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ANODIC AND CATHODIC COMPONENTS OF CURRENTS OF QUASIREVERSIBLE ELECTRODE REACTIONS ON ROTATING DISK ELECTRODES UNDER STEADY-STATE CONDITIONS[1]

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In a rotating disk electrode setup at constant potential, the current of a simple redox reaction becomes time-independent under steady-state conditions. This steady-state current can be expressed as a sum of two components, according to Butler-Volmer kinetics. While these components cannot be measured experimentally, they can be calculated using simple formulae based on the formal potential of the electrode reaction, which can be determined from the potential of zero current on the steady-state current-potential curve. The components can then be used to measure the transfer coefficients of quasireversible electrode reactions.

Keywords: Tafel analysis; steady-state current; anodic and cathodic components; rotating disk electrode; kinetics of electrode reactions

АНОДНА И КАТОДНА КОМПОНЕНТА НА СТРУЈАТА НА КВАЗИРЕВЕРЗИБИЛНИ ЕЛЕКТРОДНИ РЕАКЦИИ НА РОТИРАЧКА ЕЛЕКТРОДА ВО ВРЕМЕНСКИ НЕПРОМЕНЛИВИ УСЛОВИ

Во услови на константен потенцијал приложен на ротирачка електрода, струјата како резултат на електродна реакција е временски непроменлива. Според кинетичкиот модел на Батлер-Фолмер, оваа временски независна струја може да се прикаже како сума од две компоненти. Иако не може овие струјни компоненти експериментално да се измерат, тие можат да се пресметаат врз основа на едноставна формула, користејќи го формалниот потенцијал на редокс-парот, кој пак може да се определи од потенцијалот при кој струјата има нула вредност. Струјните компоненти можат да се искористат за мерење на коефициентите на пренос на квазиреверзибилни електродни реакции.

Клучни зборови: Тафелов график; временски независна струја; анодна и катодна компонента; ротирачка електрода; кинетика на електродни реакции

1. INTRODUCTION

A modern voltammogram consists of a set of pairs of numbers representing current as a function of potential or time.[1–4] It can be numerically analyzed to obtain thermodynamic and kinetic parameters of the given electrode reaction.[5–7] In previous papers, we described methods for separating the anodic and cathodic current components in staircase voltammetry,[8] simple linear sweep voltammetry,[9] and conventional cyclic voltammetry.[10] These procedures required semi-integration of the

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current and prior knowledge of the formal potential of the studied redox couple. In this communication, we show that the components of steady-state chronoamperograms can be directly obtained by multiplying with functions of the formal potential of the investigated reaction.

2. THE MODEL

A simple quasireversible electrode reaction involving dissolved reactant and product at a constant potential on the rotating disk electrode is considered:

$$\mathrm{Ox}^{m+} + ne^{-} \leftrightarrow \mathrm{Red}^{(m-n)+} \tag{1}$$

Under steady-state conditions, the current is defined by the following equations:[11,12]

$$D\,\frac{c_{Ox}^{*}-c_{Ox}(0)}{\delta_{ss}} = -\frac{I_{ss}}{nFS} \tag{2}$$

$$D\,\frac{c_{Red}^{*}-c_{Red}(0)}{\delta_{ss}} = \frac{I_{ss}}{nFS} \tag{3}$$

$$\frac{I_{ss}}{nFS} = -k_s e^{-\alpha\varphi}\left[c_{Ox}(0) - c_{Red}(0)\, e^{\varphi}\right] \tag{4}$$

$$\varphi = \frac{nF}{RT}\left(E - E^{0}\right) \tag{5}$$

$$\delta_{ss} = 1.61 D^{1/3} \nu^{1/6} \omega^{-1/2} \tag{6}$$

The symbols c_{Ox}^{*} and c_{Red}^{*} represent the bulk concentrations of the reactant and product and $c_{Ox}(0)$ and $c_{Red}(0)$ are their concentrations at the electrode surface, α is the transfer coefficient, D is the common diffusion coefficient, δ_{ss} is the steady-state diffusion layer thickness, E is the potential, E^{0} is the formal potential, F is the Faraday constant, I_{ss} is the steady-state current, k_s is the standard rate constant, n is the number of electrons, ν is the kinematic viscosity, R is the gas constant, S is the electrode surface area, T is the temperature, and ω is the rotation rate of the electrode. The solution to Eqs. 2 through 4 gives the well-known sigmoidal current-potential relationship:[13]

$$\Phi_{ss} = \frac{\lambda e^{-\alpha\varphi}\left[\frac{c_{Red}^{*}}{c_{Ox}^{*}} e^{\varphi} - 1\right]}{1 + \lambda e^{-\alpha\varphi}\left(1 + e^{\varphi}\right)} \tag{7}$$

$$\Phi_{ss} = \frac{I_{ss}\delta_{ss}}{nFSDc_{Ox}^{*}} \tag{8}$$

$$\lambda = \frac{k_s \delta_{ss}}{D} \tag{9}$$

The anodic and cathodic components of the current depend on the dimensionless kinetic parameter λ:

$$\Phi_a = \lambda e^{(1-\alpha)\varphi}\left[\frac{c_{Red}^{*}}{c_{Ox}^{*}} - \Phi_{ss}\right] \tag{10}$$

$$\Phi_c = -\lambda e^{-\alpha\varphi}\left(1 + \Phi_{ss}\right) \tag{11}$$

However, the ratio Φ_a/Φ_c is independent of the kinetics, and the components can be calculated directly from the current if the formal potential is known:

$$\Phi_a = \frac{e^{\varphi}\left[\frac{c_{Red}^{*}}{c_{Ox}^{*}} - \Phi_{ss}\right]\Phi_{ss}}{e^{\varphi}\left[\frac{c_{Red}^{*}}{c_{Ox}^{*}} - \Phi_{ss}\right] - (1 + \Phi_{ss})} \tag{12}$$

$$\Phi_c = \frac{-(1 + \Phi_{ss})\Phi_{ss}}{e^{\varphi}\left[\frac{c_{Red}^{*}}{c_{Ox}^{*}} - \Phi_{ss}\right] - (1 + \Phi_{ss})} \tag{13}$$

Note that the current is independent of time. The relationship between current and potential is measured using the point-by-point method, with each point corresponding to a different potential.

3. RESULTS AND DISCUSSION

The current-potential relationship defined by Eq. 7 is characterized by the limiting values:

$$\lim_{E \gg E^{0}} \Phi_{ss} = c_{Red}^{*}/c_{Ox}^{*} \text{ and } \lim_{E \ll E^{0}} \Phi_{ss} = -1$$

and by the potential of zero current:

$$E_0 = E^{0} + \frac{RT}{nF} ln\left(c_{Ox}^{*}/c_{Red}^{*}\right).$$

This is shown as the curve (1) in Figure 1, and cathodic component is defined by Eqs. 11 and 13, shown as curve (3) in Figure 1. It changes from $\Phi_c = 0$ for $E \gg E^{0}$ to $\Phi_c = -1$ for $E \ll E^{0}$. This change is because the term in brackets in Eq. 11 tends to zero at lower potentials. The anodic component, shown by curve (2) and defined by Eqs. 10 and 12, has limits of 0.5 for $E \gg E^{0}$ and zero for $E \ll E^{0}$, with a maximum at 0.048 V vs. E^{0}, caused by the term in brackets in Eq. 10.

These terms in brackets can be obtained experimentally and applied to the calculation of the cathodic and anodic components of the wave using Eqs. 12 and 13. Tafel analysis can be performed on the ratio of current component to the corresponding term in brackets. The analysis involves the relationship between the logarithm of this ratio and the potential,[8] and the resulting plot is a straight line with a slope proportional to the transfer coefficient.

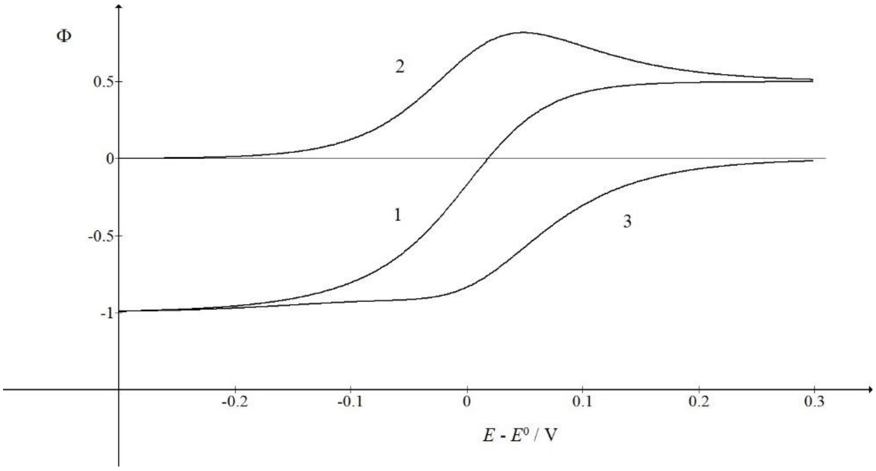

Fig. 1. Dependence of dimensionless chronoamperometric steady-state current (1) and its anodic (2) and cathodic (3) components on the electrode potential; $n = 1$, $\alpha = 0.4$, $c^*_{Red}/c^*_{Ox} = 0.5$, and $\lambda = 1$

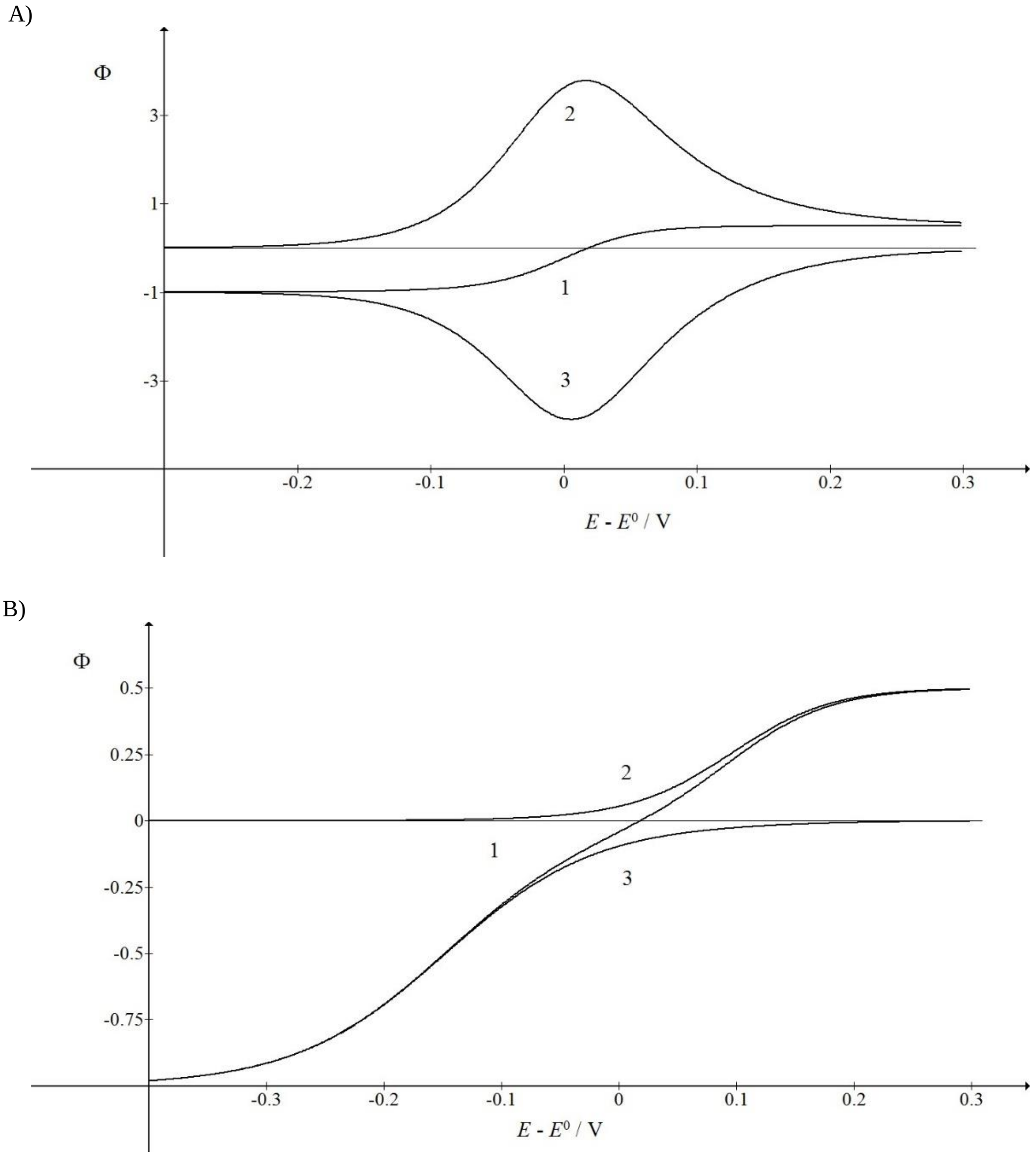

Fig. 2. The steady-state current-potential curve (1) and its anodic (2) and cathodic (3) components; $\lambda = 5$ (A) and 0.1 (B). All other parameters are as in Figure 1.

Figure 2 illustrates the influence of the kinetic parameter λ on the shape of the current components. When $\lambda = 5$, a minimum in the cathodic component and a maximum in the anodic component appear. The maximum in the anodic component is five times higher than that in Fig. 1, which aligns with previous observations.[8] The absolute values of these extremes increase with increasing λ, but tend to infinity when $\lambda > 100$. It is important to note that $\lambda = 1$ corresponds to $k_s = 10^{-2}$ cm/s, assuming $\delta_{ss} = 10^{-3}$ cm and $D = 10^{-5}$ cm^2/s. This value of k_s is characteristics of nearly all reversible electrode reactions, and Fig. 2A shows the transformation at the upper limit of the applicability of Butler-Volmer kinetics.

For electrode reactions that obey the Nernst equation under steady-state conditions, these components are not defined. Therefore, the maxima and minima of the components in quasireversible reactions can tend to infinity near the equilibrium potential if the rate constant is increased. However, Eqs. 10 and 11 show that ln λ does not affect the slope of the Tafel plot of the components.

If the electrode reaction is ten times slower than in Figure 1, the components exhibit simple wave-like current-potential curves that are suitable for Tafel analysis. As the wave begins to separate into the anodic (upper part) and cathodic (lower part) components, these components overlap the wave over a wider potential range. In this case, a completely irreversible chronoamperogram contains only one component.

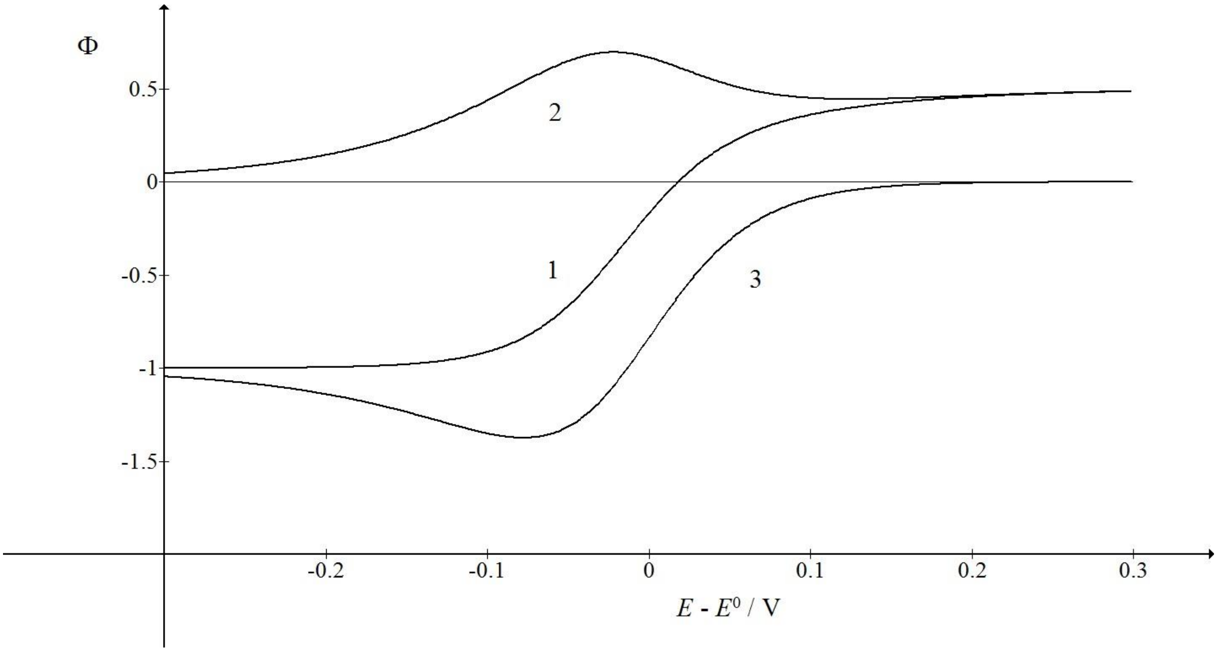

Fig. 3. The steady-state wave (1) and its anodic (2) and cathodic (3) components; $\alpha = 0.7$. All other data are as in Figure 1.

The influence of the transfer coefficient is shown in Fig. 3. Comparing to Figure 1, a minimum appears in the cathodic component because, at this degree of asymmetry, the reduction occurs faster than in the reverse case ($\alpha = 0.4$). Finally, the response calculated for the absence of the product in the bulk electrolyte and for symmetrical electron transfer is shown in Figure 4. The limiting currents of the wave and the cathodic component are zero and –1, respectively, with no minimum observed in the latter one. The anodic component starts and ends at zero, with a maximum at the formal potential.

The limiting currents of the steady-state chronoamperogram can be used to estimate the diffusion coefficients of the reactant and product, while the potential of zero current serves as a means to determine the formal potential of the electrode reaction. This formal potential is essential for calculating the anodic and cathodic components of the response. In addition to repetitive chronoamperometry, the current-potential curve can be recorded using very slow staircase voltammetry, ensuring that the steady-state conditions are maintained.[14]

For experimental verification of the proposed methodology, it has been successfully demonstrated with the electrooxidation of hexacyanoferrate(II) ions on a platinum electrode[8] and the electroreduction of the hexaammineruthenium(III) complex ions on a glassy carbon electrode.[10] The rotating disk electrode is considered here as a tool for obtaining steady-state responses, which can be analyzed directly without requiring semi-integration, rather than as the primary experimental tool.

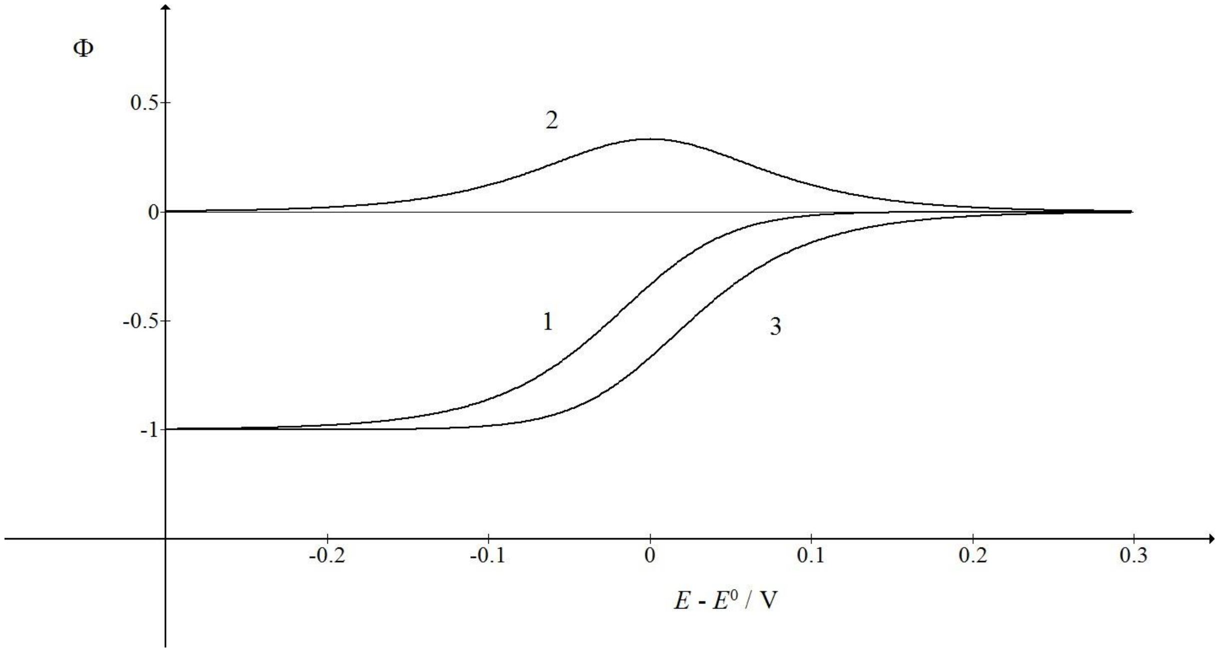

Fig. 4. The steady-state wave (1) and its anodic (2) and cathodic (3) components; $\alpha = 0.5$ and $c_{Red}^{*} = 0$. All other data are as in Figure 1.

4. CONCLUSIONS

In chronoamperometry using a rotating disk electrode, the current decreases with time until a steady state is established, where the current becomes independent of time. By repeating this measurement at various potentials, a wave-like steady-state response can be recorded. This response can be considered the sum of anodic and cathodic components, as described by Butler-Volmer kinetics. Since the ratio of these components is independent of kinetic parameters, they can be explicitly expressed as functions of the net current and the electrode potential.

These explicit functions provide a deeper understanding of similar relationships in cyclic voltammetry and other electrochemical techniques. The current calculations show conditions suitable for Tafel analysis and illustrate how the form of the components evolves as the rate constant of the electrode reaction increases.

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REFERENCES

(1) A. V. Oppenheim, R. W. Schafer, *Discrete Time Signal Processing*. Prentice Hall, New Jersey, USA, 1999.

(2) H. H. Willard, L. L. Merritt, J. A. Dean, F. A. Settle, *Instrumental Methods of Analysis*. Wadsworth, California, USA, 1988.

(3) O. Smutok, E. Katz, Electroanalytical instrumentation – how it all started: history of electrochemical instrumentation. *J. Solid State Electrochem*. **2024**, *28*, 683–710. https://doi.org/10.1007/s10008-023-05375-3

(4) P. J. T. Morris, The history of chemical laboratories: a thematic approach. *ChemTexts* **2021**, ***7***, 21. https://doi.org/10.1007/s40828-021-00146-x

(5) K. B. Oldham, How Grünwald unified and generalized the calculus, and how his discovery helps electrochemists. *ChemTexts*, **2018**, *4*, 1. https://link.springer.com/article/10.1007/s40828-017-0055-7

(6) P. J. Mahon, K. B. Oldham, Convolutive modelling of electrochemical processes based on the relationship between the current and the surface concentration. *J. Electroanal. Chem*. **1999**, *464*, 1–13. https://doi.org/10.1016/S0022-0728(98)00450-1

(7) J. Gonzalez, E. Laborda, A. Molina, Voltammetric kinetic studies of electrode reactions: guidelines for detailed understanding of their fundamentals. *J. Chem. Educ*. **2023**, *100*, 697–706. https://doi.org/10.1021/acs.jchemed.2c00944?urlappend=%3Fref%3DPDF&jav=VoR&rel=cite-asV.

(8) V. Mirceski, M. Lovric, R. G. Compton, N. Ullah, Revisiting the Butler – Volmer electrode kinetics: separating the anodic and cathodic current components of a quasi-reversible electrode reaction in staircase voltammetry. *J. Electroanal. Chem*. **2024**, *957*, 118111. http://dx.doi.org/10.1016/j.jelechem.2024.118111

(9) V. Mirceski, M. Lovric, Genuine differential voltammetry. *Talanta* **2024**, *279*, 126560. https://doi.org/10.1016/j.talanta.2024.126560

(10) V. Mirceski, D. Guziejewski, R. Gulaboski, Genuine anodic and cathodic current components in cyclic voltammetry. *Sci. Rep*. **2024**, *14*, 17314. https://doi.org/10.1038/s41598-024-67840-x

(11) H. Chen, E. Kätelhön, R. G. Compton, Rotating disk electrodes beyond the Levich approximation. Physics-informed neural networks reveal and quantify edge effects. *Anal. Chem*. **2023**, *95*, 12826–12834. https://doi.org/10.1021/acs.analchem.3c01936?urlappend=%3Fref%3DPDF&jav=VoR&rel=cite-as

(12) R. Saravanakumar, P. Pirabaharan, L. Rajendran, The theory of steady state current for chronoamperometric and cyclic voltammetry on rotating disk electrodes for EC' and ECE reactions. *Electrochim. Acta* **2019**, *313*, 441–456. https://doi.org/10.1016/j.electacta.2019.05.033

(13) Z. Galus, Fundamentals of electrochemical analysis, Ellis Horwood, New York, and Polish Scientific Publ., Warsaw, 1994.

(14) F. Opekar, P. Beran, Rotating disk electrodes. *J. Electroanal. Chem*. **1976**, *69*, 1–105.