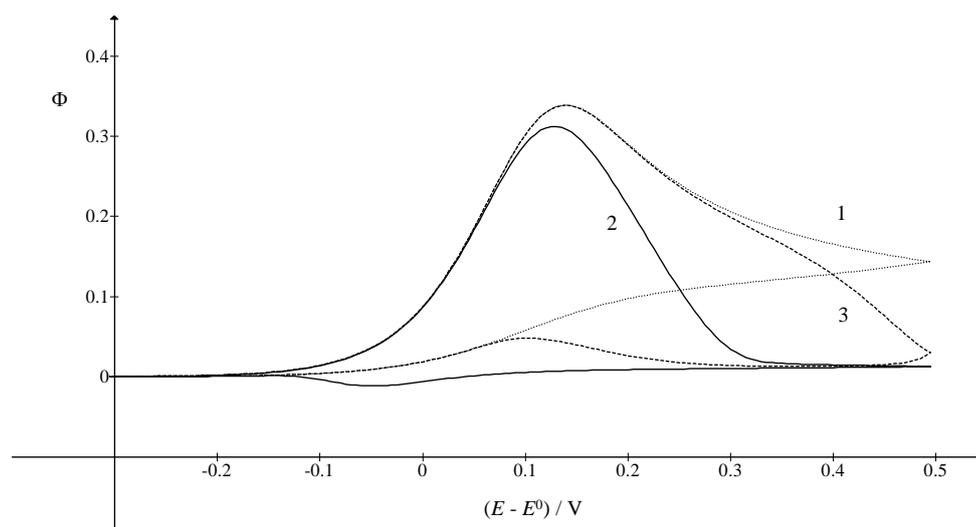


Fig. 6. Influence of the inhibiting surface complex on cyclic voltammograms of electrode reaction (1); $\kappa = 0.1$, $\alpha = 0.5$, $dE = 5$ mV, $\kappa_{MO} = 0.03$, $\alpha_{MO} = 0.5$, $Kc_R^* = 0$ (1) and 10 (2 and 3), $q = 1$ and $E_2^0 - E^0 = 0.1$ (2) and 0.3 V (3)

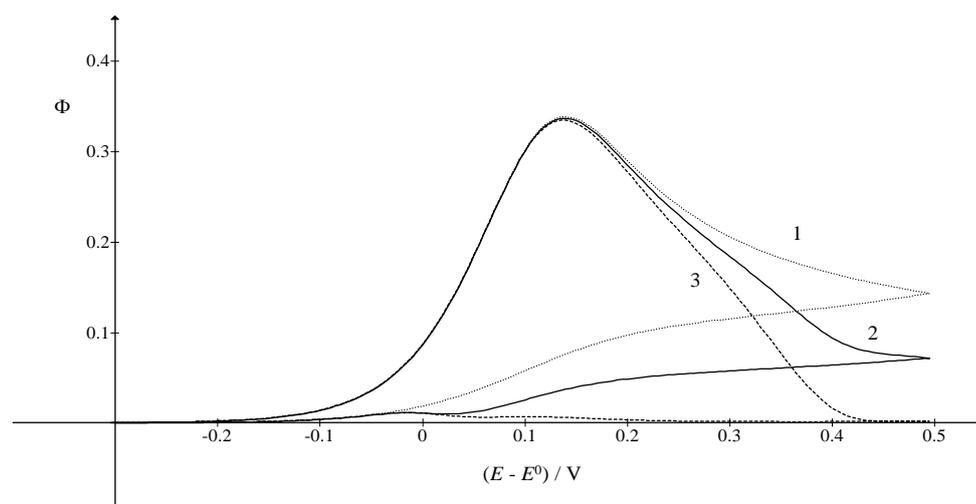


Fig. 7. Influence of the product Kc_R^* on the inhibiting effect of the surface complex. $E_2^0 - E^0 = 0.2$ V and $Kc_R^* = 0$ (1), 1 (2) and 100 (3). All other data are as in Fig. 6

The surface concentration of the inhibiting complex can be changed by the variation of the bulk concentration of the reactant of electrode reaction (1). Figure 7 shows that the current at the switching potential decreases with the increasing product Kc_R^* . Considering equations (38) and (41), the relationship between inhibited and non-inhibited currents is the following one:

$$\Phi/\Phi_{non} = 1/(1 + Kc_R^*) \quad (42)$$

If two currents Φ_1 and Φ_2 are measured at two concentrations c_R^* and $10c_R^*$, the

equilibrium constant of the surface complex can be estimated by the following equation:

$$K = (\Phi_1 - \Phi_2)/c_R^*(10\Phi_2 - \Phi_1) \quad (43)$$

However, the models developed in this paper are qualitative in a way that no lateral diffusion towards partially blocked electrode is considered [25].

Table 1. Meanings of symbols

c_R, c_O	Concentrations of reactant and product of electrode reaction (1)
c_R^*	Bulk concentration of the reactant
d	Time increment
D	Diffusion coefficient
E	Electrode potential
E^0	Standard potential
F	Faraday constant
I	Current
k_s	Standard rate constant
R	Gas constant
S	Active area of electrode surface
S_0	Total area of electrode surface
T	Temperature
t	Time
v	Scan rate
x	Distance from electrode
α	Transfer coefficient
β	Adsorption constant
Γ_O	Surface concentration of adsorbed product
$\Gamma_{O,max}$	Maximum surface concentration
τ	Step duration in the staircase cyclic voltammetry

4. CONCLUSION

A direct adsorption of the product of irreversible electro-oxidation leads to the permanent inhibition of electron transfer and the response in cyclic voltammetry is diminished, but without any anomaly. For the appearance of the second anodic peak in the reverse branch of voltammogram, the inhibition must be potential dependent and reversible. This means that the inhibiting monolayer must be formed at higher potentials, but must vanish at lower potentials. These conditions can be satisfied if the electrode surface is reversibly covered by the oxide monolayer and if the product of investigated electro-oxidation forms the inhibiting complex with the oxide. The surface concentration of the complex depends on the concentration of oxide. Hence, the complex disappears when the oxide is reduced. The response depends on the difference between standard potentials of electro-oxidation and oxide formation. The second anodic peak is more pronounced if this difference is higher. Under favourable conditions the equilibrium constant of the surface complex can be estimated by the variation of the bulk concentration of the reactant of electro-oxidation.

Dedication

Dedicated to the memory of dr. Šebojka Komorsky-Lovrić.

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