

# Square-Wave Voltammetry: A Review on the Recent Progress

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Received: July 29, 2013

Accepted: September 20, 2013

Published online: ■■■, 2013

## Abstract

A review on the recent progress of square-wave voltammetry is presented, covering the period of the last five years. The review addresses the new theoretical development of the technique as well as its application for mechanistic purposes, electrode kinetic measurements, biochemical and analytical applications. Besides, a few novel methodological modifications are proposed that might expand the scope and application of the technique.

**Keywords:** Square-wave voltammetry, Theory, Electrode mechanisms, Electrode kinetics

DOI: 10.1002/elan.201300369

## 1 Introduction

Square-wave voltammetry (SWV) is a powerful electrochemical technique suitable for analytical application, mechanistic study of electrode processes and electrokinetic measurements [1–6]. Nowadays it is considered as one of the most advanced voltammetric techniques, which unifies the advantages of pulse techniques (enhanced sensitivity), cyclic voltammetry (insight into the electrode mechanism) and impedance techniques (kinetic information of very fast electrode processes). In a historical context, it originates from the Kalousek commutator [7] and Barker's square-wave polarography [8–10]. The modern SWV, incorporated in digital electrochemical instruments [1, 11], utilizes a combination of a staircase potential modulation and periodic square-shaped potential function, applied at a stationary electrode. In this review, we address the recent advances and application of SWV covering the period from 2007 up to date, i.e. the period after publication of the monograph dedicated solely to this technique [6].

Besides addressing the basic features of SWV, we also propose a few novel methodological modifications that might expand the scope and application of the technique. In addition to, we address recent contributions in the theory of SWV, studies where SWV was applied for mechanistic and electrokinetic purposes, biochemically oriented studies, as well as a few typical studies where SWV was used for analytical determination. Clearly, covering all studies involving SWV as a working analytical tool is hardly possible.

## 2 Basic Features and New Methodological Concepts in SWV

### 2.1 Basic Characteristics of SWV

Typical potential modulation used in SWV consists of a staircase potential ramp modified with square-shaped potential pulses (Figure 1A). At each step of the staircase ramp, two equal in height and oppositely directed potential pulses are imposed. The latter two potential pulses complete a single *potential cycle* in SWV (Figure 1B). The potential cycle in SWV is repeated at each step of the staircase ramp in the course of the voltammetric experiment. For historical reasons, the height of a single potential pulse is termed as SW *amplitude* ( $E_{sw}$ ). Relative to the direction of the staircase ramp, one recognizes forward and backward potential pulses. More specifically, the potential pulses with odd serial number are forward pulses, whereas those with even serial numbers are assigned as backward (or reverse) pulses. In the course of a single potential cycle, the electrode reaction is driven in both anodic and cathodic directions, thus providing an insight into the electrode mechanism. Consequently, the critical time of the voltammetric experiment is represented by the duration of a single potential cycle ( $\tau$ ), or the duration of a single potential pulse,  $t_p = \tau/2$ . The voltammetric data can be interpreted in terms of  $\tau$ ,  $t_p$ , or the *frequency* of the potential modulation  $f$ , defined as  $f = 1/\tau$ . The physical meaning of the frequency can be understood as a number of potential cycles in a unit of time. Typical frequency range provided by commercially available instrumentation is from 5 to 2000 Hz, which corresponds to

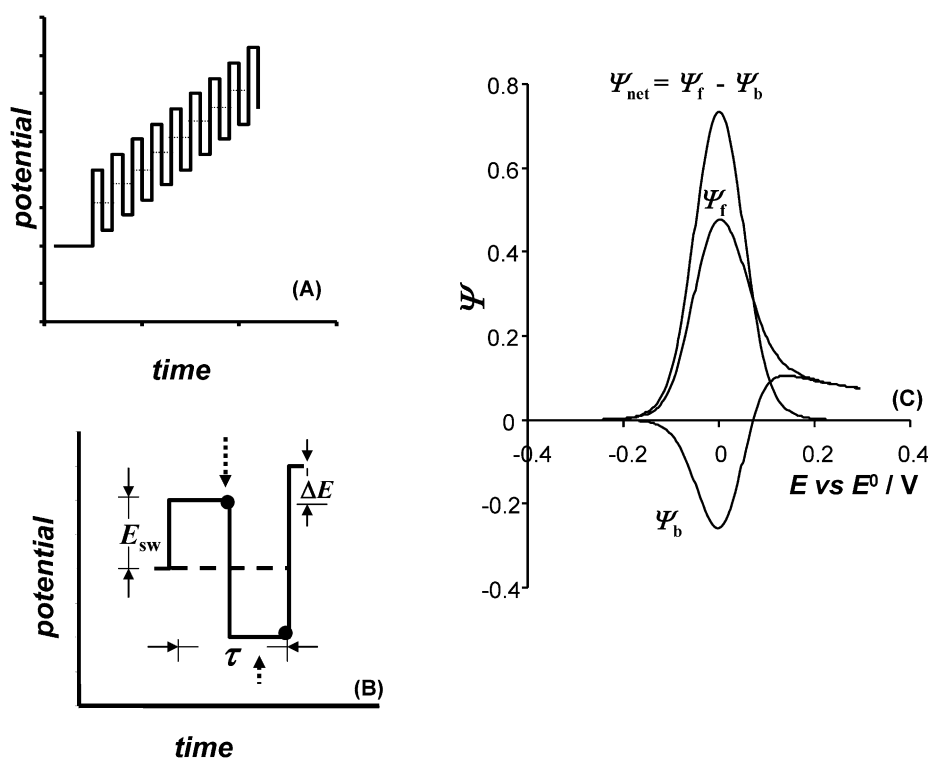


Fig. 1. Potential waveform (A), one potential cycle (B), and typical voltammogram in square-wave voltammetry (C). The response consists of a forward (anodic,  $\Psi_f$ ), backward (cathodic,  $\Psi_b$ ) and net ( $\Psi_{net}$ ) component.

the duration of a single potential pulse from 0.25 to 100 ms.

The overall potential modulation can be attributed with scan rate defined as  $v = f \Delta E$ , where  $\Delta E$  is the step of the staircase ramp (cf. Figure 1B). Hence, certain analogy between the SW frequency and the scan rate in cyclic voltammetry can be found. However, a care must be taken in establishing direct analogy between the scan rate of CV and the frequency of SWV. For instance, an experiment in SWV could be conducted at a very high frequency, i.e. a short potential cycle (e.g.  $f = 500$  Hz;  $\tau = 1$  ms), but yet at a very slow scan rate, provided the scan increment is small (e.g.  $\Delta E = 0.1$  mV). For  $f = 500$  Hz and  $\Delta E = 0.1$  mV the scan rate is moderate ( $v = 50$  mV/s) although the electrode reaction is driven in both anodic and cathodic directions over very short period of time (1 ms). A corresponding experiment in CV, assuming a potential window of 300 mV, would require scan rate of 6000 mV/s.

In order to discriminate against the charging current, the current sampling is performed at the end of each potential pulse. The currents associated with forward and backward potential pulses compose the *forward* and *backward (reverse)* component of the SW voltammogram, respectively (Figure 1C). It is important to stress that both forward and backward components are plotted versus the potential of the staircase ramp, i.e. the mid potential of the two neighboring pulses composing one potential cycle. Thus, to each step potential, two current values are assigned. Obviously, there is a difference between the

actual potential at which the current is measured and the one given in the SW voltammogram. Subtracting the forward and backward currents of a single potential pulse, a net current value is obtained. The net currents corresponding to each potential cycle compose the *net component* of the SW voltammogram (Figure 1C). For most electrode mechanisms, the net SW component is a bell-shaped curve, enabling precise determination of its position and height. We note that the charging current depends on the potential of zero charge; hence, in most of the cases the charging current is almost identical at two neighboring pulses, provided the SW amplitude is low. Hence, the subtraction procedure of the forward and backward currents contributes further in canceling out the remaining charging current, which is one of the reasons for the high quality and enhanced sensitivity of experimentally collected net SW voltammograms.

## 2.2 Potential-Corrected SW Voltammograms

As previously noted, an important feature of a SW voltammogram is the difference of the plotted potential and the actual potential of the current measurement. The difference equals the value of the amplitude used, which is becoming significant for amplitudes higher than 50 mV. For these reasons, the role of the amplitude is not enough understood and SW voltammograms usually feature peculiar behavior under the influence of the varying amplitude. To illustrate this, Figure 2A shows a SW voltammetric pattern of a surface confined electrode reaction of

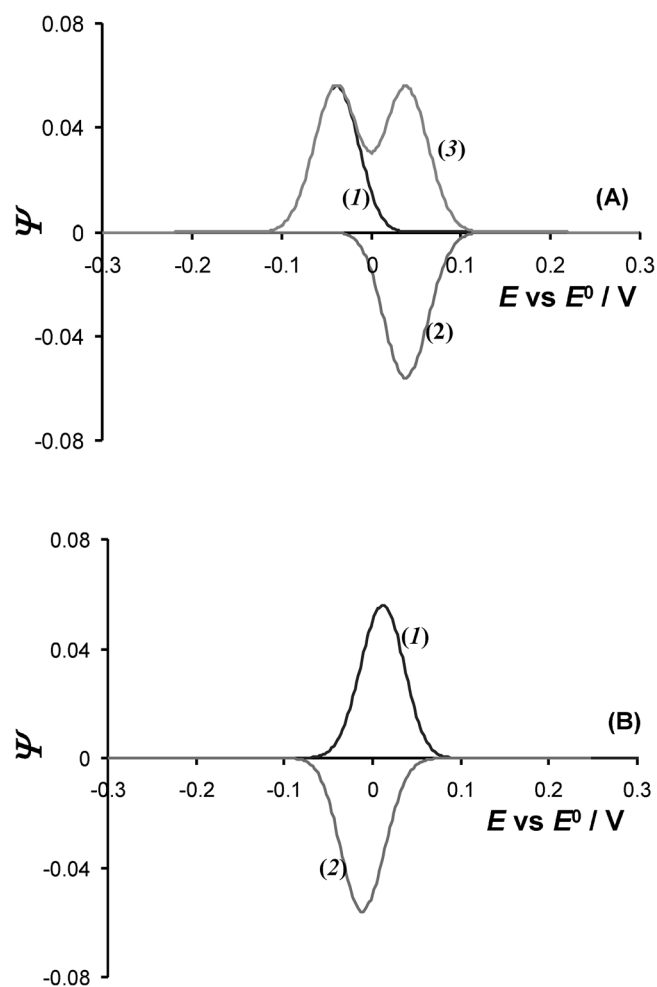


Fig. 2. (A) Typical theoretical SW voltammogram response of a surface confined electrode reaction consisting of the forward (anodic) (1), reverse (cathodic) (2) and net (3), components plotted as a function of the corresponding potential of the staircase ramp. (B) Potential-corrected SW voltammogram showing anodic (1) and cathodic (2) SW components versus the actual potential of SW pulses, at which the current is sampled. The parameters of the simulations are:  $\omega = 5$  ( $\omega = k_{\text{sur}}/f$ , where  $k_{\text{sur}}$  ( $\text{s}^{-1}$ ) is the standard rate constant), electron transfer coefficient  $\alpha = 0.5$ ,  $n = 1$ ,  $E_{\text{sw}} = 50$  mV, and step potential  $\Delta E = 2$  mV. The dimensionless current is calculated according to the model given in [6], and defined as  $\Psi = I/(nFA\Gamma^*f)$ , where  $\Gamma^*$  is the total surface concentration of redox active material,  $A$  is the electrode surface area, and other symbols have their common meaning.

a relatively fast electrode reaction measured at an amplitude of 50 mV. By analogy with cyclic voltammetry, one expects a symmetric response, in which the peak potential separation of the anodic and cathodic voltammogram curves reflects the overpotential dictated by the electrode kinetics. On the contrary, the response in SWV consists of significantly separated anodic (forward) and cathodic (backward) components. Moreover, their relative position is very peculiar, as the anodic and cathodic component of the response is positioned at more negative and more positive potentials, respectively, versus the formal potential of the electrode reaction (cf. Figure 2A). However,

re-plotting the SW voltammogram versus the actual potential of the SW pulses (Figure 2B) the relative position of the anodic and cathodic components reverses, and the shape of the SW voltammogram is becoming analogous as in CV, i.e. in agreement with the common rezoning regarding the relationship between the current and potential for a kinetically controlled electrode reaction. This is so called *potential-corrected* SW voltammogram. This correction requires shifting of the anodic and cathodic components toward more positive and more negative potentials, respectively, for the value of the SW amplitude used. The interpretation of the potential-corrected SW voltammograms is more straightforward and it is in accord to the common rezoning in relating the current, as a measure of the electrode kinetics, with the electrode potential, as a measure of the main driving force of the electrode reaction. We believe that potential-corrected SW voltammograms will expand the scope of SWV for both mechanistic and electrokinetic application, as briefly illustrated in the next section.

### 2.3 Electrode Kinetic Measurements at a Constant Frequency (Constant Scan Rate)

In most of the studies dedicated to electrode kinetic measurements with SWV, the frequency or duration of potential cycle is the main experimental tool for estimation of electrode kinetic parameters. However, the second powerful tool in hand is the SW amplitude, which, unfortunately is seldom used for electrode kinetic measurements. An exception is the work published by one of us almost two decades ago [12]. Expanding the latter methodology, we stress that electrokinetic measurements can be effectively performed by varying the SW amplitude and by analyzing the peak potential separation between the forward and backward components of the SW voltammogram. This methodology can be applied utilizing conventional or potential-corrected SW voltammograms, although our recent theoretical study favors the latter. Figure 3 shows representative examples of such analysis referring to electrode reactions of a surface confined and dissolved redox couple. For both mechanisms, potential-corrected SW voltammograms have been utilized, in order to avoid artificial peak potential separation, as explained in the previous section. The peak potential separation ( $\Delta E_p$ ) is a function of normalized amplitude ( $nE_{\text{sw}}$ ,  $n$  is the number of electrons exchanged in the electrode reaction). As can be seen from Figure 3, the exact relationship between  $\Delta E_p$  and  $nE_{\text{sw}}$  depends on the electrode kinetic parameter, which provides the basis for estimation of the standard rate constant. We recall that the electrode kinetic parameter is defined as  $\omega = k_{\text{sur}}/f$  and  $\kappa = k_s/(Df)^{0.5}$  for electrode reaction of surface immobilized and dissolved redox couple, respectively, where  $k_{\text{sur}}$  ( $\text{s}^{-1}$ ) is the standard rate constant for the surface electrode reaction and  $k_s$  ( $\text{cm s}^{-1}$ ) is the standard rate constant for the reaction of a dissolved redox couple. Therefore, for a given frequency, curves in Figure 3 can be understood as a com-

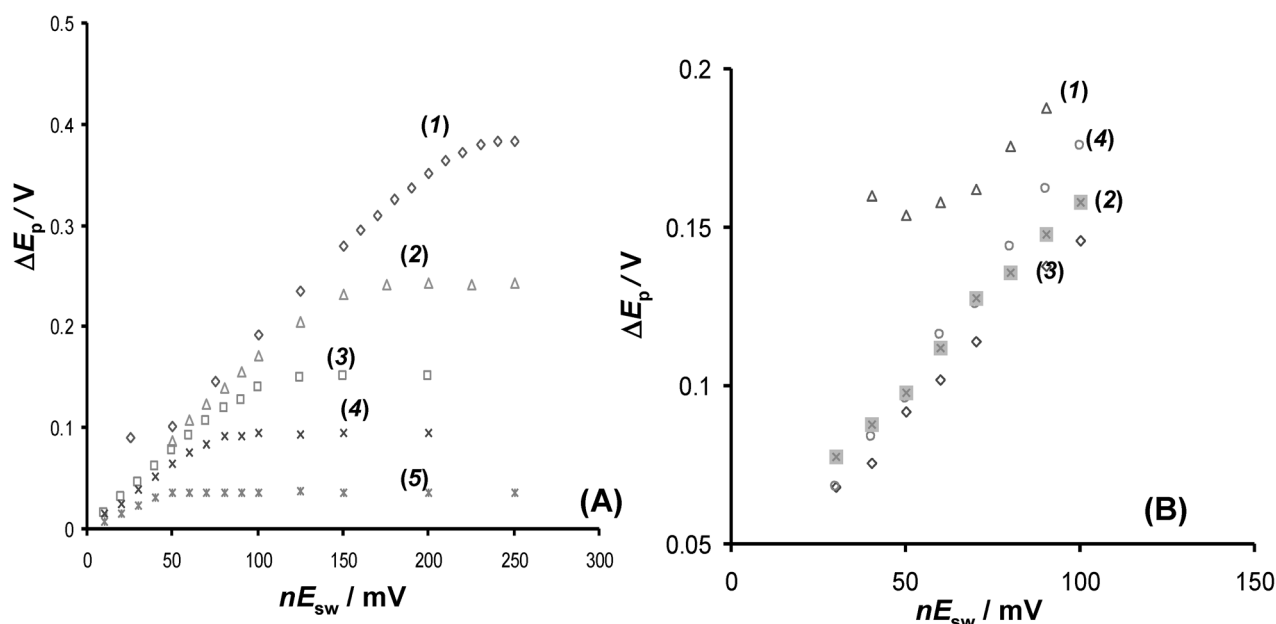


Fig. 3. The dependence of the peak potential separation  $\Delta E_p = (E_{p,a} - E_{p,c})$  of the potential-corrected SW voltammograms on the SW amplitude, for different values of the electrode kinetic parameter of the electrode reaction of a surface confined (A) and dissolved redox couple (B). For (A) the kinetic parameter is  $\omega = 0.05$  (1); 0.2 (2); 0.5 (3); 1 (4) and 3 (5), while for (B) it is  $\kappa = 0.1$  (1); 0.5 (2); 1 (3) and 10 (4) ( $\kappa = k_s / (Df)^{0.5}$ ;  $k_s$  (cm s<sup>-1</sup>) is the standard rate constant and  $D$  is the common diffusion coefficient). The conditions of the simulations for both electrode reactions are:  $n = 1$ ,  $\alpha = 0.5$ , and  $\Delta E = 2$  mV. The dimensionless current for surface reaction is defined as for Figure 2, whereas for the electrode reaction of a dissolved redox couple it is  $\Psi = I / (nFAc^*)(Df)^{1/2}$ , where  $c^*$  is the bulk concentration of initially present redox species [6].

parison of electrode reactions attributed with different standard rate constants. On the other hand, when a single electrode reaction is considered, which is attributed with a typical value of the standard rate constant, the data in Figure 3 can be reproduced by adjusting the SW frequency, which affect the value of the electrode kinetic parameter. The value of the standard rate constant can be estimated by fitting the experimental and theoretical data obtained by varying the SW amplitude for a fixed value of the frequency.

Another novel approach for electrokinetic determination at a fixed frequency (i.e. fixed scan rate) can be based on the new feature called “amplitude-based quasireversible maximum” [13]. The term “quasireversible maximum” (QRM) is related to all electrode mechanisms in which at least one component of the redox couple is immobilized on the electrode surface [6]. Conventional QRM is obtained by varying the frequency, and it is manifested as a parabolic dependence of the frequency normalized net peak current versus the logarithm of the frequency. The position of QRM is highly sensitive to standard rate constant, thus enabling estimation of the latter kinetic parameter. In our recent theoretical work we showed that a similar feature exists when the SW amplitude is varied for a fixed frequency. This is illustrated in Figure 4, where the amplitude normalized net peak current is plotted versus the values of the amplitude, again for the surface and electrode reaction of a dissolved redox couple. The position of the new, amplitude based QRM, is sensitive to the standard rate constant, thus ena-

bling its determination. An important advantage of the new maximum is the fact that it is not limited to surface processes, rather than it is equally applicable for electrode mechanisms of surface confined and dissolved redox couple. Moreover, a kinetic method at a fixed fre-

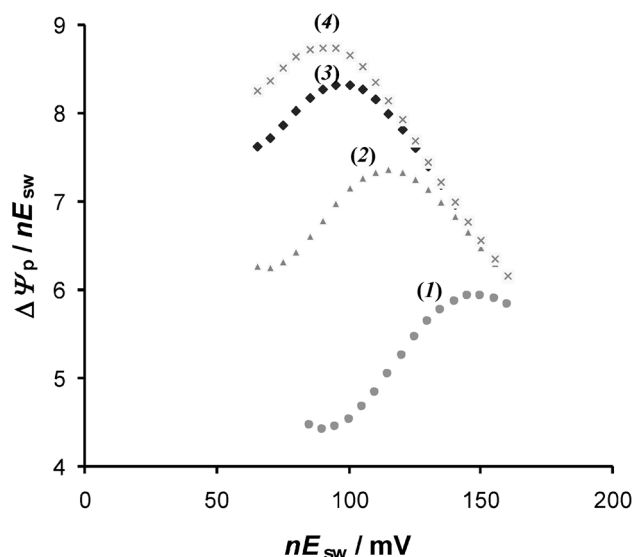


Fig. 4. Amplitude based quasireversible maximum of a dissolved redox couple electrode reaction [13]. The dependence of the ratio of the net peak current and the amplitude ( $\Delta \Psi_p / nE_{sw}$ ) on the SW amplitude, for different values of the electrode kinetic parameter  $\kappa = 0.01$  (1); 0.03 (2); 0.05 (3) and 0.06 (4). The other conditions of the simulations are:  $\alpha = 0.5$ ,  $\Delta E = 5$  mV.

quency of the potential modulation, i.e. at a constant scan rate of the voltammetric experiment, is highly advantageous in particular for complex electrode mechanisms the response of which depends on several frequency-related kinetic parameters. When the frequency is used for kinetic measurements all frequency-related kinetic parameters are simultaneously altered, causing frequently very complex voltammetric behavior of the system under study. A detailed elaboration of the new electrokinetic method based on the amplitude variation can be found elsewhere [13].

## 2.4 Cyclic Square-Wave Voltammetry

Performing a SW voltammetric experiment in a fashion of cyclic voltammetry can be regarded as a new technique termed as *cyclic square-wave voltammetry* (CSWV). The basis of this highly promising technique is found in the works of Chen [14], Xinsheng [15], Bottomley [16], Molina [17], as well as in a series of studies in which SWV was applied in a reverse mode [18–21]. Typical potential waveform of CSWV is depicted in Figure 5A, consisting of direct and reverse SW potential waveforms. The

voltammetric outcome of a CSW voltammetric experiment provides a wealthy of electrochemical information, which might consist of six voltammetric curves, i.e. forward, backward and net components for both direct and reverse scan (Figure 5B). Likewise to the spectroscopic techniques, typical CSW voltammetric pattern can be considered as a fingerprint of the studied experimental system. Typical example of a surface confined electrode reaction under conditions of CSWV is given in Figure 5B. The net components of the direct and reverse scan are symmetric curves, at equally height, thus being analogous to the expected voltammetric pattern in conventional cyclic voltammetry. For the sake of simplicity, the CSW voltammogram might feature only the net components of the direct and reverse scan only. Hence, the way of thinking developed for conventional cyclic voltammetry might be applied to resolve the outcome of the CSW voltammetric experiment, which is attributed with high sensitivity and quality of the voltammetric data. Thus, there is necessity for the analysis of a variety of electrode mechanisms under conditions of CSWV in order to establish qualitative diagnostic criteria as well as methods for determination of thermodynamic and kinetic parameters of electrode reactions.

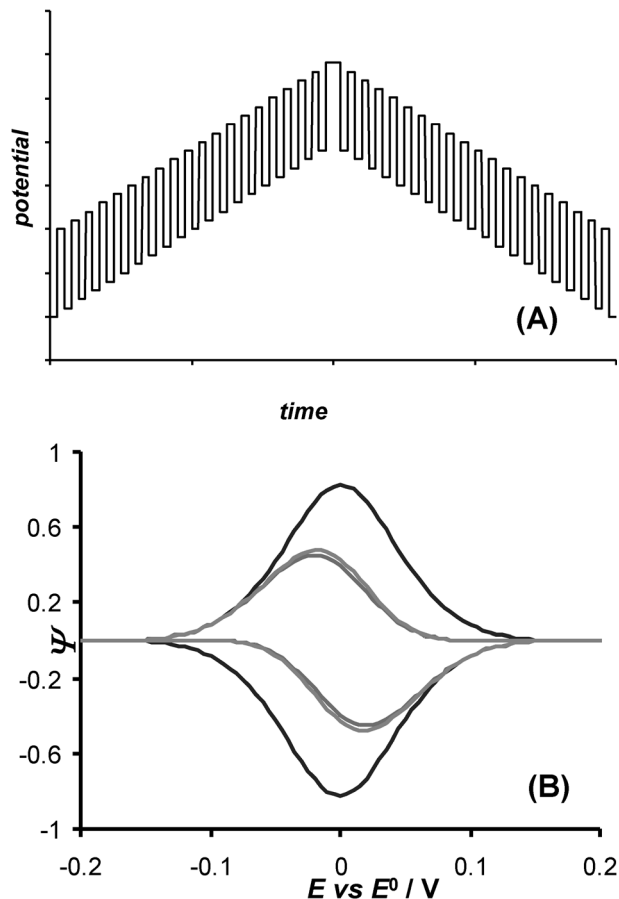


Fig. 5. (A) A potential waveform of cyclic square-wave voltammetry. (B) Typical response of a surface confined electrode reaction in cyclic square-wave voltammetry, consisting of a net, forward and backward components of both direct and reverse scan. The conditions of the simulations are:  $\omega=1$ ,  $n=1$ ,  $\alpha=0.5$ ,  $\Delta E=5 \text{ mV}$ .

## 3 Electrode Mechanisms Studied with SWV

In the reviewed period significant contributions in the theory of SWV have been done by the research groups of Lovric [18–20,22–29], Molina [17,30–35], Compton [36–39], Mirceski [40–43], Gulaboski [44–47], and others [48–50]. The theory refers to a variety of electrode mechanisms including dissolved or immobilized redox couples at macroscopic planar or microelectrodes, as well as processes undergoing in a restricted diffusion space. Due to their relevance for biochemical systems, multistep, consecutive electron transfers [17,22–24,33,44] and catalytic mechanisms [30,31,34,45] have received considerable attention. Importantly, a series of works have been dedicated to the study the electrode processes in the frame of Marcus-Hush electron transfer kinetic model [36–39]. In addition, several works have been published addressing general methodological issues in SWV such as the role of the scan rate [27] and the influence of the ohmic drop effect [51,52]. Works of merit are those where Fourier transformed SWV has been applied for estimation of electrode kinetics [50,53,54] and charge transfer kinetics at liquid/liquid interfaces [48,55].

Lovric et al. [22] analyzed a two-step consecutive electron transfer mechanism at a planar electrode of a dissolved redox couple, i.e. an EE mechanism, where the two electron transfer steps are quasireversible. The formal potential of the second step is lower in the absolute value compared to the first one, thus the intermediate of the mechanism appears thermodynamically unstable in the potential region where the first electron transfer step occurs. In [23], a reversible EE mechanism at a planar

electrode has been considered, where both the initial reactant and the intermediary are stabilized with complexation reactions. The relative position of the first and second peak of the net response depends on the thermodynamic stability of complexes, standard potentials of individual electron transfers and the concentration of the complexing ligand, which is in excess in the studied system. Molina et al. developed the theory for an EE mechanism, consisting of two electrochemically reversible steps for microdisc electrode geometry [33]. The same group considered a general case of a consecutive multi-electron transfer mechanism, where all steps are reversible, for a spherical electrode [17]. The latter solution is given in a general form, enabling to predict the outcome of the experiment for any electrode size, ranging from the case of a planar electrode to the microsphere electrode geometry. A special case of EE mechanism, where an overall transfer of three electrons is assumed, i.e. the first one-electron transfer is followed by the second two-electron transfer step, has been also studied [24]. The latter model is applicable for electrochemical deposition of bismuth and antimony, two important processes for preparation of popular bismuth and antimony film electrodes used in modern anodic stripping voltammetry [43].

Motivated by electrode mechanisms encountered in protein-film voltammetry, Gulaboski et al. have studied two specific surface mechanisms, designated as ECE [44], and the catalytic EEC' system [45]. In the model for ECE mechanism, two quasireversible electron transfer steps are linked with kinetically controlled irreversible first order chemical reaction, while in the EEC' mechanism, the second electron transfer step is coupled with a follow-up first order regenerative chemical reaction.

A detailed analysis of a variety of catalytic mechanisms is presented in works of Molina et al. [30,31,34]. They studied theoretically a simple EC' catalytic reaction scheme at a disc electrode [34], where the electrode reaction is reversible process, whereas the regenerative follow-up chemical reaction is chemically reversible, attributed with first-order kinetics. In [34], a simple surface EC' mechanism is studied, the reaction scheme being identical with the previous work of Mirceski and Gulaboski [56]. However, the work of Molina [29] is enriched by the analysis of the electric charge consumption in the course of the SW voltammetric experiment, which is termed as square-wave voltammetry (SWVC). They found that SWVC provides a direct insight into the kinetics of the first-order follow-up regenerative chemical reaction independent on the SW amplitude and the reversibility of the electrode reaction. In [30], a more complex catalytic mechanism has been considered at spherical microelectrodes, where a reversible redox couple is immobilized on the electrode surface, catalyzing a dissolved substrate through a second order follow up chemical reaction. In this model, the diffusion mass transport of the substrate has been considered, which makes the model more general compared to the common first-order surface catalytic mechanism.

In addition to the theory of catalytic mechanisms, Mirceski et al. [40] performed a comparative analysis of the electrocatalytic mechanisms of the first and second kind at a planar electrode, considering quasireversible electrode reactions. The catalytic mechanism of the first kind is represented by a simple regenerative EC' reaction scheme, whereas the electrocatalysis of the second kind assumes first formation of an electroactive complex YS between the catalyst Y and the electroinactive substrate S, followed by an irreversible electrochemical reaction of YS that yields the catalyst Y and the final electroinactive product P.

A few contributions in the theory of cathodic stripping processes of insoluble salts have been also published [42,57]. In these specific mechanisms one assumes formation of an insoluble salt between the electrode material, e.g. mercury electrode, and an electroinactive reacting ligand present in the electrolyte solution. In [57], besides deposition of the insoluble salt, the adsorption of the reacting ligand is considered as well, complicated by lateral interactions between adsorbed species. Whereas the model in [42] refers to a mechanism free of ligand adsorption, but coupled with a homogeneous first-order chemical reaction producing the reacting ligand, i.e. a sort of CE electrode mechanism in cathodic stripping voltammetry of insoluble salts. In this context, the contribution in the theory of anodic stripping processes at bismuth-film electrodes has to be also mentioned [43,58], which, from the modeling point of view, follows the previous theory for cathodic stripping processes of insoluble salts.

Lovric conducted particularly interesting theoretical work in which SWV has been applied for the first time to analyze surface active, but redox inactive, species [26]. This work is particularly significant in contrast to the generally accepted implication that SWV effectively discriminates against the capacitive current. While the latter is generally true, one must also take care for the appearance of tensammetric response under conditions of SWV, in particular when adsorption complicated electrode mechanisms are considered. A general qualitative criterion to differentiate the pure tensammetric response from the voltammetric response of an electrode reaction in which the reactant is partially adsorbed is established [26].

In a separate group of studies SWV has been applied for mechanistic and electrokinetic purposes, invoking the existing theoretical models [46,47,53,54,59]. Gulaboski et al. [47] developed a simple strategy for estimation of the standard rate constant by measuring the half-peak width of the net SW peak for electrode mechanisms of an immobilized and dissolved redox couple. In addition, the effect of the temperature has been examined in detail for a surface electrode reaction, in order to predict peculiar voltammetric features in protein-film stripping voltammetry [46]. Wang et al. [53,54] developed a new procedure for evaluation of the kinetics of a surface confined electrode reaction by means on Fourier transformed SWV (FT-SWV). The proposed method relies on the quasireversible maximum, a well-known feature of the conventional

SW voltammetric response of surface electrode processes; nevertheless the method of Wang is highly promising as it is rapid and sensitive. This is an extent of the previous works of merit of Bond et al. [60,61] who developed originally the methodology for FT-SWV. Fernandez, Zon et al. combined the method of quasireversible maximum and split SW peaks for complete thermodynamic and kinetic characterization of the surface reaction of flavonoid rutin, immobilized on the surface of glassy carbon electrode [62]. Molina, Correa et al. developed an important methodology for determination of partition constant of 1-naphthol between water and unilamellar phospholipid vesicles, based the electrochemical response of the redox compound at macroscopic platinum and glassy carbon electrodes [63]. Compton et al. studied oxidation of nitrite anion at a variety of electrodes, addressing the mechanism and kinetics of the electrode reaction. They demonstrated the critical importance of the knowledge of the electrode mechanism and kinetics for optimization and development of advanced electroanalytical methodology for quantitative determination [64].

As demonstrated in several studies [65–67], SWV is particularly suitable method for studying the electrode processes coupled with chemical reactions. Yan et al. [65] determined the formation constants of lead with humic and fulvic acids, utilizing anodic stripping response of labile lead ions at mercury film electrodes. Bento et al. [66] developed deconvolution based methodology for determination of dissociated and undissociated acid forms at microdisc platinum electrode. In [67], the accumulation and recognition of Fe(III) ions by self-assembled deferoxamine, a bacterial hydroxamic siderophore, has been studied for the purpose of development of a highly sensitive sensor for quantitative determination of Fe(III).

The last decade has been also marked by important contributions of SWV in studying the charge transfer processes across liquid/liquid interfaces (L/L) [35,48,55,68–80]. Most of these studies are related with thin-organic film [70,73–76,78,79] and three-phase electrodes [71,72,77]. The theoretical modelling relevant to film-electrodes requires consideration of electrode processes in a restricted diffusion space [41]. In [74], a comparative analysis of two electrocatalytic mechanisms at film electrodes has been conducted, referring to the heterogeneous electrocatalysis involving electron transfer across the L/L interface, and a simple EC' electrocatalytic mechanism confined within the thin film. Diagnostic criteria to differentiate between the two mechanisms have been developed. Previously mentioned FT-SWV has been also applied to estimate the kinetics of ion transfer across the L/L interface at thin-film electrodes [55,68]. Again, the feature of quasireversible maximum has been exploited, which was originally predicted for thin-film quasireversible electrode processes [81]. Molina et al. [35] studied both theoretically and experimentally the ion transfer processes at electrodes with two polarisable liquid interfaces, emphasizing the advantages of this system compared to the conventional systems with a single liquid interface.

#### 4 Analytical and Biochemical Applications of Square-Wave Voltammetry

Square-wave voltammetry, as one of the most advanced voltammetric techniques is frequently used in analytical applications and fundamental studies of various compounds recognized as medicaments, physiologically important systems, biologically active substances, pesticides and many more. When used for analytical applications, SWV shows a broad range of advantages over other voltammetric techniques. These are recognized in the greater sensitivity, short analysis time and the ability for significant reduction of capacitance currents. Advantages of SWV are also found in the sensitivities of different modes that can be applied for enrichment of the electroactive (or studied) material to be determined. SW cathodic, anodic and adsorptive stripping voltammetry are seen as preconcentration modes enabling enrichments of the analytes and their determination up to picomolar concentration level. In the recent years, the SW voltammetry has emerged as a viable and cheap alternative to the expensive and time-consuming techniques (such as chromatography, or spectrophotometry, for example) for the determination of inorganic and biologically important compounds. The simple working set-up, the quick time of performing the measurements, the different modes that can be applied, together with its sensitivity, make the SWV a technique of choice for quantification of important classes of compounds such as proteins [82], vitamins [83], phenols [84–88], benzoquinones [89], pesticides, herbicides and fungicides [90–98], alkaloids [99], terpenoids [100], heavy metals [101–116], and drugs [117,118]. One of the most valuable ability of SWV is its application for simultaneous determination of compounds with similar structures present in various pharmaceutical and physiological samples. Svorc et al. reported successful simultaneous determination of paracetamol and peniciline by using SWV at bare boron-doped diamond electrode [119]. In another work [120] a simultaneous determination of ascorbic acid, acetaminophen and tryptophan has been achieved by using SWV graphite electrode modified with carbon nanotubes. In a similar manner, Tian et al. [121] have reported a method for simultaneous determination of ascorbic acid, dopamine and uric acid by using SWV with graphene electrode modified by gold nanoparticles and beta-cyclodextrin.

In the works of Pohanka et al. [122,123] it has been shown that SWV performed on screen printed electrodes can be successfully explored as a suitable tools for the direct determination of low-molecular-weight antioxidants such as glutathione, ascorbic and uric acids in blood. The SWV method for the determination of these low-molecular antioxidants has been found superior over the well-established spectrophotometric techniques, while having major advantage in respect to the low influence coming from the matrix interferants. Very recently, the SWV has been applied as a powerful tool for the detection of phenols, as another class of important antioxi-

dants. Seven phenolic compounds, i.e. the *o*-phenilendiamine, *p*-chlorophenol, *p*-aminophenol hydroquinone, pyrocatechol, phenol and 3,3'-5,5'-tetramethylbenzidine were tested as co-substrates of the enzymatic reaction of the horseradish peroxidase [124]. The linear dependence between the net SWV peak currents and the phenolic substrates concentration was found even in the sub-nanomolar concentration range of studied phenols. Polyphenols from the group of flavonols present in various plants have been also determined by using SWV with solid electrodes [125,126]. Various catechins such as epigallocatechin gallate, epicatechin, epicatechin gallate, gallic acid and epigallocatechin were directly quantified in various green teas in submicromolar concentration ranges by using SWV with a glassy carbon as a working electrode. The accuracy of the results has been compared by HPLC technique. In these works of Komorsky-Lovric et al. [125,126] it has been shown that SWV sensitivity and selectivity is comparable to that obtained by chromatographic techniques. In another work, SWV has been explored for quantification of polyphenols from the class of flavonolignans [127]. Isosilybin, silybin and some of its derivatives (2,3-dehydrosilybin, 7-methylsilybin, 20-*O*-methylsilybin) have been detected by exploring their oxidation peaks in adsorptive stripping square-wave voltammetric mode. Moreover, in the work of Zatloukalova et al. [127] it has been shown that silybin forms 1:2 complexes with  $\text{Cu}^{2+}$  ions capable to selectively bind to DNA molecules. Resveratrol is another important polyphenolic antioxidant present in the red wine. Its detection from various red wine samples has been achieved by using adsorptive stripping square-wave voltammetry in high concentrated perchloric media [128]. The detection limit of resveratrol in ng/mL range has been reported that is comparable to that obtained by chromatographic techniques.

In the last decade, protein-film voltammetry emerged as a simple but powerful tool to getting insight into the redox chemistry of various enzymes [129]. The square-wave voltammetry applied in a protein-film voltammetric set-up has proven to be a simple and powerful technique that provides information to the mechanistic pathways, but also to the thermodynamic and kinetics of many important proteins. Very recently, Duwensee et al. [130] have described a remarkable achievement of SWV performed on heated microwires to detect the products of the asymmetric convective polymerase chain reaction performed in a tube containing very small volume. The polymerase chain reaction is an important approach in molecular biology, serving for the detection of some genetic diseases or genetically modified plants. By using a gold electrode modified with a complementary single-stranded capture probe immobilized via a thiol-linker, a labeled product of the polymerase chain reaction could be successfully detected. The product of polymerase chain reaction was selectively labeled by bipyridine complex of osmium(VIII). With this approach, the authors have obtained significant discrimination between complementary and noncomplementary targets by exploring different im-

mobilized probes. The method is reported to be very simple and quick (5–10 minutes), and superior in many aspects over the commonly explored microfluid chips with external pumps. Another important achievement of the SWV in the protein detection is reported in the work of Krizkova et al [131]. In this work, electrophoretic and voltammetric methods have been developed for the determination of the protein avidin (responsible for crop's protection). The reaction between avidin (glycosylated protein) and vitamin H (biotin) has been explored to establish a sensitive method for avidin quantification. The authors have shown that the method is specific, while its sensitivity is comparable to the electrophoretic methods developed for avidin determination in the transgenic plants. In another work [132] the authors have reported on ultra-sensitive detection of streptoavidin (from *Streptomyces avidinii*) in a zeptomolar concentrations by using carbon paste electrode.

Next to its role for kinetic and thermodynamic characterization of various proteins, SWV was also explored as a technique for detection of other important physiological organic compounds [133,134]. Arevalo et al. [135] have recently reported a sensitive adsorptive stripping SWV method for detection of the steroid progesterone on a glassy carbon electrode. The authors of the latter work also paid attention on the adsorption of progesterone on the working electrode surface, while evaluating thermodynamic parameters of the adsorption strength. The same group [136] has previously reported a comprehensive SWV study about the reduction of progesterone in acetonitrile at glassy carbon electrode. Electrochemical transformation of progesterone in a nonaqueous medium is accompanied by formation of stable radical anions. In another work, Goyal et al [137] reported on a SWV method for simultaneous detection of adenosine and adenosine-5-triphosphate on a ITO electrode modified with gold nanoparticles. The specific catalytic effect of gold nanoparticles was a crucial factor that led in separating the voltammetric signals of adenosine and adenosine-5-triphosphate, thus their simultaneous determination was achievable. A simple but efficient SWV method has been developed for quantification of yeast RNA (yRNA) on a cetylpyridine bromide-cellulose modified ITO electrode [138]. The yRNA strongly adsorbed on the cellulose modified electrode, and its oxidation in such an arrangement is a chemically irreversible process. The kinetic parameters of the electrochemical reaction or yRNA have been evaluated from SW voltammetric response. A fast Furrier transformed square-wave voltammetry has been applied to detect the amino acid levodopa that is precursor required by the brain to produce dopamine [139]. With the help of this technique, L-dopamine has been detected in urine and human serum in micromolar concentration range by using microelectrode.

Nowadays, SWV is also exploited as a tool for routine measurements of some ecotoxic compounds. The detection of organophosphorous pesticides was achieved by following the electrochemical activity of dichloroindophe-



nol with thiocholine that was a product created by enzymatic reaction of acetylthiocholine with cholinesterase [140]. A two-phase square-wave voltammetry has been employed as a tool for the detection of other similar ecotoxic compounds. SWV method for the detection of organophosphorous pesticides has been recently reported based on inhibition of the enzyme cholinesterase in a biphasic system [141]. The activity of the enzyme cholinesterase creates a redox active compound indophenol in the water phase emerging as a product of the enzymatic hydrolysis of the water insoluble indophenol acetate. The indophenol has been subsequently detected on a graphite electrode by square-wave voltammetry.

Square-wave voltammetry is a technique of choice not only for the detection of organic and inorganic compounds, but also for assessing the number of some bacterial cultures in real samples. Carpani et al. [142] recently reported on a SWV method for quantification of bacterial load of *Escherichia coli Pseudomonas aeruginosa* in non-treated water samples. A microelectrode array has been used for this purpose, while direct detection of the investigated bacterial cultures was possible at the epoxy glue impregnated reticulated vitreous carbon electrode. The method reported is selective, simple and fast and it does not need pretreatment of the water samples. In another work, traces of *Escherichia coli* population have been detected by coupling square-wave voltammetry on a glassy carbon electrode modified with multiwalled carbon nanotubes [143]. The detection of these living microbial cultures is based on measuring the activity of oxidizable components present in *Escherichia coli*, whose release from the bacteria is catalyzed by the carbon nanotubes.

One of the advantages of SWV is also seen in its abilities to be applied for the direct detection of some redox active compounds even in complex organic matrixes or food products. Recently, the detection of antibiotic certiofur has been achieved by applying square-wave voltammetry directly in milk samples following the hydrolysis of certiofur [144]. Owing to its performances for determination of various polyphenolic antioxidants, useful and cheap SW voltammetric methods have been developed for the determination of the total antioxidative capacity in food products such as edible oils [145] and beverages [146]. Alkaloids are other class of natural compounds that attract considerable interest due to their wide range of applications in the pharmaceutical industry. The adsorptive stripping SW voltammetric quantification of the isoquinoline alkaloid, protopine has been achieved in an alkaline media, while following its oxidation at pyrolytic graphite electrode [147].

## 5 Outlook for the Future

SWV remains a superior technique for analytical application. Outstanding performances are expected to foster further its application in the analysis of complex biochemical systems. However, the wide application of SWV

for mechanistic study of electrode processes remains a challenge. Yet, recent intensive development of the theory justifies expectations that staircase cyclic voltammetry could be soon replaced by square-wave voltammetry in the investigation of electrode mechanisms. Some of the existing examples are the application of SWV in the redox speciation measurements [25,148], detection of the adsorption of the intermediate of a complex two step electrode reaction [149], or mechanistic studies of chlorophyllin [150] and myricetin [151]. We do hope that the novel methodological concepts presented in section 2 might expand the scope of SWV and facilitate its application for mechanistic and electrokinetic studies. Potential-corrected SWV avoids peculiar voltammetric features, in particular when the technique is applied to study surface confined electrode processes; hence, potential-corrected SWV is expected to provide more direct insight into the mechanistic aspects of electrode reactions. Particularly promising is cyclic square-wave voltammetry [16]. Hence, there is a necessity of analyzing a variety of electrode mechanisms in order to establish diagnostic criteria under conditions of cyclic square-wave voltammetry. Finally, methods for electrode kinetic measurements at a constant scan rate deserve further attention as they can provide kinetic information in a new and unique approach [13].

## Acknowledgements

This work was funded by the *Alexander von Humboldt (AvH)* foundation via the joint German-Macedonian Project, 3.4-Fokoop-DEU/1128670 (to VM and RG). This project was also supported by the “*Deutsche Forschungsgemeinschaft*” (SFB894 Project A1 to MH and SFB 1027 Project C4 to IB).

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