

Transient currents in the staircase voltammetry of electro-catalytic reaction on the rotating disk electrode

Milivoj Lovrić

Divkovićeve 13, Zagreb 10090, Croatia

mlovric@irb.hr

Abstract

The method of variable diffusion layer thickness is applied in the calculation of staircase voltammetry of electro-catalytic reactions on the rotating disk electrode. It is shown that voltammograms exhibit either maximum or limiting current, but rarely both. This is because the potential range within which a certain reaction is recorded is limited and must be scanned rather slowly to allow the diffusion layer to extend to the steady state limit. If the scan rate is high, this condition is not satisfied and the response is recorded under transient conditions. The relationship between current maxima and the experimental conditions are analysed theoretically.

Keywords

Electro-catalytic reaction; Mathematical model; Rotating disk electrode; Variable diffusion layer thickness.

1. Introduction

Staircase voltammetry is a digital version of a linear scan voltammetry [1-6]. The difference between responses of these two techniques depends on the mechanism of electrode reaction [7-10]. In the previous paper [11] the theory of staircase voltammetry of reversible charge transfers on the rotating disk electrode was reported, and in the present communication the calculations are extended to the electro-catalytic processes on the same electrode. These reactions are important for the investigation of enzymatic electron transfers in the protein-film voltammetry [12-14].

2. Model

It is assumed that a certain redox couple is strongly adsorbed on the surface of rotating disk electrode and that in the solution there is a compound Y which can be oxidized by the product of the surface redox reaction:



The electrode reaction (1) is fast and reversible, while the catalysed oxidation (2) is totally irreversible. In the investigated potential range the compound Y cannot be electro-oxidized on the bare electrode surface due to very slow electron transfer. The mass transport towards the surface of rotating disk electrode is defined by the following system of equations:

$$\frac{\partial c_Y}{\partial t} = D \frac{\partial^2 c_Y}{\partial x^2} + \kappa x^2 \frac{\partial c_Y}{\partial x} \quad (3)$$

$$\kappa = 0.51 \sqrt{\omega^3 / \nu} \quad (4)$$

$$D \left(\frac{\partial c_Y}{\partial x} \right)_{x=0} = k_f \Gamma_{\text{Ox}} c_{Y,x=0} \quad (5)$$

$$\Gamma_{\text{Ox}} = \Gamma_{\text{Red}} \exp(\varphi) \quad (6)$$

$$\varphi = \frac{nF}{RT} (E - E^0_{\text{Ox/Red}}) \quad (7)$$

$$\Gamma_{\text{Ox}} + \Gamma_{\text{Red}} = \Gamma_{\text{Red}}^* \quad (8)$$

$$\frac{I}{nFS} = k_f \Gamma_{\text{Ox}} c_{Y,x=0} \quad (9)$$

The meanings of all symbols are reported in the Table 1.

Table 1

Meanings of symbols

c_Y	Concentration of compound Y
c_Y^*	Bulk concentration of compound Y
D	Diffusion coefficient
δ	Diffusion layer thickness
E	Electrode potential
$E_{Ox/Red}^0$	Standard potential
F	Faraday constant
Γ_{Ox}	Surface concentration of oxidized form of adsorbed catalyst
Γ_{Red}	Surface concentration of reduced form of adsorbed catalyst
Γ_{Red}^*	Initial surface concentration of the adsorbed catalyst
I	Current
k_f	Rate constant of catalytic reaction
n	Number of electrons
ν	Kinematic viscosity
ω	Rate of rotation
S	Electrode surface area
t	Time
x	Distance from electrode surface

Differential equation (3) is solved by the method of variable diffusion layer thickness that was described previously [11, 15]. The method is based on the assumption that the concentration of compound Y can be described by the following equation:

$$c_Y = c_{Y,x=0} + (c_Y^* - c_{Y,x=0}) \frac{x}{\delta} \quad (0 \leq x \leq \delta) \quad (10)$$

$$c_Y = c_Y^* \quad (x > \delta) \quad (11)$$

In these equations the symbol δ stays for the diffusion layer thickness that depends on time. Differential equation (3) is integrated from $x = 0$ to $x \rightarrow \infty$ and transformed into the following differential equation:

$$\frac{du}{dt} = 4 - \frac{4}{3} k u^{3/2} + \frac{2u}{c_Y^* - c_{Y,x=0}} \frac{dc_{Y,x=0}}{dt} \quad (12)$$

$$u = \frac{\delta^2}{D} \quad (13)$$

$$k = 0.51 \omega^{3/2} \sqrt{D/\nu} \quad (14)$$

The combination of equations (6) and (8) as well as (5) and (10) give the following results:

$$\Gamma_{Ox} = \frac{\Gamma_{Red}^* \exp(\varphi)}{1 + \exp(\varphi)} \quad (15)$$

$$c_{Y,x=0} = \frac{c_Y^* D}{D + k_f \Gamma_{Ox} \delta} \quad (16)$$

$$\frac{dc_{Y,x=0}}{dt} = - \frac{c_Y^* k_f D}{(D + k_f \Gamma_{Ox} \delta)} \left[\delta \frac{d\Gamma_{Ox}}{dt} + \Gamma_{Ox} \frac{d\delta}{dt} \right] \quad (17)$$

The surface concentration Γ_{Ox} depends only on the electrode potential. The latter is changed in a stepwise manner, for the increment ΔE at the beginning of each step period τ . The current is defined by equation (9). It depends on time because the quantities $c_{Y,x=0}$ and δ are functions of time. The current is measured at the end of the step period. The change of Γ_{Ox} occurring in the beginning of step has no influence on the current [8, 11]. The quantity u changes from zero, for $t = 0$, to the maximum

$$\sqrt{u_{ss}} = \left(\frac{3}{k}\right)^{1/3} \quad (18)$$

that appears under steady state conditions. The equation (12) is solved numerically by the approximation $du/dt \approx \Delta u/\Delta t$. The result of calculations is a dimensionless current ratio:

$$\frac{I}{I_{dif}} = \frac{\lambda \sqrt{u_{ss}} \exp(\varphi)}{1 + \exp(\varphi) + \lambda \sqrt{u} \exp(\varphi)} \quad (19)$$

$$I_{dif} = nFS c_Y^* \sqrt{D/u_{ss}} \quad (20)$$

$$\lambda = k_f \Gamma_{Red}^* / \sqrt{D} \quad (21)$$

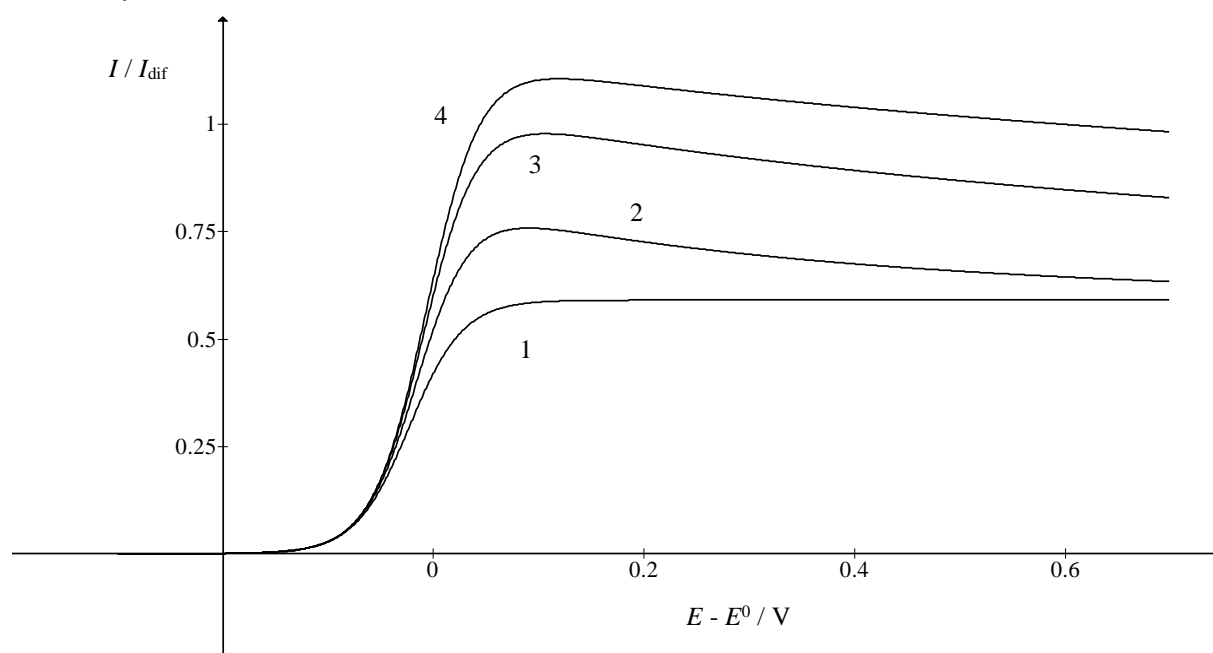


Fig. 1 Staircase voltammograms calculated for various scan rates. $\Delta E = 1$ mV, $n = 1$, $\Delta t = 10^{-5}$ s, $k = 1$ s $^{-3/2}$, $\lambda = 1$ s $^{-1/2}$ and v (V/s) = 0.1 (1), 1 (2), 4 (3) and 10 (4).

3. Results and discussion

Staircase voltammogram of electro-catalytic reaction on the rotating disk electrode is a curve characterized by the maximum and the limiting current. This is shown in Fig. 1. The difference between the maximum and the limiting currents is linearly proportional to the square root of scan rate:

$$\left(\frac{I}{I_{dif}}\right)_{max} - \left(\frac{I}{I_{dif}}\right)_{lim} = 0.18 \sqrt{v} \quad (22)$$

The factor of proportionality applies only for the parameters used in the calculations of Fig. 1, and only for the scan rates higher than 0.5 V/s. The potentials of maxima depend linearly on the logarithm of scan rate:

$$E_{max} - E_{Ox/Red}^0 = 0.029 \log(v) + 0.090 \text{ V} \quad (23)$$

If the scan rate is lower than 0.2 V/s, the maximum disappears and the response resembles the polarographic wave. The limiting current appears under steady state conditions:

$$\lim_{\substack{E \gg E^0 \\ t \rightarrow \infty}} \left(\frac{I}{I_{dif}}\right) = \frac{\lambda(3/k)^{1/3}}{1 + \lambda(3/k)^{1/3}} \quad (24)$$

This equation is the combination of equations (18) and (19).

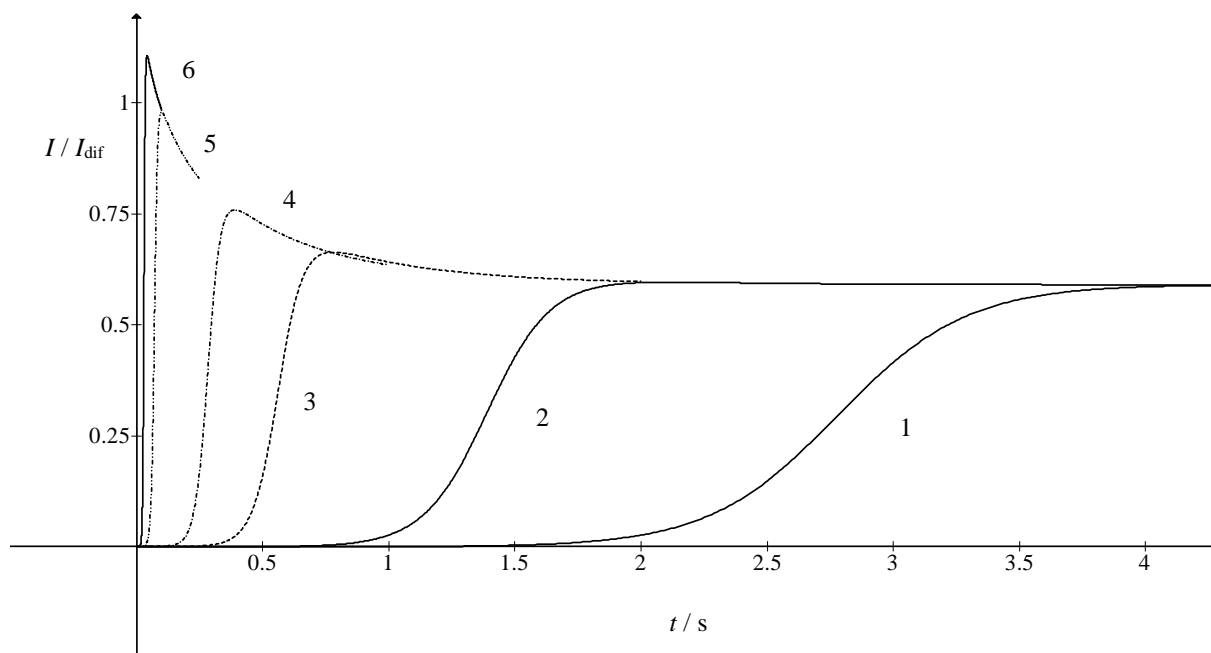


Fig. 2 Voltammograms presented in the current – time form; $v/(V/s) = 0.1$ (1), 0.2 (2), 0.5 (3), 1 (4), 4 (5) and 10 (6). All other data are as in Fig. 1.

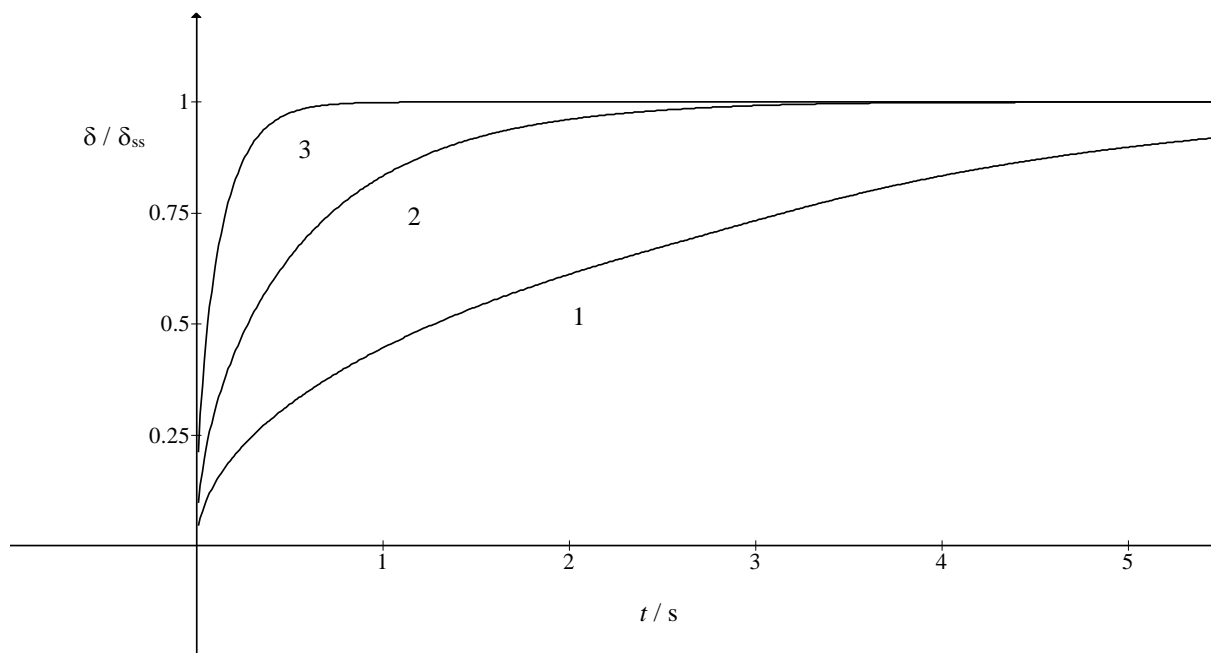


Fig. 3 Relative diffusion layer thickness as a function of time; $v = 0.1$ V/s and $k/s^{-3/2} = 0.1$ (1), 1 (2) and 10 (3). All other data are as in Fig. 1.

The development of the diffusion layer takes time and the responses shown in Fig. 1 can be better compared if the current is reported as a function of time. This can be seen in Fig. 2. If the scan rate is 1 V/s (see curve 4) the maximum appears after 0.391 second and the whole voltammogram is recorded in one second. Within this period the diffusion layer thickness increases to 0.834 of the maximum value. This is shown by the curve 2 in Fig. 3. In the next second the ratio δ/δ_{ss} increases to 0.961 . Hence, below two seconds the transient conditions prevail if $k = 1$ s^{-3/2}. Furthermore, if $v = 0.1$ V/s (see curve 1 in Fig. 2) the response starts to develop after 1.5 s and reaches the limiting value after 4 s. In this period $\delta \approx \delta_{ss}$ and the conditions are close to the steady state. So, no maximum appears. If, however, the scan rate is increased to 0.2 V/s (curve 2), the response is developed

between 1 and 2 seconds and a small maximum (0.596 comparing to the limiting value 0.590) appears after 2.12 seconds.

Looking at Fig. 3, one can propose an empirical rule for the appearance of maxima in voltammograms. If $k = 1 \text{ s}^{-3/2}$ the steady state conditions are established after 3 seconds. If the starting potential is 0.3 V lower than the standard potential, the time that is needed to scan over this 0.3 V is $0.3/\nu$ and this time must be smaller than 3 seconds for the maximum to appear: $0.3/\nu < 3$ and $\nu > 0.1 \text{ V/s}$. If $k = 0.1 \text{ s}^{-3/2}$ the transient conditions last 7 seconds and the rule is $0.3/\nu < 7$ and $\nu > 0.04 \text{ V/s}$. If $k = 10 \text{ s}^{-3/2}$ the steady state is established after 0.4 seconds and the voltammograms with maxima appears if $\nu > 0.75 \text{ V/s}$.

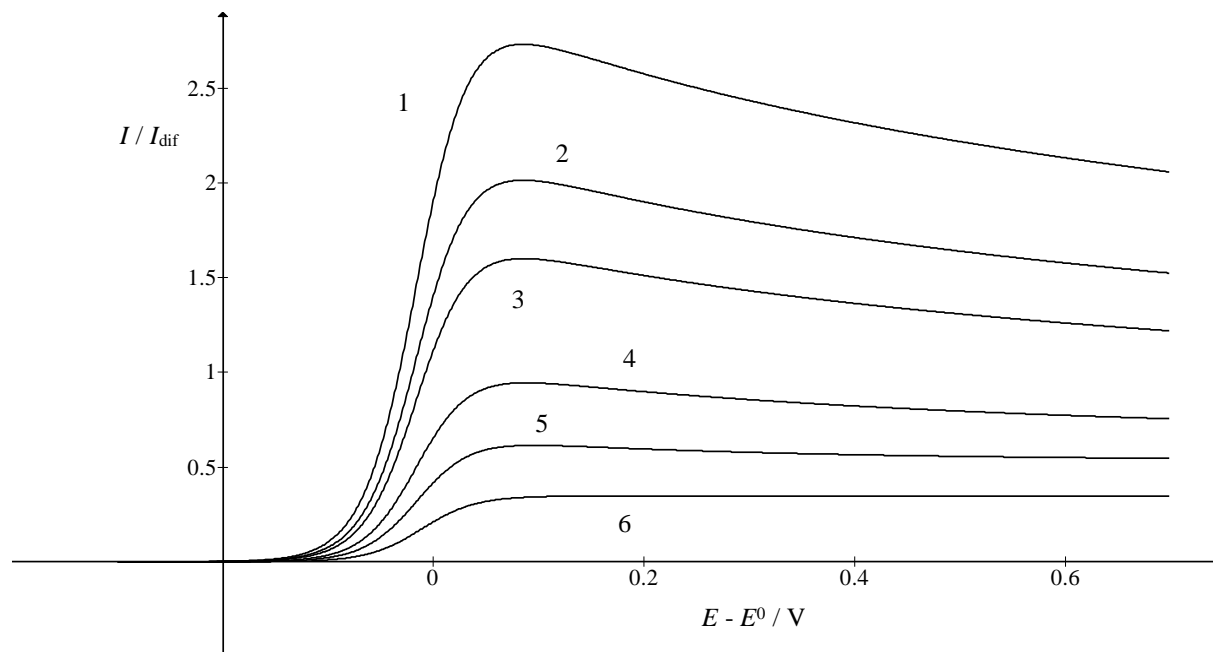


Fig. 4 Influence of the rotation rate on the voltammograms; $\nu = 1 \text{ V/s}$ and $k/s^{-3/2} = 0.02$ (1), 0.05 (2), 0.1 (3), 0.5 (4), 2 (5) and 20 (6). All other data are as in Fig. 1.

Partial confirmation of this proposition can be found in Fig. 4 which shows voltammograms recorded at the same scan rate, but different rotation rates. For $k = 20 \text{ s}^{-3/2}$ the response is a wave although $\nu = 1 \text{ V/s}$. Very small maximum (0.405 comparing to the limiting 0.401) appears if $k = 10 \text{ s}^{-3/2}$, which is similar to the curve 2 in Fig. 2 and satisfies the prediction. With the diminishing values of k both the maximum and limiting currents increase, as well as the difference between them, but the potentials of maxima do not change. The net peak currents satisfy the following relationship:

$$\log \left[\left(\frac{I}{I_{dif}} \right)_{max} - \left(\frac{I}{I_{dif}} \right)_{lim} \right] = -0.66 \log(k) - 0.774 \quad (25)$$

This means that this difference is inversely proportional to the rotation rate:

$$\left(\frac{I}{I_{dif}} \right)_{max} - \left(\frac{I}{I_{dif}} \right)_{lim} = 0.27 (\nu/D)^{1/3} \omega^{-1} \quad (26)$$

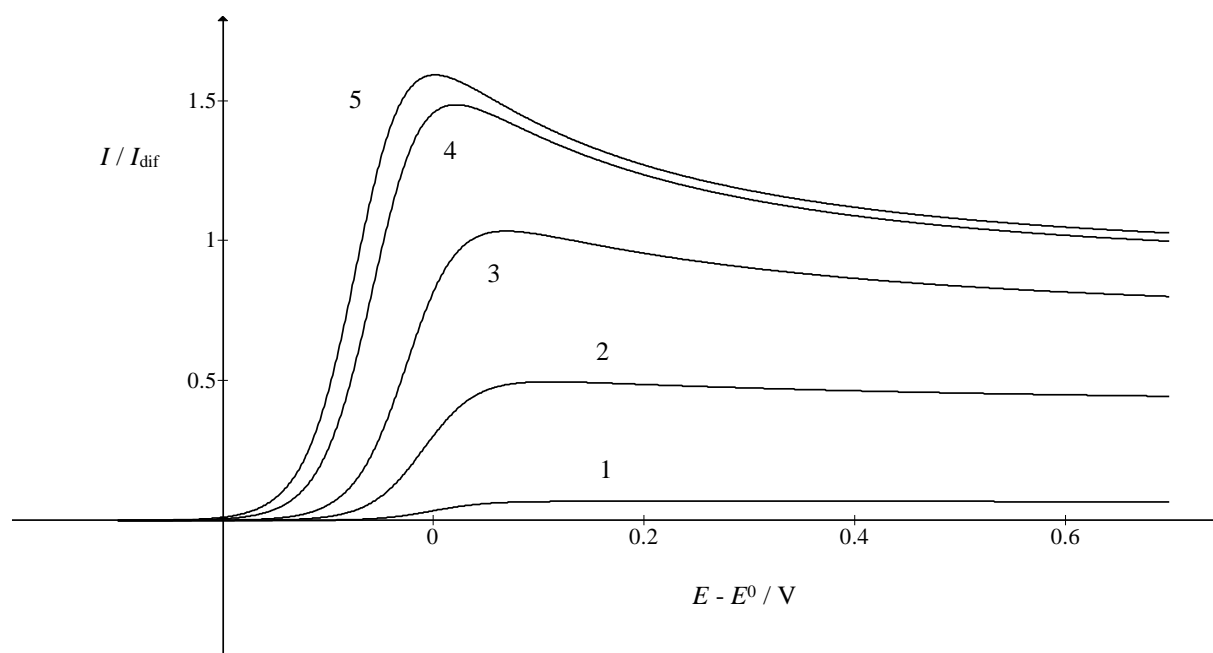


Fig. 5 Influence of the kinetics of catalytic oxidation on the staircase voltammograms; $v = 1$ V/s and $\lambda/s^{-1/2} = 0.05$ (1), 0.5 (2), 2 (3), 10 (4) and 20 (5). All other data are as in Fig. 1.

The influence of the rate constant λ is shown in Fig. 5. These results compare either different catalytic reactions (k_f) or different experimental conditions (Γ_{Red}^*). The parameter λ determines the limiting currents primarily, as can be seen in eq. (24). For instance, $(I/I_{dif})_{lim} > 0.9$ if $k = 1$ s^{-3/2} and $\lambda > 6.25$ s^{-1/2}. However, this parameter defines the transient currents as well because it influences the development of the diffusion layer (see eq. 12 and 17). If $\lambda < 0.1$ s^{-1/2} the response is a wave at the scan rate of 1 V/s. If $\lambda < 2$ s^{-1/2} the net peak current $(I/I_{dif})_{max} - (I/I_{dif})_{lim}$ is directly proportional to the increasing λ value, but if $\lambda > 5$ s^{-1/2} the current increases with $\lambda^{0.2}$. The potentials of maxima depend linearly on the logarithm of λ :

$$E_{max} - E_{Ox/Red}^0 = -0.068 \log(\lambda) + 0.090 \text{ V} \quad (27)$$

In the staircase voltammetry transient currents originate from the electro-catalytic reaction entirely, while in the linear scan voltammetry they are mixed with the oxidation current of adsorbed catalyst [15]. This is the main difference between these two techniques if the electrode reaction of catalyst appears fast and reversible at any scan rate. Under the influence of kinetics of surface electrode reaction, the response in the staircase voltammetry includes more or less surface current [8] and the above mentioned difference is diminished.

As the staircase voltammetry is insensitive to capacitive and pseudo-capacitive currents, it is very probable that generally the maximum current is linearly proportional to the bulk concentration of the compound Y and that this straight line passes through the origin:

$$I_{max} = \frac{nFS\lambda\sqrt{D} \exp(\varphi_{max})}{1 + \exp(\varphi_{max}) + \lambda\sqrt{u_{max}} \exp(\varphi_{max})} c_Y^* \quad (28)$$

For these reasons the maximum current can be used for the determination of unknown concentration of Y by the standard addition method. The limiting current can be also used for this purpose, but the amperometric constant of maxima is higher.

4. Conclusions

The investigated transient currents appear in the form of maxima that are linearly proportional to the bulk concentration of substrate. The net peak currents depend linearly on the square root of scan rate and on the inverse value of the rotation rate. Also, they are exponential function of the rate constant of catalytic reaction. The peak potentials are linear functions of logarithms of scan rate and the catalytic reaction rate constant. These responses can be used for the analytical purpose.

Dedication

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

Conflict of interest

No conflict of interest is declared.

Data availability statement

All relevant data are available on demand.

References

1. J. H. Christie, P. J. Lingane, *J. Electroanal. Chem.* 10 (1965) 176. (doi.org/10.1016/0022-0728(65)85021-5)
2. G. Jasinski, A. Strzelczyk, B. Chachulski, P. Jasinski, *Procedia Engineering* 47 (2012) 1422. (doi.org/10.1016/j.proeng.2012.09.424)
3. C. Montella, *J. Electroanal. Chem.* 808 (2018) 348. (doi.org/10.1016/j.jelechem.2017.12.016)
4. M. Saralathan, R. Osteryoung, J. Osteryoung, *J. Electroanal. Chem.* 214 (1986) 141. (doi.org/10.1016/0022-0728(86)80093-6)
5. R. Kant, *Electrochim. Acta* 111 (2013) 223. (doi.org/10.1016/j.electacta.2013.07.163)
6. E. Laborda, J. Gonzalez, A. Molina, *Electrochem. Commun.* 43 (2014) 25. (doi.org/10.1016/j.elecom.2014.03.004)
7. R. Gulaboski, P. Kokoškarova, S. Mitrev, *Electrochim. Acta* 69 (2012) 86. (doi.org/10.1016/j.electacta.2012.02.086)
8. Š. Komorsky-Lovrić, M. Lovrić, *Electroanalysis* 8 (1996) 959. (doi.org/10.1002/elan.1140081022)
9. C. Montella, *J. Electroanal. Chem.* 796 (2017) 96. (doi.org/10.1016/j.jelechem.2017.04.048)
10. D. Jadreško, M. Zelić, M. Lovrić, *J. Electroanal. Chem.* 645 (2010) 103. (doi.org/10.1016/j.jelechem.2010.04.016)
11. M. Lovrić, Š. Komorsky-Lovrić, *To Chem. J.* 1 (2018) 370.
12. R. Gulaboski, S. Petkovska, *Anal. Bioanal. Electrochem.* 10 (2018) 566.
13. V. Mirčeski, R. Gulaboski, *J. Solid State Electrochem.* 7 (2003) 157. (doi.org/10.1007/s10008-002-0290-7)
14. A. Molina, C. Serna, J. Gonzalez, *J. Electroanal. Chem.* 454 (1998) 15. (doi.org/10.1016/S0022-0728(98)00251-4)
15. M. Lovrić, M. Branica, *Electrochim. Acta* 28 (1983) 1261. (doi.org/10.1016/0013-4686(83)85014-2)