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ELECTRODE KINETICS FROM A SINGLE SQUARE-WAVE VOLTAMMOGRAM[♦]

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A novel methodological approach for processing electrochemical data measured under conditions of square-wave voltammetry (SWV) is proposed. The methodology takes advantage of the chronoamperometric characteristics of the electrochemical system observed in the course of the voltammetric experiment, which are commonly not considered in conventional SWV. The method requires processing of a single voltammogram only, measured under given set of the potential modulation parameters (i.e. SW frequency and height of the potential pulses). The core idea is to analyze the variation of the current with time, considering the last quarter time period of each potential pulse of the potential modulation, instead of measuring the single current value from the very end of the pulses. Hence, a single point current measurement is replaced with a multisampling current procedure, leading to a series of new SW voltammograms measured at different time increments of each potential pulse. The novel method is illustrated by the theoretical analysis of a quasireversible electrode reaction of a dissolved and surface confined redox couple, as well as a reversible electrode reaction preceded by a chemical equilibrium reaction (C_rE_r mechanism).

Keywords: square-wave voltammetry; electrode kinetics; chronoamperometry; simulations

ОПРЕДЕЛУВАЊЕ НА КИНЕТИКАТА НА ЕЛЕКТРОДНИ РЕАКЦИИ ОД ЕДИНИЧЕН КВАДРАТНОБРАНОВ ВОЛТАМОГРАМ

Во овој труд е предложен нов метод за процесирање на податоците од електрохемиските мерења во услови на квадратнобранова волтаметрија. Методот се базира на хроноамперометриските својства на електрохемиските системи што се забележуваат во текот на волтаметрискиот експеримент, а кои најчесто не се разгледуваат во конвенционалната квадратнобранова волтаметрија. Методот подразбира процесирање на единичен волтамограм што е измерен при дадени инструментални параметри (квадратнобранова фреквенција и амплитуда). Главната идеја на овој пристап е да се анализираат промените во измерената струја како функција од времето, притоа земајќи ја предвид само последната четвртина од временскиот интервал на секој потенцијален пулс, наместо мерењето на единична вредност на струјата на крајот од секој потенцијален пулс. На овој начин класичната процедура во квадратнобрановата волтаметрија на мерење на струјата во една точка се заменува со повеќекратно мерење на струјата, што резултира со серија волтамограми измерени во различни временски интервали од секој потенцијален пулс. Новиот метод е тестиран преку теоретска анализа на волтамограмите на квазиреверзибилна електродна реакција симулирана за електродни реакции што се одвиваат од растворена и атсорбирана состојба на учесниците во електродната реакција, како и на реверзибилна електродна реакција што е поврзана со претходна хемиска реакција (C_rE_r механизам).

Клучни зборови: квадратнобранова волтаметрија; кинетика на електродни реакции; хроноамперометрија; теоретски симулации

[♦] Dedicated to Academician Gligor Jovanovski on the occasion of his 70th birthday.

1. INTRODUCTION

Square-wave voltammetry (SWV) is a well established electroanalytical technique in the family of pulsed voltammetric techniques attributed with superior performances from both analytical and electrokinetic perspectives [1–6]. As could be deduced from the shape of the potential modulation (Fig. 1A) and the current sampling procedure in the course of a single potential cycle (Fig. 1B), SWV could be seen as a repetitive double-step chronoamperometric technique, as at each step of the staircase ramp, two equal, oppositely directed potential pulses are imposed. Yet, though the current variation could be monitored in the whole duration of the voltammetric experiment (Fig. 1C), the current is sampled only at the end of each potential pulse (Fig. 1B) in order to construct the conventional SW voltammogram, as presented in Figure 1D. The strategy to sample the current at the end of a potential pulse is well justified as it is a means to discriminate against the charging current and to enhance the noise-to-signal ratio as a critical determinant of the sensitivity of any analytical technique. Besides, calculation of a net component (Ψ_{net}) of the SW voltammetric response as a difference between the measured forward (Ψ_f) and backward (Ψ_c) voltammetric component (Fig. 1D) further participates in the enhanced sensitivity of the technique. On the other hand, similar to cyclic voltammetry, the forward and backward voltammetric components (Fig. 1D) provide mechanistic information on the studied electrode reaction.

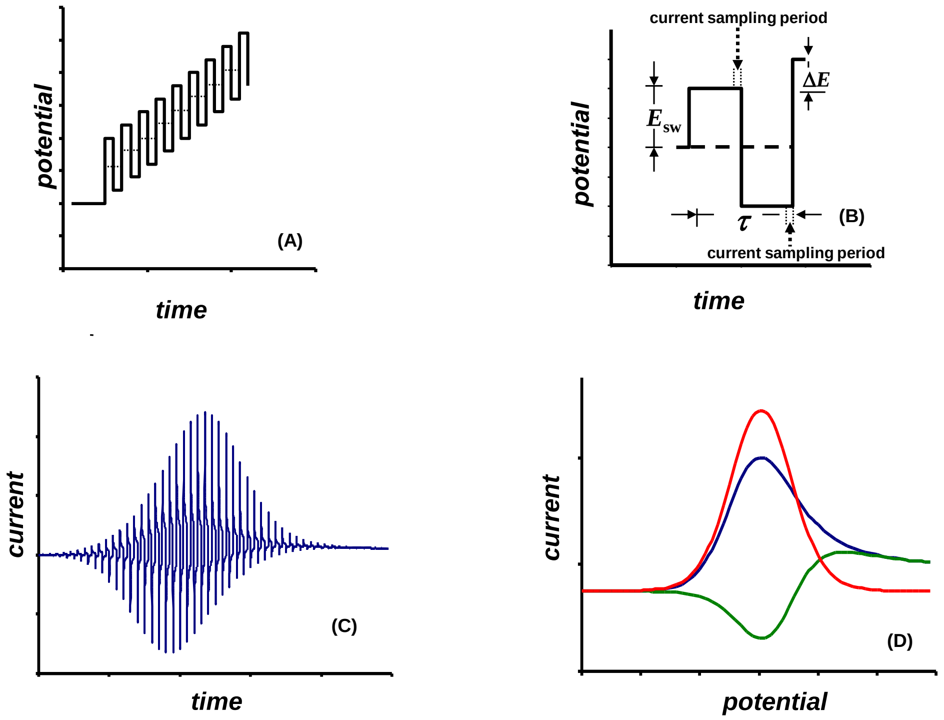

Fig. 1. (A) Potential waveform, **(B)** single potential cycle, **(C)** variation of the current with time and **(D)** typical dimensionless voltammogram in square-wave voltammetry. The dimensionless response in (D) consists of a forward (Ψ_f –blue line), backward (Ψ_b – green line) and net (Ψ_{net} – red line) component.

When applied for mechanistic [7–11] and electrokinetic studies [12–16], SWV is most frequently conducted by varying the frequency (*f*) of the potential modulation, as the most critical time parameter of the voltammetric experiment, determining the duration of a single potential cycle τ ($f = 1/\tau$), during which the studied electrode reaction is shifted in both anodic and cathodic directions. Together with the step potential (ΔE, cf. Fig. 1B), the frequency determines scan rate (v) of the staircase potential ramp ($v = f\,\Delta E$), hence the overall time of the voltammetric experiment. We have, however, recently demonstrated that kinetic measurements are even possible at a constant time of the voltammetric experiment only by virtue of the potential pulses height (i.e. the SW amplitude, E_{sw}, cf. Fig. 1B) variation [15, 16]. The latter methods revealed how versatile SWV is, from both mechanistic and electrokinetic point of view.

A careful analysis of the theory of SWV revealed that a variety of electrode mechanisms are attributed with unique, frequently peculiar, voltammetric features, originating mainly from specific chronoamperometric characteristics of studied electrode reactions [17–19] combined with the current sampling procedure in SWV. A typical example is the so called “quasireversible maximum” of surface confined [20, 21] and adsorption complicated electrode mechanisms [22–24], where the maximum of the frequency normalized voltammetric response is achieved for quasireversible processes with a moderate rate of the charge transfer reaction. Another example is the splitting of the response of fast surface confined electrode processes [25], or processes occurring in a limiting diffusion space [26], where the relative position of the anodic and cathodic SW voltammetric components is opposite compared to the typical voltammetric pattern observed under conditions of cyclic voltammetry [27]. Moreover, the most peculiar voltammetric feature was observed for adsorption complicated EC_i mechanism [18, 19], where the backward voltammetric component, affected by the irreversible follow-up chemical reaction (i.e. C_i step), increases by accelerating the chemical reaction, being completely opposite to the common cyclic voltammetric behaviour.

Given the high sensitivity of SWV to the chronoamperometric characteristics of a studied electrode reaction, it is reasonable to assume that more detailed analysis of the current variation with time in the course of potential pulses will be beneficial for electrokinetic purposes. In the present communication a novel and simple methodological approach for analyzing SW voltammetric data is proposed based on the analysis of the current variation with time, considering the last portion of each potential pulse. As will be demonstrated, a wealth of kinetic information could be derived from the chronoamperometric analysis of a SW voltammogram, enabling estimation of the electrode kinetics from a single voltammogram. The proposed methodology is illustrated by a theoretical analysis of a quasireversible electrode reaction of a dissolved redox couple, surface confined electrode reaction, and an electrode reaction coupled with a preceding chemical reaction, i.e. an C_rE_r mechanism.

2. RESULTS AND DISCUSSION

A quasireversible electrode reaction of two chemically stable, dissolved (sol) redox species (Ox/Red) at a planar macroscopic electrode is considered (eq. 1). The mathematical modelling and the solution for numerical simulations are given elsewhere [1, 3, 5].

$$\mathrm{R(sol)} \leftrightarrow \mathrm{O(sol)} + ne^- \qquad (1)$$

Theoretical results are presented in a form of dimensionless current defined as $\Psi = I(nFAc^*)^{-1}(Df)^{-0.5}$, where I is the current, n is the number of exchanged electrons, A is the electrode surface area, c^* is the bulk concentration of initially present Red species, D is the common diffusion coefficient for both Ox and Red, and f is the frequency of the potential modulation. Voltammetric features of the system are well known [1, 3, 5, 15], being predominantly determined by the electrode kinetic parameter $\kappa = \frac{k_s}{\sqrt{Df}}$, which relates the rate of the electrode reaction, represented by the standard rate constant k_s (cm s^{-1}), with the diffusion rate ($\sqrt{Df}$). Net peak currents of conventional SW voltammograms ($\Delta\Psi_p$) depend sigmoidally on $\log(\kappa)$. For a normalized amplitude of nE_{sw} = 50 mV, $\Delta\Psi_p$ increases linearly with $\log(\kappa)$ over the interval $-0.7 \le \log(\kappa) \le -0.2$ [15]. The latter kinetic region can be used for estimation of the standard rate constant k_s. To this goal, a series of SW voltammograms need to be recorded by varying the SW frequency, which affects the value of the electrode kinetic parameter ($\kappa = \frac{k_s}{\sqrt{Df}}$), keeping in mind that k_s and D are typical constants for a single electrode reaction under given experimental conditions.

In the present methodology only a single voltammogram is required for kinetic analysis of the system. Specifically, a single voltammogram is simulated for a given set of kinetic parameters (k_s, D, and electron transfer coefficient α) and constant values of the potential modulation parameters (f, E_{sw} and ΔE). However, instead of applying a common single-sampling procedure and using the current from the very end of each potential pulses to construct a conventional SW voltammogram, all currents measured at the last quarter portion of each potential pulse are considered. Purposely, in the present simulations each potential pulse is divided into 50 time increments and a multisampling current procedure is conducted in order to use all currents from the last ten time increments. In other words, the currents are measured at 40th, 41st, 42nd etc. up to the last 50th time increment. Corresponding SW voltammograms, constructed out of the currents measured at different time increments, are shown in Figure 2A. Obviously, the voltammogram corresponding to the 50th time increment is the conventional SW voltammogram. As shown in Fig. 2A, new net SW voltammograms diminish with the time increments as a consequence of the chronoamperometric characteristics of the system, reflecting the diminishing of the current with time during each potential pulse. On the other hand, all net voltammograms shown on Figure 2A are identical with respect to the peak potential and half-peak width.

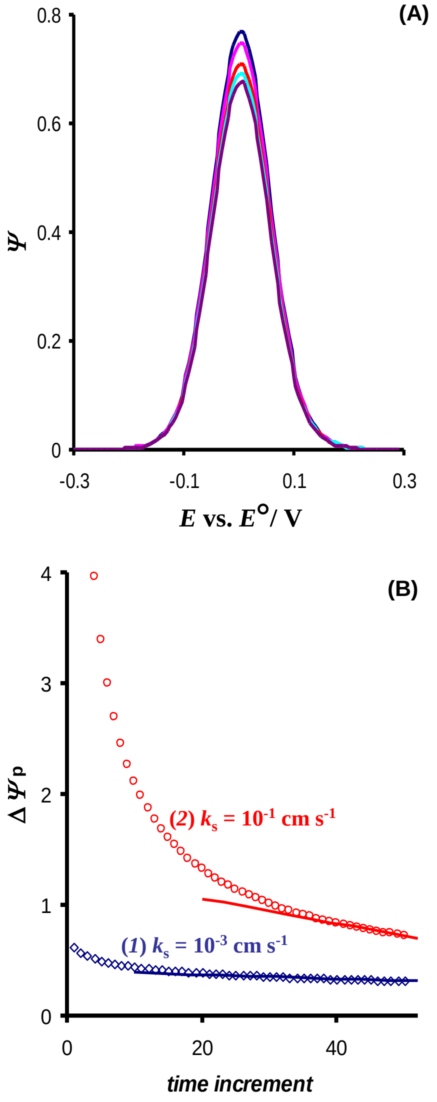

Fig. 2. Quasireversible electrode reaction of a dissolved redox couple. **(A)** Net voltammograms constructed by sampling the current at 40th, 42nd, 46th, 48th and 50th time increment of each potential pulse (from top to the bottom). The total time increments of each pulse are 50. The conditions of the simulations are: frequency $f = 10$ Hz, amplitude $E_{sw} = 50$ mV, step potential $\Delta E = 10$ mV, electron transfer coefficient $\alpha = 0.5$, standard rate constant $k_s = 0.01$ cm s^{-1}, diffusion coefficient $D = 5 \times 10^{-6}$ cm^2 s^{-1}, and number of exchanged electrons $n = 1$. **(B)** Variation of the net peak current of voltammograms constructed at different time increments of potential pulses versus time increments for the standard rate constant of 10^{-3} (*1*) and 10^{-1} cm s^{-1} (*2*). The other conditions of the simulations are identical as for panel **(A)**.

In addition, Figure 2B represents the variation of net peak currents of all new SW voltammograms with time increments, considering the whole duration of potential pulses, for two different rate constants of the electrode reaction. The last portion of the curves of Figure 2B, which corresponds to the last quarter of each potential pulse, could be approximated with a line, the slope of which depends on the electrode kinetics. Thus, the analysis of net peak currents of new SW voltammograms, constructed by multisampling the current at the last portion of each potential pulse, could provide an access to the electrode kinetics. More detailed analysis is presented in Figure 3, conducted for different reversibility of the electrode reaction. Obviously, for electrode reactions featuring fast electron transfer ($\log(\kappa) > 1$) the line is independent on the electrode reaction rate, as the decreasing of the current in the course of potential pulses depends on the rate of diffusion only. For the electrode reactions featuring moderate electrode transfer, characterized with $-2 \le \log(\kappa) \le 1$, the lines of Figure 3 are sensitive to the electrode kinetics, taking into account both the slope and the intercept. Thus, the latter dependency can serve for electrode kinetics measurements, as the variation of the current in the course of potential pulses is affected by both electrode kinetics and diffusional mass transport. For electrode reactions with a very slow electron transfer step ($\log(\kappa) < -2$) the line is hardly dependent on the electrode kinetics again, and only approximate estimation of the electrode kinetics can be done.

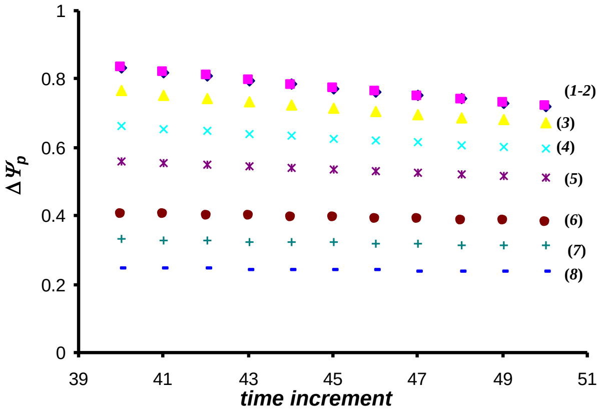

Fig. 3. Quasireversible electrode reaction of a dissolved redox couple. Variation of the net peak current of voltammograms constructed by sampling the currents at different time increments of potential pulses versus time increments, for the electrode kinetic parameter $\log(\kappa)$: 2.15 (*1*); 1.15 (*2*); 0.15 (*3*); –0.15 (*4*); –0.35 (*5*); –0.65 (*6*); –0.85 (*7*), and –1.8 (*8*). The other conditions of the simulations are identical as for Fig. 2.

In further analysis, another typical and important electrode mechanism is considered, i.e. a quasireversible surface confined electrode reaction of two chemically stable species [5, 25] (eq. 2).

$$\mathrm{R(ads)} \leftrightarrow \mathrm{O(ads)} + n\mathrm{e}^{-} \qquad (2)$$

For this mechanism, sampling the current at different time intervals of potential pulses results in dramatic changes in the morphology of the response, as depicted in Figures 4A and B. Obviously, the latter figure shows the phenomenon of splitting of the net multi-sampled net voltammograms, achieved by increasing the time of the current sampling [25]. The phenomena of splitting is well-known and it is one of the most intriguing feature of SWV of surface confined electrode reactions attributed with high electron transfer rate [25]. The splitting is a peculiar, but useful phenomenon that can be utilized for complete thermodynamic and kinetic characterization of the surface electrode reaction, by analyzing the peak potential separation between split peaks. The present analysis reveals that the phenomenon of splitting is a direct consequence of the specific chronoamperometric features of the surface electrode reaction, and it could be even demonstrated by measuring a single SW voltammogram and applying a multi-sampling current procedure. The voltammetric profile presented in Figures 4A and B is attributed with a typical value of the electrode kinetic parameter, i.e. the electrode kinetic parameter $\omega = 3$ and the normalized amplitude $nE_{sw} = 50$ mV. For these parameters the splitting appears at net SW voltammogram corresponding to 44th time increment. For $\omega > 3$, the splitting appears at 40th time increment, while for $\omega \leq 2.5$ the splitting vanishes and it could be observed only under conditions of large amplitudes, $nE_{sw} > 50$ mV. Hence, the evolution of the voltammetric profile of multisampled net SW voltammograms can be effectively exploited for estimation of the electrode kinetics. Let us recall that the electrode kinetic parameter in the case of a surface confined electrode reaction is defined as $\omega = \dfrac{k_{\mathrm{sur}}}{f}$, where k_{sur} is the surface standard rate constant (s^{-1}) [25]. Figure 4B shows the linear variation of the peak currents of multi-sampled net voltammograms with time, for different standard rate constants. Obviously, both slope and intercept of the liner functions are strongly sensitive to the electrode kinetics, the phenomenon being more pronounced compared to the electrode reaction of dissolved redox species (cf. Fig. 3). These results are well understandable as the chronoamperometric characteristics of a surface confined electrode reaction are dependent on the electrode reaction rate only, while in the case of the electrode reaction of dissolved redox species the chronoamperometric features are affected by both electrode kinetics and mass transport.

Finally, the proposed methodology is tested on the electrode mechanism coupled with a chemical reaction. Specifically, reversible $\mathrm{C_rE_r}$ mechanism is assessed, where the reversible electrode reaction ($\mathrm{E_r}$) (eq. 4) is preceded by a chemical reaction ($\mathrm{C_r}$) (eq. 3), characterized with a first order forward (k_f) and backward (k_b) rate constants (s^{-1}), and the equilibrium constant $K = k_f / k_b$ [1, 5].

$$\mathrm{Y} \underset{k_{\mathrm{b}}}{\overset{k_{\mathrm{f}}}{\leftrightarrow}} \mathrm{R} \qquad (3)$$

$$\mathrm{R} \leftrightarrow \mathrm{O} + n\mathrm{e}^{-} \qquad (4)$$

It is worth recalling that the voltammetric features of the $\mathrm{C_rE_r}$ are predominantly dictated by the chemical kinetic parameter $\varepsilon = \dfrac{k_f + k_b}{f}$ and the equilibrium constant K. While the latter parameter determines the position of the chemical equilibrium (eq. 3), the ε represents the rate constant of re-establishing the chemical equilibrium during the time-frame of the current measurement in every single pulse. In the course of the voltammetric experiment, the chemical equilibrium is disturbed by proceeding of the electrode reaction (eq. 4), prompting the chemical reaction to reestablish the equilibrium conditions at rate dictated by ε.

Figure 5A depicts the evolution of SW voltammograms constructed by the multisampling procedure for the $\mathrm{C_rE_r}$ mechanism. The simulations represent a specific case attributed with $\log(K) = -3$ and $\log(\varepsilon) = 2$, which means that the chemical equilibrium is significantly shifted toward the initial electrochemically inactive reactant *Y*, while the chemical system is able rapidly to re-establish the disturbed equilibrium. Figure 5A reveals that the declining of net voltammograms is very slow by increasing the sampling time. In particular, the net peak current of the voltammograms measured at the end of the potential pulse (50th time increment) is only 10% less than the voltammogram measured at the 40th time increment (i.e. the beginning of the last quarter of the potential pulse). For comparison, the decreasing of the current for simple reversible electrode reaction (eq. 1) is about 14% for the corresponding conditions. Moreover, in the case of the surface confined electrode reaction (eq. 2), the corresponding decrease could be up to 50% (cf. Fig. 4A).

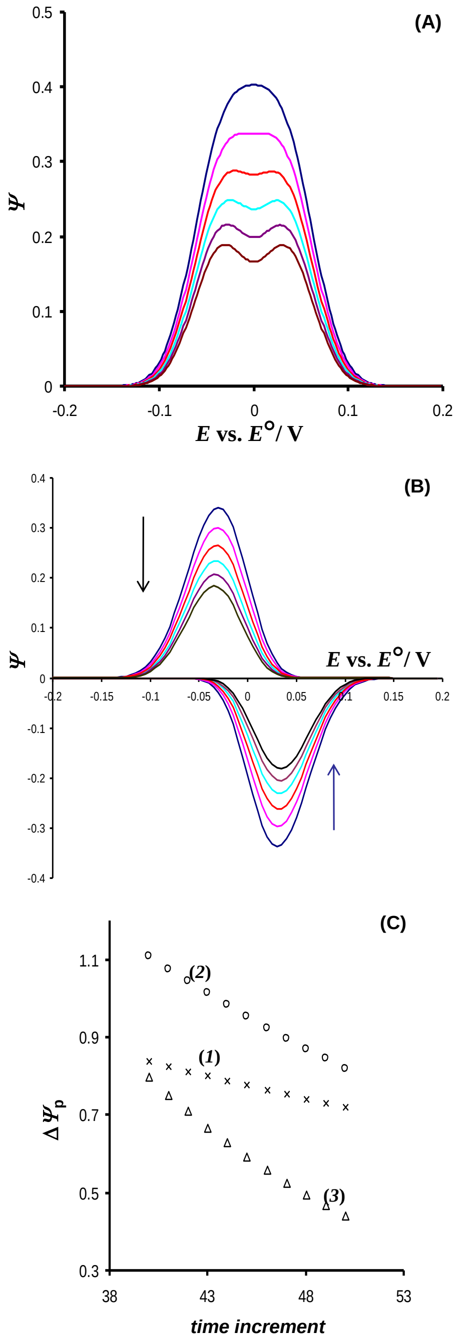

Fig. 4. Quasireversible surface confined electrode reaction. **(A)** Dimensionless net voltammograms constructed by sampling the current at 40th, 42nd, 44th, 46th, 48th and 50th time increment of each potential pulse (from top to the bottom). **(B)** Forward and backward SW voltammetric components corresponding to the net SW voltammograms depicted in panel (A). The time increment increases in the direction of the arrows. The total number of time increments of each pulse is 50. The conditions of the simulations are: frequency f = 10 Hz, normalized amplitude nE_{sw} = 50 mV, step potential ΔE = 2 mV, electron transfer coefficient $\alpha = 0.5$, and standard rate constant k_{sur} = 30 s^{-1}. **(C)** Variation of the net peak current of voltammograms constructed at different time increments of potential pulses versus time increments for the surface standard rate constant of 5 (*1*), 10 (*2*), and 20 s^{-1} (*3*). The other conditions of the simulations are identical as for panel **(A)**. The dimensionless current is defined as $\Psi = I(nFA\Gamma^* f)^{-1}$, where Γ^* is the total surface concentration.

Thus, the chronoamperometric characteristics of C_rE_r mechanism are significantly different compared to the simple reversible reaction of a dissolved redox couple (eq. 1), which is clearly revealed by the multisampled SW voltammograms. Indeed, the exhaustion of the diffusion layer with electroactive material is significantly compensated by the chemical reaction (eq. 3), which causes a slow decreasing of the current in the course of potential pulses. As shown by panel B of Figure 5, the decreasing of the net peak currents of multisalmpled voltammograms is insignificant for equilibrium constant log(K) ≤ –2 and is becoming obvious for log(K) ≥ –1, implying that the present methodology can be utilized for measuring the kinetics and thermodynamics of the chemical reaction coupled to the reversible electrode reaction by fitting of the experimental and simulated data.

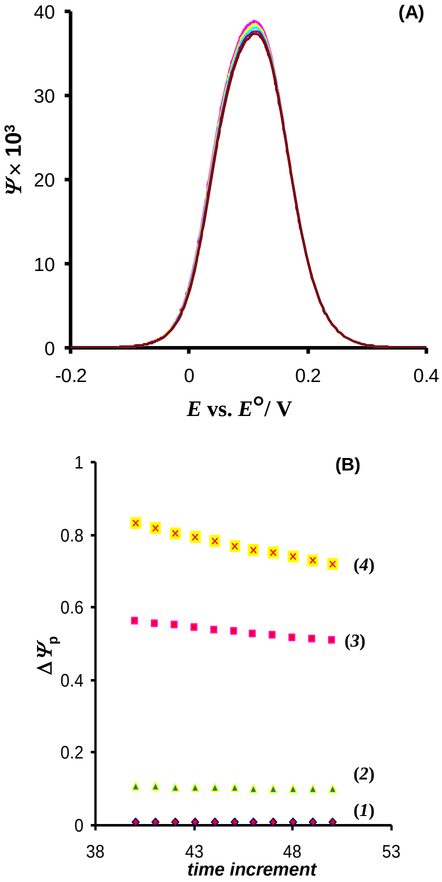

Fig. 5. Reversible C_rE_r electrode mechanism of a dissolved redox couple. **(A)** Net voltammograms constructed by sampling the current at 40th, 42nd, 46th, 48th and 50th time increment of each potential pulse (from top to the bottom). Chemical kinetic parameter is log(ε) = 2 and the equilibrium constant is log(K) = –3. The parameters of the potential modulation are nE_{sw} = 50 mV and the step potential is ΔE = 2 mV. **(B)** Variation of the net peak current of voltammograms constructed at different time increments of potential pulses versus time increments for the equilibrium constant log(K) = –3 (*1*); –2 (*2*), –1 (*3*), and 0 (*4*). The other conditions of the simulations are identical as for panel **(A)**.

3. CONCLUSIONS

The foregoing theoretical analysis of three different electrode mechanisms confirmed that chronoamperometric analysis of SW voltammograms is possible, resulting in novel and beneficial methodology in electrode kinetics. An important advantage of the proposed methodology is that it requires analysis of a single voltammogram only. Another important aspect is that the proposed methodology is based on a multisampling current procedure at a constant frequency of the potential modulation (i.e., at a constant duration of potential pulses), which is different than the conventional analysis in which the frequency of the potential modulation is changed. In the latter conventional approach all frequency-related kinetic parameters of the studied electrode mechanism are changed in the course of the experiment, whereas in the present methodology these parameters are kept unaltered, which simplifies the electrokinetic analysis. The proposed methodology is based on a completely new concept, which was not considered so far either in the theory or in the experimental analysis. The implementation of the method in the experimental analysis is expected to be simple, requiring the used potentiostat to provide all measured current data in the course of each potential pulse, instead of selecting only the current values from the very end of potential pulses, as commonly done in conventional SWV so far.

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