

A Model of a Two-step Three-electron Surface Redox Reaction

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Abstract

A theory of a two-step surface redox mechanism, involving both single-electron and two-electron transfers, is developed for cyclic voltammetry. It is assumed that the first step is kinetically controlled, while the second one is reversible. Depending on the difference in standard potentials, three types of responses appear as functions of the kinetic parameters. Calculation of the transfer coefficients and the standard rate constant is explained.

Keywords

Two-step electron transfers, surface-confined electrode reaction, cyclic voltammetry, successive electrode reactions, theoretical model

1 Introduction

Redox reactions, wherein both the reactant and product are confined to the electrode surface, occur in electro-catalytic systems^{1–3}, protein-film voltammetry^{4,5}, investigations of electro-active self-assembled monolayers,⁶ electro-kinetic measurements of chemically prepared electrodes^{7–9}, and electro-analysis with adsorptive accumulation.^{10,11} In these reactions, the relationship between current and potential is not complicated by mass transfer, allowing for the determination of their thermodynamic and kinetic parameters through voltammetric measurements.^{12–14} Systems involving two successive surface electrode reactions are particularly interesting, as they appear in the redox transformations of many surface-active and electro-active organic substances.^{15–19} Cyclic voltammograms of these reactions depend on two rate constants, two transfer coefficients, and two standard potentials, all of which can be freely combined, resulting in a large number of possible responses that require complex methods of analysis.^{15,16,18} Generally, multi-step electrode reactions consist of single-electron and concerted multi-electron transfers, dependent on the stability of intermediates.^{20–22} This paper describes an example of a three-electron surface redox reaction comprising two steps, in which a single and two electrons are transferred. The purpose is to report the conditions under which the second step does not prevent the determination of the kinetic parameters of the first electron transfer.

1.1 Model

It is assumed that a certain electro-active and surface-active compound (Red) is strongly adsorbed to the electrode

surface in the form of a monolayer, wherein its activity is proportional to the surface concentration. It is further assumed that the products of the electrode reaction of this compound (Int^+ , Ox^{3+}) remain adsorbed on the surface, allowing desorption to be neglected during voltammetric measurement. During this period, the additional accumulation of the reactant is also disregarded. The electrode reaction comprises two steps: the first being the kinetically controlled transfer of a single electron, while the second step involves a fast, reversible, and concerted transfer of two electrons.



The charges of species are compensated by anions in the double layer or by the dissociation of protons in the well-buffered electrolyte. The standard potentials of these two steps are independent, and they determine the form of the response in cyclic voltammetry. The current is calculated using the following differential equations:

$$\frac{d\Gamma_{\text{Red}}}{dt} = -\frac{i_1}{FS} \quad (3)$$

$$\frac{d\Gamma_{\text{Int}}}{dt} = \frac{i_1}{FS} - \frac{i_2}{2FS} \quad (4)$$

$$\frac{d\Gamma_{\text{Ox}}}{dt} = \frac{i_2}{2FS} \quad (5)$$

$$\frac{i_1}{FS} = -k_s e^{-\alpha\phi_1} [\Gamma_{\text{Int}} - \Gamma_{\text{Red}} e^{\phi_1}] \quad (6)$$

$$\phi_1 = \frac{F}{RT} (E - E_1^0) \quad (7)$$

$$\Gamma_{\text{Ox}} = \Gamma_{\text{Int}} e^{\phi_2} \quad (8)$$

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$$\varphi_2 = \frac{2F}{RT}(E - E_2^0) \quad (9)$$

$$\Gamma_{\text{Red}} + \Gamma_{\text{Int}} + \Gamma_{\text{Ox}} = \Gamma^* \quad (10)$$

At time $t = 0$, the following applies:

$$\Gamma_{\text{Red}} = \Gamma^* \quad (11)$$

$$\Gamma_{\text{Int}} = 0 \quad (12)$$

$$\Gamma_{\text{Ox}} = 0 \quad (13)$$

The meanings of all symbols are provided in the List of symbols. The dimensionless currents in cyclic voltammetry are defined as follows:

$$\Phi_j = \frac{I_j}{FS \Gamma^* v (F/RT)} \quad (j = 1 \text{ and } 2) \quad (14)$$

$$\Phi = \Phi_1 + \Phi_2 \quad (15)$$

The time is divided into m increments, and the solutions are obtained in the recursive form:

$$\Phi_{1,m} = \frac{e^{\varphi_{1,m}} - \Delta E (F/RT) \left[1 + e^{\varphi_{1,m}} - \frac{e^{\varphi_{2,m}}}{1 + e^{\varphi_{2,m}}} \right] \sum_{j=1}^{m-1} \Phi_{1,j}}{\frac{e^{\alpha\varphi_{1,m}}}{\lambda} + \Delta E (F/RT) \left[1 + e^{\varphi_{1,m}} - \frac{e^{\varphi_{2,m}}}{1 + e^{\varphi_{2,m}}} \right]} \quad (16)$$

$$\Phi_{2,m} = \frac{2e^{\varphi_{2,m}}}{1 + e^{\varphi_{2,m}}} \sum_{j=1}^m \Phi_{1,j} - \sum_{j=1}^{m-1} \Phi_{2,j} \quad (17)$$

$$\lambda = \frac{k_s}{v(F/RT)} \quad (18)$$

In the calculations, the potential increment $\Delta E = 10^{-4}$ V was used.

2 Results and Discussion

Electrode reactions consisting of two steps are referred to as the EE mechanism.¹³ The response in cyclic voltammetry of the EE mechanism considered in this paper depends on the difference in standard potentials of the two steps and on the dimensionless kinetic parameter of the first step.

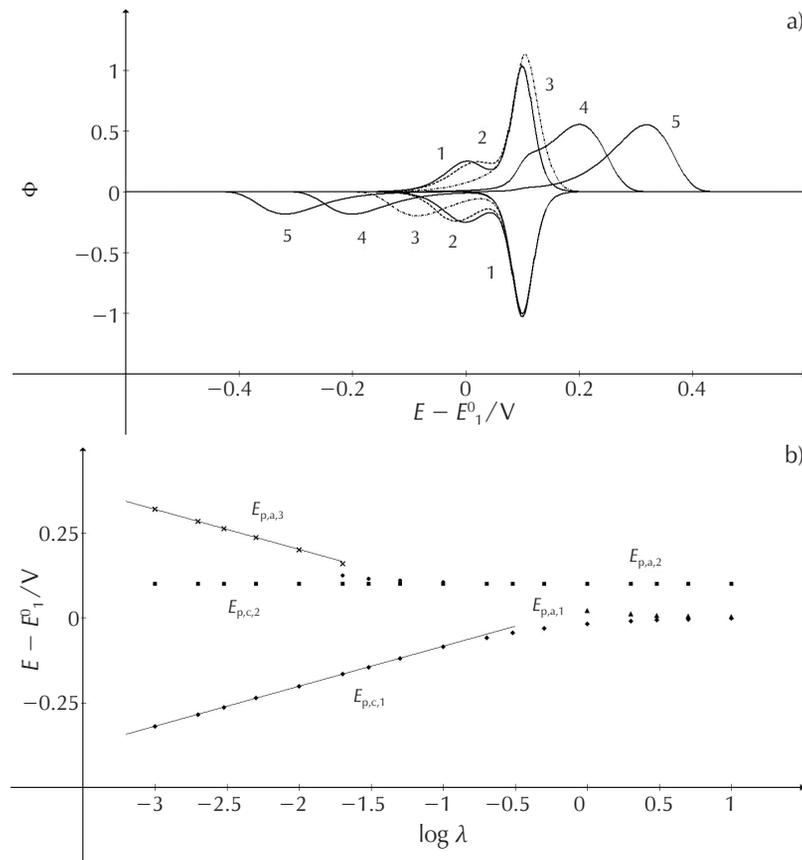


Fig. 1 – Cyclic voltammograms of (a) the surface EE mechanism, and (b) the dependence of peak potentials on the logarithm of dimensionless kinetic parameter. $E_2^0 - E_1^0 = 0.1$ V, $\alpha = 0.5$ and $\lambda = 10$ (1), 1 (2), 0.1 (3), 0.01 (4) and 0.001 (5).

Slika 1 – Ciklički voltamogrami površinskog EE mehanizma (a) i zavisnost vršnih potencijala o logaritmu bezdimenzijskog kinetičkog parametra (b). $E_2^0 - E_1^0 = 0,1$ V, $\alpha = 0,5$ te $\lambda = (1), 1 (2), 0,1 (3), 0,01 (4)$ i $0,001 (5)$

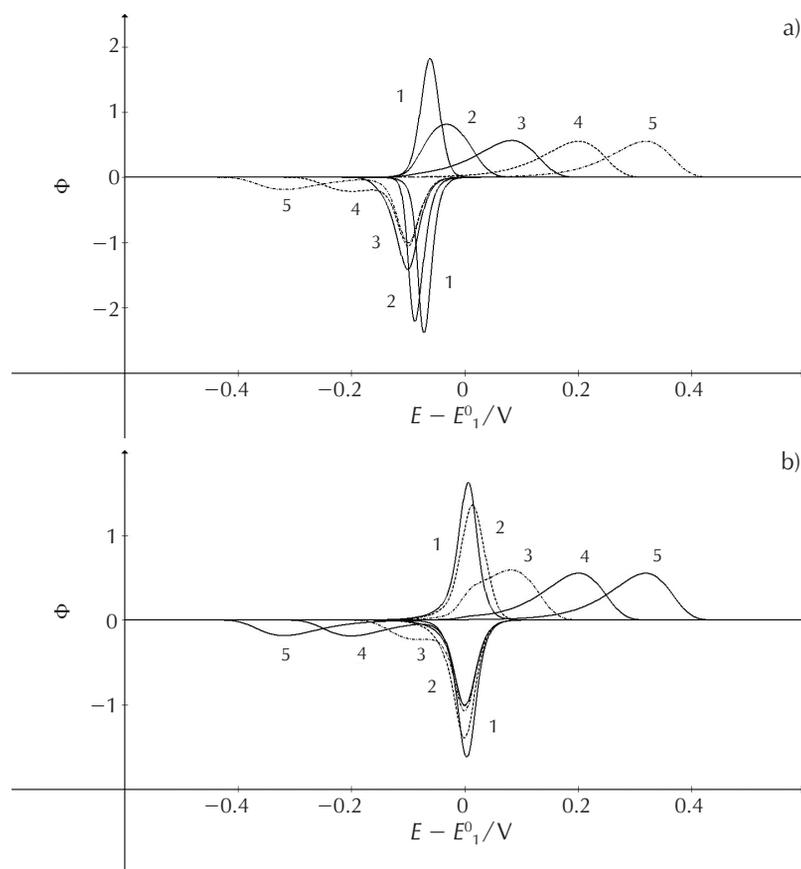


Fig. 2 – Cyclic voltammograms of the surface EE mechanism; $\alpha = 0.5$, $E_2^0 - E_1^0/V = -0.1$ (a) and 0.0 (b) and $\lambda = 10$ (1), 1 (2) 0.1 (3), 0.01 (4) and 0.001 (5).

Slika 2 – Ciklička voltamogrami površinskog EE mehanizma; $\alpha = 0,5$, $E_2^0 - E_1^0/V = -0,1$ (a) i $0,0$ (b) te $\lambda = 10$ (1), 1 (2) $0,1$ (3), $0,01$ (4) i $0,001$ (5)

If $E_2^0 - E_1^0 \geq 0.1$ V and both reactions are fast and reversible ($\lambda \geq 10$), the voltammogram exhibits two pairs of peaks at E_1^0 and E_2^0 , with dimensionless peak currents $\Phi_p = \pm n^2/4$, where n is a number of simultaneously transferred electrons.²³ This can be observed on curve 1 in Fig. 1A. If the parameter λ is diminished by the increasing scan rate, the first anodic peak merges with the second one, while the separation of cathodic peaks increases. If the first reaction is very slow ($\lambda < 10^{-2}$), the cathodic peak current is equal to -0.184 , which aligns with the theoretical value $-\alpha/e$, where e is the base of the natural logarithm, while the anodic peak current is equal to 0.552 . This number corresponds to an irreversible three-electron EE mechanism if $\alpha = 0.5$ and $E_2^0 - E_1^0 \geq 0.1$ V. The peak potentials are shown in Fig. 1B. The first cathodic peak potential is a linear function of the argument: $E_{p,c,1} - E_1^0 = 0.118 \log \lambda + 0.035$ V. The slope is equal to $2.3RT/(\alpha F)$ while the intercept is equal to $-2.3(RT/(\alpha F)) \cdot \log \alpha$. Hence, if $E_{p,c,1} = E_1^0$ then $\lambda_{crit} = \alpha$ and $k_s = \alpha v_{crit}(F/RT)$. If the intermediate is stable, the standard rate constant and the transfer coefficient of the first step can be determined by varying the scan rate. The peak potentials of irreversible three-electron oxidation are a mirror image of a single electron reduction: $E_{p,a,3} - E_1^0 = -0.118 \log \lambda - 0.035$ V. However, this slope is

equal to $-2.3RT/((1-\alpha)F)$, while the intercept is equal to $2.3(RT/((1-\alpha)F)) \cdot \log(1-\alpha)$.

If the difference between standard potentials is increased to 0.2 V, the anodic peaks of EE response are well separated if $\lambda > 0.1$, and merged if $-2.5 < \log \lambda < -1$. The peak current of irreversible three-electron oxidation is 0.552 , as in Fig. 1.

Fig. 2 shows responses calculated for unstable intermediates. If $E_2^0 - E_1^0 = -0.1$ V and both reactions are reversible, a single pair of peaks appears at -0.066 V, with the peak currents equal to ± 2.18 . The peak potential agrees with the theoretical value for the simultaneous transfer of three electrons, that is $(E_1^0 + 2E_2^0)/3$, but the peak currents are smaller than $\pm n^2/4$. This is because the theoretical value is achieved only if $E_2^0 - E_1^0 \leq -0.2$ V. For $\lambda = 10$, the anodic peak current is 1.82 , while the cathodic one is -2.38 , and the peak potentials are -0.062 and -0.072 V, respectively. Reduction of the parameter λ causes the transformation of the reversible three-electron EE mechanism into an irreversible one. In the anodic branch, a new peak appears if $\lambda \leq 10^{-1}$. Its peak current is 0.552 and its peak potential depends on λ . In the cathodic branch, the response is split

into reversible two-electron and irreversible single electron reduction peaks if $\lambda \leq 10^{-2}$. For $E_2^0 = E_1^0$, this separation occurs at $\lambda \leq 10^{-1}$. Under this condition, the peak current of irreversible three-electron oxidation is also 0.552, indicating independence from the standard potentials difference.

The relationship between peak potentials of the responses shown in Fig. 2 and the logarithm of dimensionless scan rate is shown in Fig. 3. The straight lines in this figure are defined by the same equations as the straight lines in Fig. 1B, allowing for the determination of transfer coefficients from their slopes. The rate constant can be calculated using the peak potentials of the reversible EE mechanism ($E_{p,3,rev} = (E_1^0 + 2E_2^0)/3$) and the peak potential of reversible two-electron reduction: $E_{p,c,2} - E_1^0 = E_2^0 - E_1^0$. The first standard potential is determined by the following equation: $E_1^0 = 3E_{p,3,rev} - 2E_{p,c,2}$. The condition is that $\lambda \geq 10$ at the lowest scan rate, enabling the measurement of $E_{p,3,rev} = (E_{p,a,3} + E_{p,c,3})/2$. If $v_{min} = 10^{-3} \text{ V s}^{-1}$, the lowest standard rate constant measurable is equal to 0.4 s^{-1} . The critical scan rate occurs when $E_{p,a,3} = E_1^0$, or $E_{p,c,1} = E_1^0$. If $E_2^0 - E_1^0 > 0$, it is preferable to use the cathodic branch for kinetic measurements, but if $E_2^0 - E_1^0 < 0$, the anodic branch is more suitable.

If the intermediate is highly unstable, in the anodic branch of cyclic voltammogram, the second and the third electron follow the first one immediately. However, in the cathodic branch, the first electron may follow the third and the second one immediately only if the electrode potential is high enough to surpass the kinetic limitations of its transfer. Fig. 4 shows that the cathodic response may or may not split, depending on the reduction transfer coefficient. If $\alpha = 0.7$ and the oxidation transfer coefficient is 0.3, there is no splitting if $E_2^0 - E_1^0 = -0.3 \text{ V}$. A single peak of three-electron reduction appears between -0.212 V and -0.295 V vs. E_1^0 , and its minimum current changes from -2.79 ($\lambda = 10$) to -2.95 ($\lambda = 1$) and to -2.1 at $\lambda = 10^{-3}$. In the anodic branch, the quasi-reversible three-electron peak appearing at -0.191 V decreases into the irreversible one with the peak current equal to 0.331 and the peak potential satisfying the equation: $E_{p,a,3} - E_1^0 = -0.197 \log \lambda - 0.103 \text{ V}$. In Fig. 4b, the peak current of this response is 0.772 and the equation of peak potential is: $E_{p,a,3} - E_1^0 = -0.084 \log \lambda - 0.013 \text{ V}$. The cathodic peak potential changes between -0.245 V and -0.3 V vs. E_1^0 . If $\lambda = 10^{-3}$, a new peak appears at -0.488 V , similar to Fig. 2. Regarding the dependence of the irreversible three-electron oxidation peak on the transfer coefficient, it is obvious that its peak current is defined by the following equation:

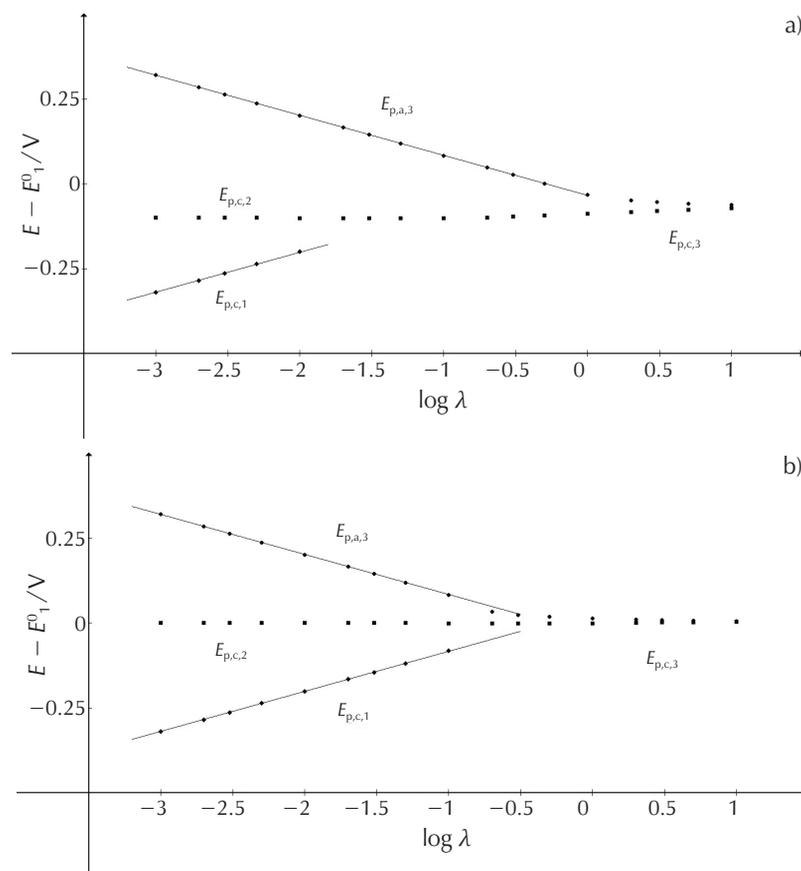


Fig. 3 – Dependence of peak potentials of the surface EE mechanism on the logarithm of the dimensionless kinetic parameter; $\alpha = 0.5$ and $E_2^0 - E_1^0/V = -0.1$ (a) and 0.0 (b).

Slika 3 – Zavisnost vršnih potencijala površinskog EE mehanizma o logaritmu bezdimenzijskog kinetičkog parametra; $\alpha = 0,5$ i $E_2^0 - E_1^0/V = -0,1$ (a) i $0,0$ (b)

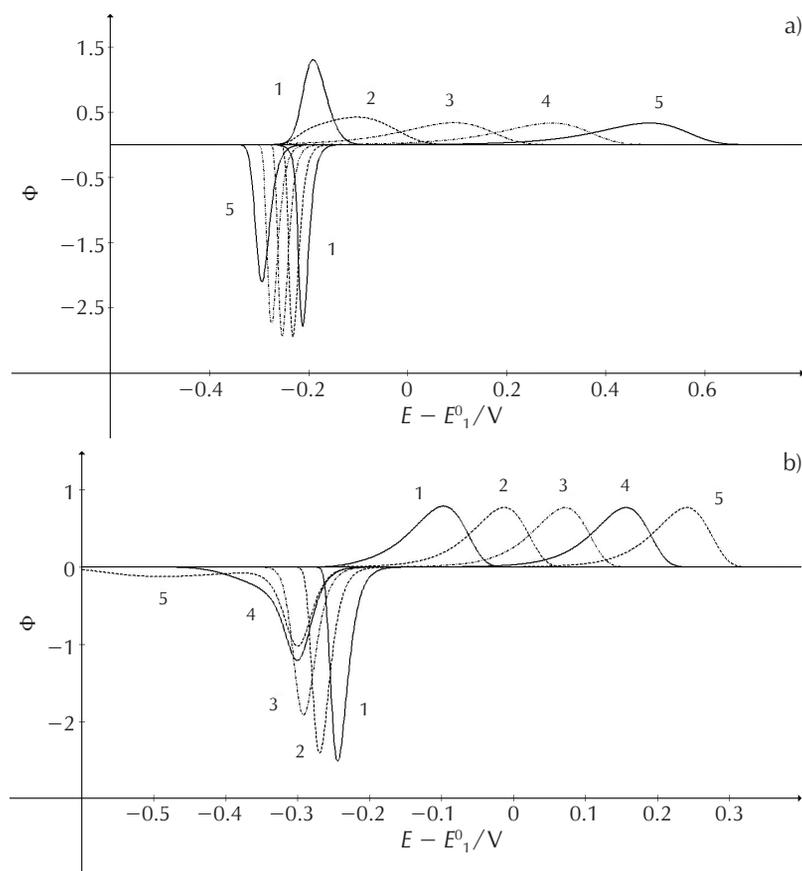


Fig. 4 – Cyclic voltammograms of the surface EE mechanism. $E_2^0 - E_1^0 = -0.3$ V, $\alpha = 0.7$ (a), and 0.3 (b), and $\lambda = 10$ (1), 1 (2), 0.1 (3), 0.01 (4) and 0.001 (5).

Slika 4 – Ciklički voltamogrami površinskog EE mehanizma; $E_2^0 - E_1^0 = -0,3$ V, $\alpha = 0,7$ (a) i $0,3$ (b) i $\lambda = 10$ (1), 1 (2), $0,1$ (3), $0,01$ (4) i $0,001$ (5)

$$\Phi_{p,3,irrev} = 3(1-\alpha)/e \quad (19)$$

In the absence of split cathodic response, the second standard potential cannot be estimated. Furthermore, the EE mechanism appears less reversible if the intermediate is less stable,²⁴ making it challenging to estimate the reversible potential of the EE mechanism as well. Without this information, the standard rate constant cannot be calculated.

3 Conclusions

The presented model represents the simplest combination of kinetically controlled and reversible electron transfers. This EE mechanism exhibits three types of voltammetric responses: reversible and irreversible single-electron peaks, reversible two-electron peaks, and reversible and irreversible three-electron peaks. The first two responses are clearly separated in the cathodic branch if the intermediate is stable. In principle, varying the scan rate allows for the recording of both reversible and irreversible peaks, facilitating calculation of the kinetic parameters. When the intermediate is moderately unstable, this can be achieved

by measuring the three-electron peaks, which depend on the kinetics of the first step but have a peak current three times higher. A highly unstable intermediate may result in the appearance of a single pair of peaks at every scan rate, hindering the calculation of the standard rate constant.

List of symbols Popis simbola

- α – cathodic transfer coefficient
- ΔE – potential increment
- E – potential
- E^0 – standard potential
- E_p – peak potential
- EE – two-step electrode reaction
- F – Faraday constant
- Φ – dimensionless current
- Γ – surface concentration
- Γ^* – sum of surface concentrations
- I – current

- k_s – standard rate constant
 λ – dimensionless kinetic parameter
 n – number of electrons
 R – gas constant
 S – electrode surface area
 t – time
 T – temperature
 v – scan rate
 φ – dimensionless potential

DEDICATION

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

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SAŽETAK

Model dvostupanjske troelektronske površinske redoks-reakcije

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Razvijena je teorija cikličke voltametrije površinskog redoks-mehanizma, koji se sastoji od uzastopnih prijenosa jednog i dvaju elektrona. Pretpostavljeno je da prvi korak zavisi o kinetici prijenosa, a da je drugi reverzibilan. Javljaju se tri tipa odziva koji zavise o kinetičkim parametrima i različiti standardnih potencijala. Objasnjeno je kako se mogu izračunati koeficijenti prijelaza i standardna konstanta brzine prve elektrodne reakcije.

Ključne riječi

Dvostupanjski prijenos elektrona, površinska elektrodna reakcija, ciklička voltametrija, uzastopne elektrodne reakcije, teoretski model

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