Simulation of electrocatalytic mechanism followed by chemical reaction

Lara Čižmek, Milivoj Lovrić *

Division of Materials Chemistry, "Ruđer Bošković" Institute, 10000 Zagreb, Croatia

ABSTRACT

The second order, reversible electrocatalytic mechanism followed by irreversible transformation of oxidized substrate is analyzed for chronoamperometry. The dependences of limiting current and half-wave potential on the measurement time and the concentrations of catalyst and substrate are investigated theoretically. These relationships can be used for the redox characterization of substrate and the measurement of its concentration.

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1. Introduction

In electrocatalytic mechanism the catalyst is regenerated on the electrode surface [1–5]. So, the heterogeneous charge transfer from the electrode to the catalyst is followed by the homogeneous electron transfer between the catalyst and the substrate. The characteristics of redox reaction of substrate is investigated by its influence on the electrode reaction of the catalyst. The theory of this mechanism is developed for chronoamperometry [6–10] and alternating current [1, 11], linear scan [3,4,12–14], cyclic [2,5,15–18], differential pulse [19] and square wave voltammetry [20–26]. Examples of electrocatalyzed reactions are reductions of hydrogen peroxide [3,23], hydroxylamine [4,20,22,27] and ruthenium(III) [18] and iron(III) [28] complex ions in the presence of iron(III/II) and molybdene(V/IV) redox couples and azobenzene, respectively, and oxidations of plastocyanin [15], fructose [29], dopamine [30], ascorbic acid [8] and cysteine [16,31] catalyzed by cytochrome c, cobalt hydroxide, catechin hydrate and iron(III/II) complexes, respectively. Amperometric biosensors in which redox enzymes and proteins are immobilized on electrode surface and catalyze redox reactions of various substrates are particularly important [32–38]. Another application of this mechanism is in the measurement of activity and concentration of natural antioxidants [39–44]. These compounds scavenge reactive oxygen species and exhibit antiviral, anti-inflammatory and antitumor effects [45–51]. The radical scavenging capacity of polyphenolic antioxidants can be correlated to chemical reaction of phenoxy radical with the solvent [52–55]. In this communication the results of simulation of reversible, second order electrocatalytic mechanism that is followed by irreversible chemical reaction of the oxidized substrate are reported. They correspond to the redox reaction of the antioxidant with electrogenerated radical and the subsequent decay of the second radical. For the calculation, the models proposed by Miaw et al. [9] and Barker et al. [15] were adapted. The purpose of the work was to investigate the analytical application of this mechanism.

2. The model

Reversible oxidation of dissolved substrate C catalyzed by the product of electrooxidation of dissolved substance A is considered. Furthermore, totally irreversible transformation of oxidized substrate is assumed.

$$A \rightleftharpoons B^+ + e^- \tag{1}$$

$$B^+ + C \rightleftharpoons A + D^+ \tag{2}$$

$$D^+ \longrightarrow P \tag{3}$$

The chemical reaction (2) is governed by the second order kinetics and the electrode reaction (1) is fast and reversible. Also, only reduced forms of the catalyst and substrate are initially present in the solution. For the stationary, planar electrode, this mechanism can be described by four partial differential equations with the following initial and boundary conditions:

$$\partial c_A/\partial t = D\partial^2 c_A/\partial x^2 + k_f c_{B^+} c_C - k_b c_A c_{D^+} \tag{4}$$

$$\partial c_{B^+}/\partial t = D\partial^2 c_{B^+}/\partial x^2 - k_f c_{B^+} c_C + k_b c_A c_{D^+} \tag{5}$$

$$\partial c_C/\partial t = D\partial^2 c_C/\partial x^2 - k_f c_{B^+} c_C + k_b c_A c_{D^+} \tag{6}$$

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* Corresponding author at: Bijenička 54, Zagreb, Croatia.
E-mail address: mlovric@irb.hr (M. Lovrić).

Table 1
Meanings of symbols.

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c_A, c_{B^+}	Concentrations of the reduced and oxidized forms of the catalyst
c_C, c_{D^+}	Concentrations of the reduced and oxidized forms of the substrate
c_A^*	Bulk concentration of the reduced catalyst
c_C^*	Bulk concentration of the reduced substrate
D	Common diffusion coefficient
E	Electrode potential
E^0	Standard potential of electrode reaction (1)
F	Faraday constant
Φ	Dimensionless current
I	Current
k_f, k_b	Forward and backward rate constants of reaction (2)
k_3	Forward rate constant of reaction (3)
K	Equilibrium constant of reaction (2)
κ_f^*	Dimensionless forward rate constant of reaction (2)
κ_3^*	Dimensionless forward rate constant of reaction (3)
R	Gas constant
S	Electrode surface area
t	Time
T	Temperature
τ	Measurement time
x	Distance from electrode surface
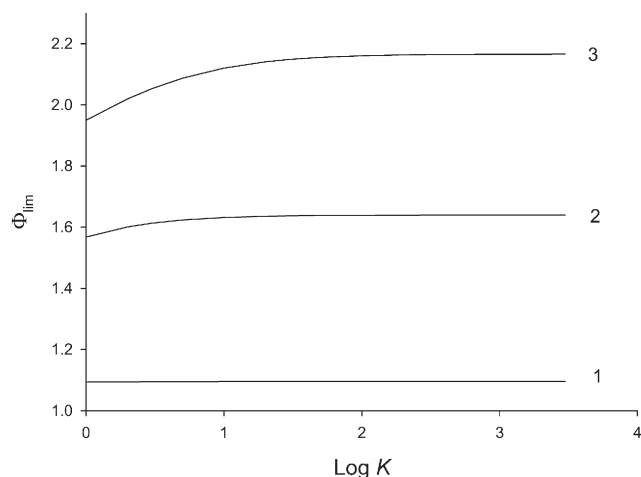
Fig. 2. Relationship between the current and the logarithm of equilibrium constant of reaction (2). $E - E^0 = 0.3$ V, $c_C^* = c_A^*$, $\kappa_3^* = 0$ and $\kappa_f^* = 0.1$ (1), 1 (2) and 10 (3).

$$\partial c_{D^+}/\partial t = D\partial^2 c_{D^+}/\partial x^2 + k_f c_{B^+} c_C - k_b c_A c_{D^+} - k_3 c_{D^+} \qquad (7)$$

$$t = 0, x \geq 0: \quad c_A = c_A^*, \quad c_{B^+} = 0, \quad c_C = c_C^*, \quad c_{D^+} = 0 \qquad (8)$$

$$t > 0, x \to \infty: \quad c_A \to c_A^*, \quad c_{B^+} \to 0, \quad c_C \to c_C^*, \quad c_{D^+} \to 0 \qquad (9)$$

$$x = 0: (c_{B^+})_{x=0} = (c_A)_{x=0} \; exp\left((F/RT)\left(E-E^0\right)\right) \qquad (10)$$

$$D(\partial c_A/\partial x)_{x=0} = I/FS \qquad (11)$$

$$D(\partial c_{B^+}/\partial x)_{x=0} = -I/FS \qquad (12)$$

$$(\partial c_C/\partial x)_{x=0} = 0 \qquad (13)$$

$$(\partial c_{D^+}/\partial x)_{x=0} = 0. \qquad (14)$$

The meanings of all symbols are reported in Table 1. The rate constants of reaction (2) are connected by equilibrium constant $K = k_f/k_b$. Differential Eqs. (4)–(7) were solved by the finite difference method [56]. The simulation parameters were $D\Delta t \Delta x^{-2} = 0.2$ and $\Delta t = \tau/1000$, where τ is the measurement time in chronoamperometry. The diffusion was calculated for 1000 space increments and the double precision was

used. The dimensionless current $\Phi = I(FSc_A^*)^{-1}\sqrt{\pi\tau/D}$ was calculated as a function of electrode potential and the dimensionless parameters K, $\kappa_f^* = k_f \tau c_A^*$ and $\kappa_3^* = k_3\tau$.

3. Results and discussion

In chronoamperometry the relationship between current and potential has a sigmoidal form: $\Phi = \Phi_{lim}/(1 + \exp(-(F/RT)(E - E_{1/2})))$ [9]. The current Φ is normalized by the square-root of τ and applies to any value of the measurement time. The half wave potential, $E_{1/2}$, is equal to the standard potential if diffusion coefficients are equal and $k_f = 0$. The current is practically independent of electrode potential if $E - E^0 > 0.25$ V. This potential independent current is called the limiting current Φ_{lim}. In this work the limiting current and half-wave potential are calculated as functions of kinetic parameters and relative bulk concentration of substrate. Fig. 1 shows sigmoidal relationship between the limiting current and the logarithm of dimensionless forward rate constant of the chemical reaction (2). It corresponds to equal bulk concentrations of the substrate and catalyst and to equal rate constants of the second reaction. Also, the rate constant of the third reaction is negligible. Under these conditions dimensionless current increases from $\Phi_{lim} = 1$, for $\kappa_f^* = 0$, to $\Phi_{lim} = 2$ for $\kappa_f^* = 500$, which is in agreement
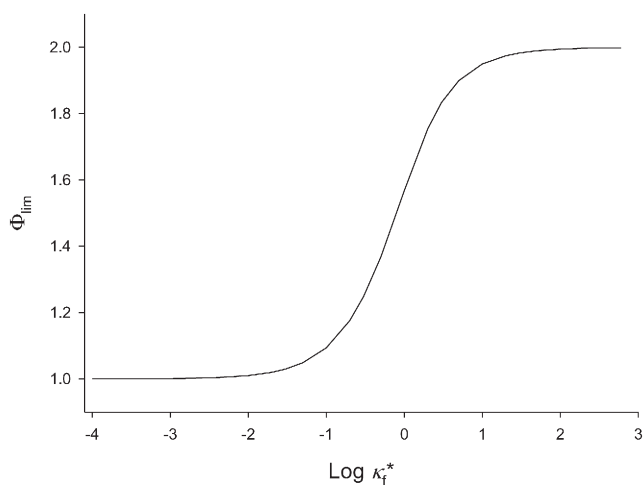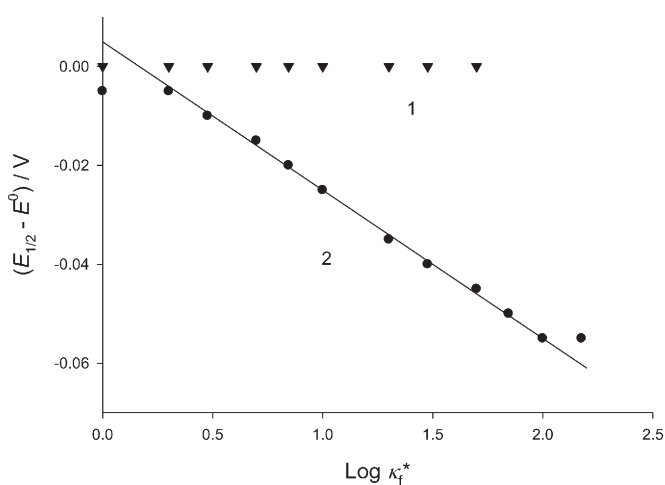

Fig. 1. Dependence of chronoamperometric dimensionless response on the logarithm of dimensionless forward rate constant of reaction (2). $E - E^0 = 0.3$ V, $K = 1$, $c_C^* = c_A^*$ and $\kappa_3^* = 0$.

Fig. 3. Dependence of half-wave potential on the logarithm of dimensionless forward rate constant of reaction (2); $c_C^* = c_A^*$, $\kappa_3^* = 0$ and $K = 1$ (1) and 1000 (2). The straight line is a linear approximation: $E_{1/2} - E^0 = -0.030\log\kappa_f^* + 0.005$ V.