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ADVANCED PROCESSING OF ELECTROCHEMICAL DATA IN SQUARE-WAVE VOLTAMMETRY

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The processing of data in voltammetry is crucial for extracting mechanistic and kinetic information about the electrode reaction under study. One of the most advanced pulse-voltammetric techniques, square-wave voltammetry (SWV), allows for the investigation of electrode mechanisms, measurement of fast electron transfer reaction rates, and quantitative detection of redox species at sub-micromolar concentration levels. To ensure reliable comparison and fitting of experimental and theoretical data, several ideas for appropriate data processing have been proposed, considering the differences between experimentally accessible current and the dimensionless current function used in the theory and mathematical modeling of electrode processes in SWV. Significantly, in the context of advanced and recently introduced double-sampled square-wave voltammetry, a novel methodology for data analysis has been introduced. This methodology transforms the conventional current-potential function (i.e., voltammogram) into a current-current function, analogous to complex numbers. By employing this methodology, the accessible kinetic interval is extended, allowing for the measurement of very fast, virtually reversible electrode reactions characterized by a standard rate constant as high as 0.1 cm s^{-1} .

Key words: square-wave voltammetry; simulations; processing of voltammetric data; electrode kinetics; double-sampled square-wave voltammetry

INTRODUCTION

Voltammetry is a fundamental experimental methodology in electrochemistry and related fields, designed to study the mechanism, kinetics, and thermodynamics of electron transfer (redox) reactions. It offers powerful analytical methods for both quantitative and qualitative determinations [1]. Voltammetry has a rich historical background, dating back over a century, and has evolved into its current state of development, primarily represented by pulse voltammetric techniques [2]. Pulse voltammetry is specifically designed to enhance sensitivity for the quantitative detection of redox compounds, even at trace levels. Among the multitude

of pulse techniques, square-wave voltammetry (SWV) stands out as one of the most advanced methods. It combines the advantages associated with cyclic voltammetry, such as mechanistic studies, with excellent analytical performance [3] (Fig. 1). As a result, SWV has become the cornerstone of highly sensitive methods in electroanalytical chemistry [4]. The theoretical foundation of this technique has been developing since the 1960s [5, 6]. However, significant methodological advancements in both theory and experimental applications have been witnessed in recent years [7–9]. Building upon the methodological improvements proposed by Krušić et al. [10], square-wave voltammetry (SWV) has recently undergone transformations to function as a

pulse-form of chronoamperometric technique. This modification aims to simplify the technique and enable advanced applications in conjunction with amperometric sensors [11]. Furthermore, a hybrid voltammetric technique has been developed by combining SWV with differential pulse voltammetry [12]. This combination enhances the effectiveness in discriminating residual current while retaining the ca-

pability to resolve electrode mechanisms and kinetics. Additionally, to enable comprehensive studies of electrode reactions within a single experiment, multisampling [13] and double-sampling [14] current protocols have been proposed. These protocols facilitate the investigation of reaction mechanisms and kinetics, as well as the advanced analysis of sluggish electron transfer processes [14].

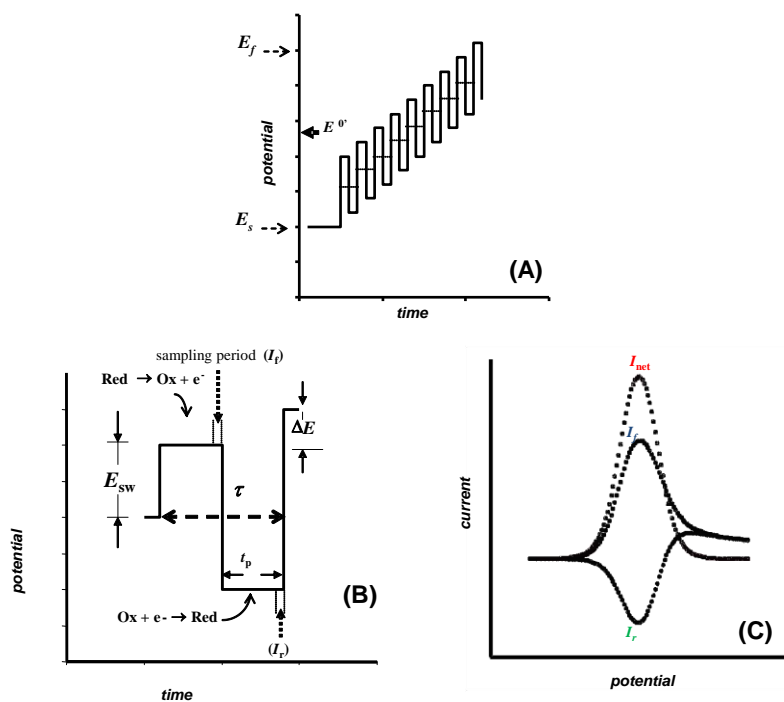


Fig. 1. (A) The potential waveform in square-wave voltammetry (SWV) can be visualized as a combination of a staircase potential and alternating potential pulses, overlaid on each step of the staircase waveform. (B) In SWV, a single potential cycle with a duration of τ comprises two opposing pulses of equal magnitude (E_{sw} , defined as the SW amplitude), each with a duration of t_p , such that $\tau = 2t_p$. The inverse of τ is the SW frequency f ($f = 1/\tau = 1/(2t_p)$). Typically, t_p ranges from 0.5 to 100 ms. ΔE represents the step potential of the staircase waveform. The opposing directions of the neighboring potential pulses induce the studied electrode reaction in both the anodic and cathodic directions, providing insights into the redox mechanism, similar to cyclic voltammetry. With respect to the overall potential modulation direction (panel A: E_s and E_f referring to the starting and final potential, respectively), forward and backward (reverse) potential pulses can be identified. Current is sampled at the end of each potential pulse (mean current of the last 5% of the current samples, for example) to discriminate against the charging current, resulting in a significant signal-to-noise ratio. (C) A typical SW voltammogram comprises forward current (I_f), reverse current (I_r), and net current (I_{net}) components. The forward and backward currents correspond to the current sampled at each forward and backward pulse, respectively (panel B), while the net component is the difference between them, $I_{net} = I_f - I_r$. All current components are plotted against the mid-potential of each potential cycle (i.e., the potential of the staircase ramp; panel A).

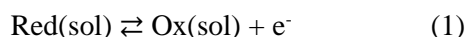
In addition to its analytical applications, when square-wave voltammetry (SWV) is employed for the fundamental study of electrode processes, the processing of voltammetric data and the comparison or fitting of theoretical and experimental data become crucial. The theoretical framework, specific to electrode mechanisms, is typically generalized by normalizing the current to a dimensionless form, which differs from the experimentally measured real

current. This discrepancy makes the correlation between theory and experiment not straightforward. Another challenge in experimental analysis is the influence of numerous parameters that are difficult to precisely control, thus hindering the estimation of the real current in theoretical models. A typical example is the active surface area of a solid electrode, which may vary between experiments conducted with the same electrode. In theoretical models, the

electrode surface area is typically neglected, as it is considered part of the parameters used for normalizing the current to a dimensionless form. Consequently, direct fitting of theoretical and experimental data is not possible. This highlights the need for appropriate processing of experimental data to uncover the underlying electrode mechanism and extract essential kinetic and thermodynamic parameters of the electrode reaction. The objective of this study is to provide a few simple guidelines to address this common issue in voltammetry, focusing on square-wave voltammetry (SWV) and its advanced variation, double-sampled square-wave voltammetry (DSSWV) [14].

RESULTS AND DISCUSSION

We consider a one-electron, quasi-reversible electrode reaction (1) involving a dissolved redox couple Red(sol)/Ox(sol) at a macroscopic planar electrode. The mathematical modeling of this reaction has been described elsewhere [3].



The real current I can be calculated as the product of Ψ , a dimensionless function derived solely through numerical simulations [15], and A , the amperometric constant. A is defined as $A = FSc(Df)^{1/2}$, where F is the Faraday constant, S is the electrode surface area, D is the common diffusion coefficient of both Red and Ox forms, c is the bulk concentration of the initially present reactant Red(sol), and f is the SW frequency. In general, the dimensionless function Ψ encompasses various aspects of the electrode mechanism, including the mass transfer regime, electrode kinetics, and other relevant phenomena like adsorption equilibria and coupled chemical reactions. This complexity makes the theory of voltammetry intricate in a broad context [3, 5, 6]. The role of theoretical analysis and mathematical modeling is to unveil the behavior of Ψ as a function of intrinsic kinetic parameters (such as the standard rate constant k_s and the electron transfer coefficient α , in the case of interfacial electron transfer modeled by the Butler-Volmer kinetic model [16]) and parameters related to the potential modulation (such as the SW frequency, amplitude (E_{sw}), and step potential (ΔE); see Fig. 1). For a single electrode reaction described by equation (1) and characterized by specific values of k_s , α , and D , when studied under a particular set of potential parameters (f , E_{sw} , and ΔE), the dimensionless function Ψ has a unique value. However, the actual current I cannot be calculated theoretically because it also

depends on the amperometric constant A , which is often unknown due to the difficulty in precisely determining the electrode surface area S . The characteristics of the dimensionless function Ψ for the electrode reaction (1) are primarily governed by the dimensionless electrode kinetic parameter $\kappa = k_s/(Df)^{1/2}$ [3, 5, 6]. This parameter combines the effects of electrode kinetics (k_s), the rate of diffusion mass transfer (D), and the critical time of the voltammetric experiment (f). To examine the impact of electrode kinetics on the intensity of the dimensionless voltammetric response (specifically, the dimensionless net-peak current $\Delta\Psi_p$), one can vary the frequency of the potential modulation, thereby altering the critical kinetic parameter κ . A typical result of such theoretical analysis is presented in the inset of Figure 2.

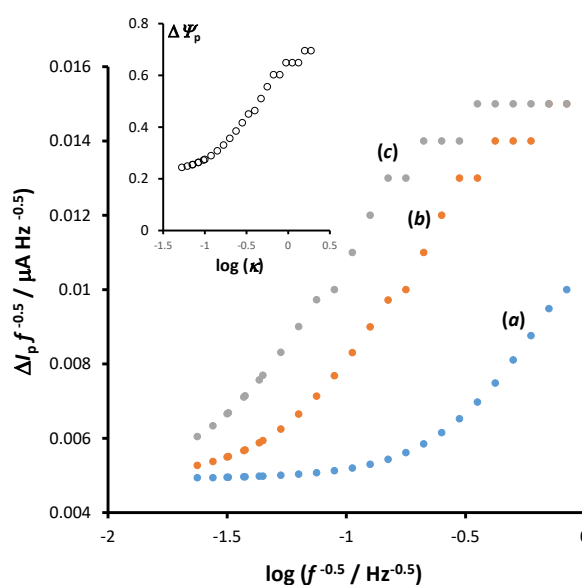


Figure 2. The figure illustrates the typical relationship between the frequency-normalized net peak current ($\Delta I_p/f^{1/2}$) and the logarithm of the inverse square root of the square-wave (SW) frequency, for three different standard rate constants: $k_s = 0.001$ (a), 0.005 (b), and 0.01 cm/s (c). The simulations were conducted under the following conditions: stoichiometric number of electrons in the electrode reaction equation $n = 1$, electron transfer coefficient $\alpha = 0.5$, common diffusion coefficient $D = 5 \times 10^{-6}$ cm²/s, bulk concentration of the reactant $c = 1 \times 10^{-7}$ mol/cm³, electrode surface area $S = 0.001$ cm², SW amplitude $E_{sw} = 50$ mV, step potential $\Delta E = 10$ mV, and temperature $T = 298.15$ K. The inset graph presents the dependence of the dimensionless net peak current ($\Delta\Psi_p$) on the logarithm of the electrode kinetic parameter $\kappa = k_s/(Df)^{1/2}$, achieved by varying the SW frequency for a standard rate constant $k_s = 0.005$ cm/s. The other conditions remain the same as in the main panel.

Considering the actual current I in the same frequency analysis, analogous to a real experiment,

one realizes that the effect of frequency is more complex, as it simultaneously affects both Ψ and A . To overcome this challenge, the real net peak current (ΔI_p) needs to be normalized with the corresponding frequency, i.e., $\Delta I_p/f^{1/2}$. The function $\Delta I_p/f^{1/2}$ vs. $1/f^{1/2}$, which qualitatively corresponds to the theoretical function $\Delta\Psi_p$ vs. κ , is illustrated in Figure 2 for three different values of the standard rate constant. Both functions, $\Delta I_p/f^{1/2}$ vs. $1/f^{1/2}$ and $\Delta\Psi_p$ vs. κ , can be used to extract the standard rate constant k_s of the studied electrode reaction. However, they cannot be directly fitted, as the real net peak current also depends on the remaining unknown parameters of the amperometric constant A .

In order to ensure a reliable and meaningful comparison between I and Ψ , it is necessary to transform the real current into a dimensionless form, despite the unknown amperometric constant. Drawing inspiration from spectroscopy [17], a straightforward approach is to employ a self-normalization procedure where both the real current and the dimensionless current are normalized using the corresponding net-peak current. Specifically, the ratio $I/\Delta I_p$ is equivalent to the ratio $\Psi/\Delta\Psi_p$, given that $\Delta I_p = \Delta\Psi_p A$. This simple normalization enables direct comparison and fitting procedures, effectively eliminating the influence of the unknown amperometric constant. Consequently, a thorough analysis of the complete SW voltammogram can be conducted, taking into account all three voltammetric components: forward, backward, and net components. Figure 3 illustrates self-normalized SW voltammograms for three different values of the SW frequency corresponding to a typically quasireversible electrode reaction. The increase in

frequency, ranging from very low ($f = 1.4$ Hz; Fig. 3a) to high values ($f = 1000$ Hz, Fig. 3c), causes the electrode reaction to transition from close-to-reversible to the characteristic electrochemically irreversible kinetic region [3, 5, 6]. This transition is evident from the morphological changes observed in the forward and backward voltammetric components. These dimensionless voltammograms can be effectively fitted with the theoretical function $\Psi/\Delta\Psi_p$ to estimate the typical kinetic parameters of the electrode reaction, such as k_s , α , and D . An alternative approach to achieve full normalization of the real current is demonstrated in Figure 4. This approach examines the frequency-normalized real net-peak current ($\Delta I_p/f^{1/2}$) as a function of frequency. The analysis in Figure 4 represents an improved version of the analysis depicted in Figure 2, as the ratio $\Delta I_p/f^{1/2}$ is further normalized by dividing it by the value measured at the lowest frequency ($\Delta I_p f^{-0.5}/\Delta I_p f^{-0.5}(f_{\min})$). In the example presented in Figure 4, the minimum frequency is denoted as $f_{\min} = 1.413$ Hz. The ratio $\Delta I_p f^{-0.5}/\Delta I_p f^{-0.5}(f_{\min})$ is dimensionless and equivalent to the ratio $\Delta\Psi_p(f)/\Delta\Psi_p(f_{\min})$, where $\Delta\Psi_p(f)$ represents the dimensionless net-peak current simulated for a given frequency, and $\Delta\Psi_p(f_{\min})$ is the dimensionless net-peak current corresponding to the first, minimum frequency within the selected frequency interval. Notably, Figure 4 demonstrates that the function $\Delta I_p f^{-0.5}/\Delta I_p f^{-0.5}(f_{\min})$ exhibits sensitivity to the standard rate constant. Consequently, this function can be directly fitted with simulated data to facilitate the kinetic characterization of the investigated electrode reaction.

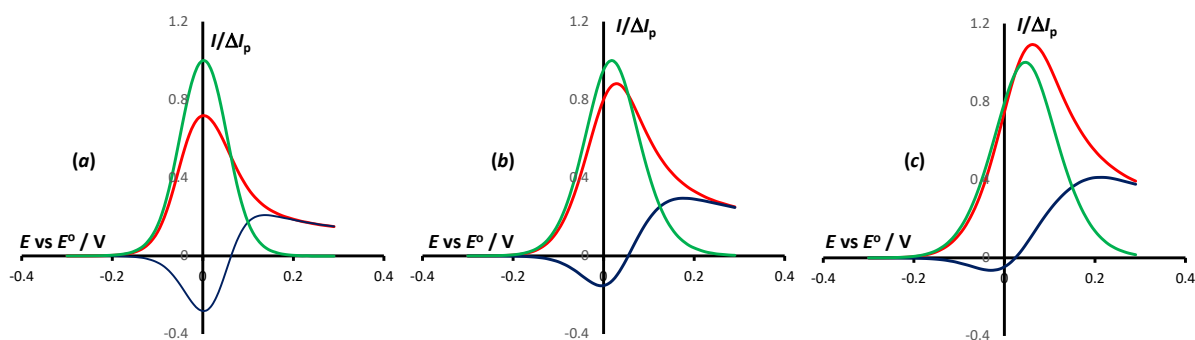


Figure 3. Representation of self-normalized SW voltammograms, illustrating the net (green), forward (red), and backward (blue) voltammetric components simulated for three different SW frequencies: $f = 1.4$ Hz (a), 251.2 Hz (b), and 1000 Hz (c). The standard rate constant is set to $k_s = 0.001$ cm s⁻¹. Self-normalization is achieved by dividing the current by the corresponding net peak-current (ΔI_p) of the voltammogram. All other conditions remain the same as in Figure 2.

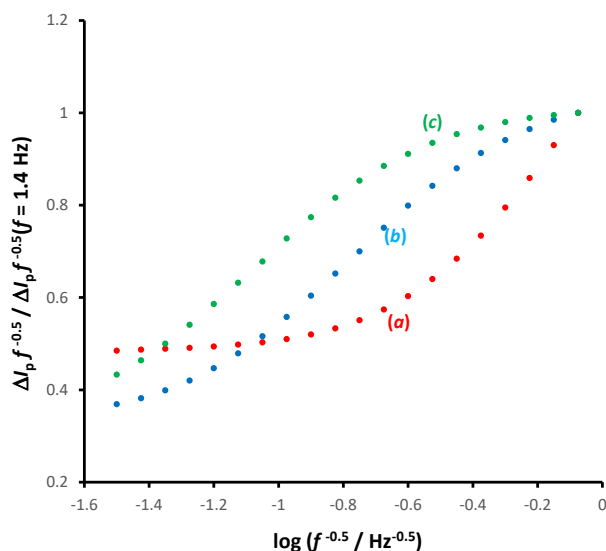


Fig. 4. The typical relationship between the frequency-normalized real net peak-current ($\Delta I_p/f^{1/2}$) and the logarithm of the inverse square root of the frequency for different standard rate constants: $k_s = 0.001 \text{ cm s}^{-1}$ (a), 0.005 cm s^{-1} (b), and 0.01 cm s^{-1} (c). Furthermore, an additional normalization step is performed by dividing all values by the corresponding value obtained at the minimum frequency, denoted as $(\Delta I_p f^{-1/2} / \Delta I_p f^{-1/2} (f = 1.477 \text{ Hz}))$. It is worth noting that all other conditions remain the same as depicted in Figure 2.

In this section, we will discuss an advanced approach to process voltammetric data, focusing on a recently introduced technique called double-sampled square-wave voltammetry (DSSWV) [14].

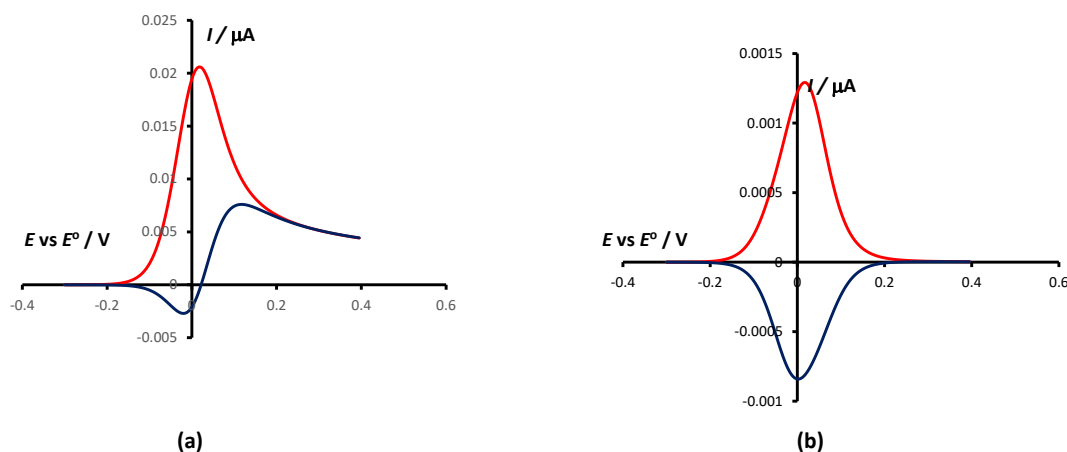


Fig. 5. A comparison of conventional (a) and double-sampled square-wave voltammograms (b), illustrating the forward (red) and backward (blue) voltammetric components. The simulations are conducted for a standard rate constant of $k_s = 0.005 \text{ cm s}^{-1}$, SW frequency of $f = 10 \text{ Hz}$, SW amplitude $E_{sw} = 25 \text{ mV}$, and step potential of $\Delta E = 5 \text{ mV}$. In the case of double-sampled square-wave voltammetry (DSSWV), the ratio of the sampling time to pulse duration is set at $t_s/t_p = 0.8$ [14]. All other conditions remain the same as depicted in Figure 2.

Since both forward and backward voltammetric components exhibit well-developed peaks regardless of the degree of electrochemical reversibility (as shown in Figure 5b), they serve as a foundation for rigorous kinetic analysis. In addition

The motivation behind developing DSSWV as an enhanced version of conventional SWV stems from the need for a comprehensive analysis of both forward and reverse components of the SW voltammogram when investigating the mechanistic and kinetic aspects of an electrode process. However, the backward component of the response often exhibits poor development, either due to sluggish electron transfer or the low amplitude of the SW pulses, as illustrated in Figure 5a. To overcome this limitation and broaden the applicability of SWV, a double-sampling current protocol was proposed. In this protocol, the current is sampled twice in the last quarter of the pulse duration, at designated times t_s and t_p (refer to Figure 1 in [14]). Subsequently, the current corresponding to each pulse is transformed into a differential current calculated as $I_{\text{dir}} = I(t_s) - I(t_p)$. The implications of this simple transformation are remarkable for both the forward and backward SW components, as demonstrated in Figure 5b. It is anticipated that this transformation of the SWV current components will enable improved mechanistic and kinetic analysis of electrode processes across various degrees of electrochemical reversibility. Furthermore, based on existing literature, there is a plausible expectation that DSSWV will enhance the analytical performance of the technique as well [18].

to the conventional approach of analyzing the relationship between their peak currents and peak potentials, it is valuable to consider all current values of both components to explore their detailed interdependence. Essentially, one can examine the

characteristics of the function I_b vs. I_f within a specific voltammogram under various conditions of the electrode reaction. To achieve this, Figure 6 displays the dimensionless function $I_b/\Delta I_p$ vs. $I_f/\Delta I_p$, where ΔI_p represents the corresponding net-peak current of the DSSW voltammogram. This dimensionless representation allows for self-normalization, as explained earlier in the context of conventional SWV. By analyzing this function, one can gain insights into the interrelationship between the forward and backward voltammetric components and study their behavior under different conditions of the electrode reaction. The function $I_b/\Delta I_p$ vs. $I_f/\Delta I_p$, which represents a current-current function, should not be confused with a voltammogram, which typically represents a current-potential function. However, this current-current function offers a novel approach for advanced analysis of voltammetric data. It provides valuable insights and exhibits high sensitivity to the standard rate constant, making it particularly useful for studying very fast electrode reactions characterized by a rate constant of $k_s = 0.1 \text{ cm s}^{-1}$ (as depicted by curve d in Figure 6). This approach expands the kinetic range of accessible standard rate constants, particularly in the direction of very fast and nearly reversible electrode reactions. This advantage sets it apart from conventional analysis methods used in SWV [3].

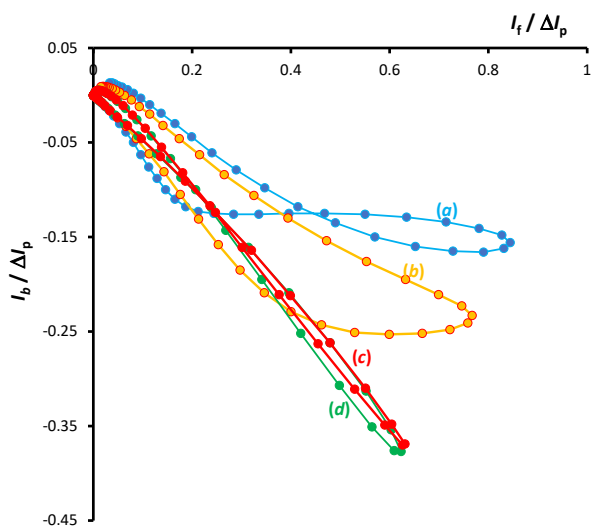


Fig. 6. Figure 6 displays the backward vs. forward voltammetric components of double-sampled square-wave voltammetry (DSSWV) for different standard rate constants: $k_s = 0.005 \text{ cm s}^{-1}$ (a), 0.01 cm s^{-1} (b), 0.05 cm s^{-1} (c), and 0.1 cm s^{-1} (d). The current values are self-normalized by dividing them by the corresponding net peak-current (ΔI_p) of the DSSW voltammogram. The simulations are conducted under the following conditions: SW frequency $f = 100 \text{ Hz}$, SW amplitude $E_{sw} = 25 \text{ mV}$, step potential $\Delta E = 10 \text{ mV}$, and a ratio of the sampling time to pulse duration $t_s/t_p = 0.8$. All other conditions remain the same as depicted in Figure 2.

It is worth noting that the current-current function depicted in Figure 6 can be mathematically interpreted within the context of complex numbers [19]. The forward and backward currents can be viewed as the real and imaginary components, respectively, of a complex current denoted as $Z = \Psi_f + i\Psi_b$. Here, Ψ_f represents the real part, Ψ_b represents the imaginary part, and $i = \sqrt{-1}$ is the imaginary unit. In order to study the behavior of Z , it is common to plot the imaginary component (Ψ_b) against the real component (Ψ_f). Therefore, the plot presented in Figure 6 represents the evolution of the complex number Z during the course of the voltammetric experiment, showcasing the relationship between Ψ_b and Ψ_f . Treating voltammetric data within the framework of complex numbers introduces a new approach for analysis, providing additional tools for advanced mechanistic and kinetic analysis of electrode processes. This perspective enhances the capabilities of voltammetric techniques and will be further elaborated upon in our future communications.

CONCLUSIONS

Accurate processing of electric current data obtained from a voltammetric experiment is essential for reliable comparison with theoretical predictions and understanding the mechanistic and kinetic aspects of an electrode process. The theory establishes a clear relationship between the experimentally measured current I and the current function Ψ , which can only be determined through numerical simulations. The relationship is defined as $I = nFSc(Df)^{1/2}\Psi$, where n represents the stoichiometric number of electrons involved, and other symbols are defined as explained in the previous section. To overcome any discrepancies between I and Ψ , a straightforward approach is to apply a self-normalization procedure to both currents using their corresponding net peak-currents. By dividing the currents by their respective net peak-currents, the functions $I/\Delta I_p$ and $\Psi/\Delta \Psi_p$ can be directly compared and fitted. This approach opens up new possibilities for analyzing voltammetric data, where the conventional current-potential function in SWV can be enriched with a novel current-current function. This new function utilizes the forward and backward components of the SW voltammogram, specifically the $I_f/\Delta I_p$ vs. $I_b/\Delta I_p$ function. The current-current function represents a promising and innovative tool for more in-depth and advanced processing of voltammetric data. It enables the expansion of the range of accessible rate constants, as demonstrated in the case of DSSWV.

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НАПРЕДНА ОБРАБОТКА НА ЕЛЕКТРОХЕМИСКИТЕ ПОДАТОЦИ ВО КВАДРАТНО-БРАНОВА ВОЛТАМЕТРИЈА

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Обработката на електрохемиските податоци во волтаметријата е од суштинска важност за изучување на реакциските механизми и кинетиката на електродните реакции. Квадратно-брановата волтаметрија е една од најнапредните пулсни волтаметриски техники која овозможува изучување на реакциските механизми, мерење брзи процеси на пренос на електрони, како и квантитативни определувања на аналити во субмикромоларно

концентрациско подрачје. Заради релевантна споредба на експерименталните со теоретските податоци, во овој труд се предложени неколку нови идеи за обработка на електрохемиските податоците, земајќи ја предвид разликата во прикажување на реалната експериментална струја и бездимензионалната функција на струјата која се користи во теоретското моделирање на електродните процеси во квадратно-брановата волтаметрија. Важно е да се истакне дека во рамките на скорешно воведената нова техника наречена квадратно-бранова волтаметрија со двојно мерење на струјата, предложена е целосно нова методологија за анализа на податоците. Имено, вообичаената функција *струја-потенцијал* (позната како волтамограм) се трансформира во функција *струја-струја*, која има своја аналогија со комплексните броеви во математиката. Со примена на оваа методологија е проширен е интервалот на мерливи брзини на пренос на електрони, при што може да се мери кинетиката на многу брзи процеси на пренос на електрони (практично реверзибилни електродни реакции) кои се одликуваат со стандардна константа на брзина на пренос на електрони од редот на 0.1 cm s^{-1} .

Клучни зборови: квадратно-бранова волтаметрија; симулации; обработка на електрохемиски податоци; електродна кинетика; квадратно-бранова волтаметрија со двојно мерење на струјата