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Review

RECENT ACHIEVEMENTS IN SQUARE-WAVE VOLTAMMETRY A REVIEW

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Recent advances in square-wave voltammetry for analytical purposes as well as for studying electrode mechanisms and kinetics are reviewed, mainly covering results published in the last decade. Analyzing only some typical analytically oriented studies, one confirms the well-known fact that the technique is attributed with superior analytical performance in the family of advance pulse voltammetric techniques. Covering all analytical studies where square-wave voltammetry is the working technique is hardly possible. For this reason, we decided to cover the relevant studies in square-wave voltammetry, mainly published in the last five to seven years. The reviewed period is marked with remarkable contributions in the theory of complex electrode mechanisms, revealing that square-wave voltammetry is one of the most powerful voltammetric techniques for both mechanistic and kinetic characterizations of electrode processes. Finally, a brief consideration is given to several methodologically oriented studies, referring mainly to cyclic-square voltammetry as well as methods based on the analysis of electrode processes by varying the amplitude of the potential modulation, which is expected to expand the scope and application of the technique in coming years.

Keywords: square-wave voltammetry; electroanalysis; electrode mechanisms; electrochemistry; kinetics of electrode reactions;

РЕВИЈАЛЕН ПРЕГЛЕД НА СКОРЕШНИОТ РАЗВОЈ НА КВАДРАТНО-БРАНОВАТА ВОЛТАМЕТРИЈА

Во овој труд е даден ревијален преглед на развојот на квадратно-брановата волтаметрија во последните неколку години, осврнувајќи се на нејзината примена како електроаналитичка техника, но и како техника за изучување на електродните механизми и електродната кинетика. Со анализа на некои покарактеристични аналитички ориентирани студии е потврден познатиот факт дека оваа техниката се одликува со супериорни особини во поширокото семејство на пулсни електроаналитички техники. Треба да се напомни дека е невозможно да се опфатат сите аналитички студии, бидејќи нивниот број е огромен. Покрај другото, овој период се одликува со значителен развој на теоријата на оваа техника за проучување на сложени електродни механизми, што е потврда дека квадратно-брановата волтаметрија е една од најмоќните алатки за студирање на механизмите и кинетиката на електродните реакции. На крајот е даден краток осврт на неколку важни методолошки ориентирани студии кои се засноваат на анализа на електродната кинетика само со промена на амплитудата на ексцитацискиот сигнал, и се очекува дека ќе го прошират опсегот на примена на оваа техника.

Клучни зборови: квадратно-бранова волтаметрија; електроанализа; електродни механизми; кинетика на електродни реакции; електрохемија

1. INTRODUCTION

Square-wave voltammetry (abbreviated here as SWV) is one of the most advanced electrochemical techniques [1–6] that, in a historical context, originates from the Kalousek commutator [7] and Barker square-wave polarography [8–10]. Though most frequently applied for analytical purposes, SWV is a superior electrochemical technique for both mechanistic and electrokinetic studies of various electrode processes. Basic features of the potential modulation, together with a simulated voltammetric response in SWV, are depicted in Figure 1. In SWV, the potential modulation comprises of a staircase potential ramp combined with square-shaped potential pulses (Figure 1A). The main parameters of a potential cycle composed of two neighboring pulses (Figure 1B) are the height of the pulses (referred as the SW amplitude, E_{sw}) and the SW frequency (*f*), defined as $f = 1/\tau$, where τ is the duration of a potential cycle. In terms of the duration of the single potential pulse t_p ($\tau = 2t_p$), the frequency could be defined as $f = 1/(2t_p)$. The potential cycle, repeated at each step of the staircase ramp, consists of a forward and backward (or reverse) potential pulse, the terms being defined relative to the direction of the staircase ramp. Obviously, in the course of each potential cycle, the electrode reaction is driven in both the anodic and cathodic directions, thus providing an insight into the electrode mechanism.

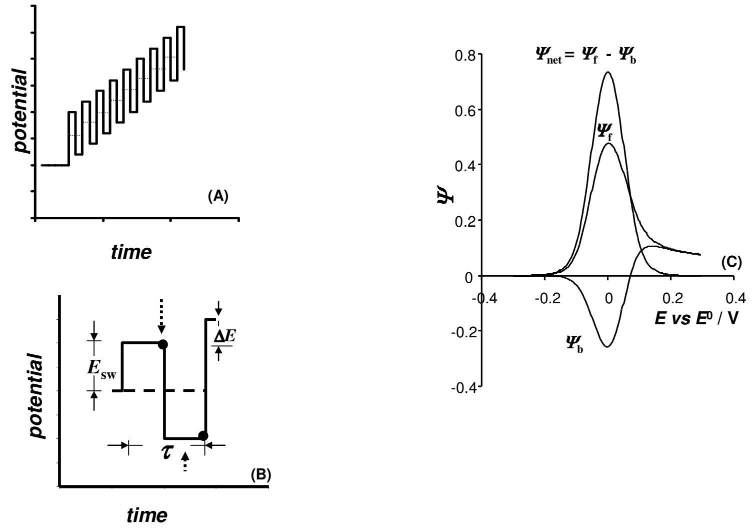

Fig. 1. **(A)** Potential waveform, **(B)** one potential cycle, and **(C)** a typical voltammogram in square-wave voltammetry. The response consists of a forward (anodic, Ψ_f), backward (cathodic, Ψ_b) and net (Ψ_{net}) component.

The SW frequency is the critical time parameter of the voltammetric experiment. The physical meaning of the frequency is understood as the number of potential cycles in a unit of time. The typical frequency range provided by commercially available instruments [1, 11] is from 5 to 2000 Hz, which corresponds to the duration of a single potential pulse t_p from 0.25 to 100 ms. Besides the frequency, the scan rate of the voltammetric experiment could be defined as $v = f\,\Delta E$, where ΔE is the step of the staircase ramp (cf. Figure 1B).

In the course of a voltammetric experiment, the current is sampled at the end of each potential pulse, aiming to discriminate against the charging current [1, 5]. Accordingly, 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. Consequently, to each step potential, two current values are assigned. Subtracting the forward and backward currents, a net component of the SW voltammogram is obtained, which is most frequently a bell-shaped curve that enables precise determination of its position and height (Figure 1C).

In the present review, an attempt is made to highlight the developments in this technique in the last several years, addressing the most typical analytically oriented studies, the theoretical studies referring to complex electrode mechanisms, as well as application of the technique for kinetic and mechanistic purposes. Finally, a brief consideration is given to several methodologically oriented studies of general importance that, to the best of our knowledge, might facilitate and expand the scope and application of the technique.

2. APPLICATION OF SQUARE-WAVE VOLTAMMETRY IN ELECTROANALYSIS

Square-wave voltammetry, as one of the superior members of the large family of pulse-voltammetric techniques, is attributed with excellent analytical sensitivity [1, 5, 6]. Hence, it is frequently applied for the quantitative determination of a variety of compounds such as medications, biomolecules, environment pollutants, antioxidants, etc. Besides the pronounced sensitivity, electroanalytical methods commonly require a short analysis time, as SWV is recognized as a very fast voltammetric technique. Furthermore, the analytical sensitivity can be enhanced by combining the technique with enrichment procedures that are well-known in electroanalysis, such as electrolytic or adsorptive accumulation. Accordingly, square-wave stripping voltammetry enables ultra-trace analytical determination down to a picomolar concentration level [5, 6]. In the last decade, in many cases, SWV has emerged as a viable and cheap alternative to other more expensive and time-consuming techniques (such as chromatography, for example) for the determination of inorganic and biologically important compounds. All these advantages make SWV a technique of choice for the quantification of important classes of compounds, such as proteins [12], vitamins [13], phenols [14–18], benzoquinones [19], pesticides, herbicides and fungicides [20–28], alkaloids [29], terpenoids [30], metal traces [31–46], and drugs [47, 48].

Due to the outstanding resolution of the voltammetric response, SWV is applied for simultaneous determination of compounds with close redox potentials, such as paracetamol and penicillin, exemplified by the work of Švorc [49], as well as for ascorbic acid, acetaminophen, and tryptophan at a graphite electrode modified with carbon nanotubes [50]. In a recent work, Tian et al. [51] reported on the simultaneous determination of ascorbic acid, dopamine, and uric acid at a gold nanoparticle-modified graphite electrode.

SWV, in combination with screen printed electrodes [52, 53], has been successfully exploited for the direct determination of low molecular weight antioxidants such as glutathione, ascorbic and uric acids in blood samples. This method is less sensitive to matrix interference and is superior compared to the well-established spectrophotometric methodology for the quantification of low molecular weight antioxidants. In addition, SWV has been successfully applied for the detection of phenols, another class of important antioxidants. Seven phenolic compounds, i.e. the *o*-phenylendiamine, *p*-chlorophenol, *p*-aminophenol hydroquinone, pyrocatechol, phenol, and 3,3-5,5-tetramethylbenzidine were tested as cosubstrates of the enzymatic reaction of the horseradish peroxidase [54]; the calibration was carried out in the subnanomolar range. Many polyphenols belonging to the group of flavonols present in various plants have been successfully determined by solid electrodes [55, 56]. Various catechins, such as epigallocatechin gallate, epicatechin, epicatechin gallate, gallic acid, and epigallocatechin were directly quantified in various green teas in the submicromolar range at a glassy carbon electrode. The accuracy, sensitivity and selectivity of the latter method were comparable to the corresponding HPLC-based methodology. In another work, SWV was explored for the quantification of polyphenols from the class of flavonolignans [57]. Additionally, SWV has been used for the determination of isosilybin, silybin and some of its derivatives in adsorptive stripping mode. Moreover, it was shown that silybin forms 1:2 complexes with Cu^{2+} ions capable of selectively binding to DNA molecules. Resveratrol is another important polyphenolic antioxidant present in red wine. Its detection in red wine samples has been achieved using an adsorptive stripping methodology in a concentrated perchloric medium [58]. The detection limit of resveratrol was in the ng/ml range, comparable to that obtained by chromatographic techniques.

In the last decade, protein-film voltammetry has emerged as a suitable technique for studying the redox chemistry of various enzymes and proteins [59]. Duwensee et al. [60] 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 a very small volume. The polymerase chain reaction is an important tool in molecular biology, used for the detection of gene-related diseases, amongst other applications. 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 labeled with an osmium(VIII) bipyridine complex. In such an approach, significant discrimination was achieved against complementary and non-complementary targets. The method was reported to be very simple and fast, and superior in many aspects over the commonly explored microfluidic chips with external pumps. Another important contribution in protein detection is the work of Křižková et al. [61]. In this study, electrophoretic and voltammetric methods were developed for the determination of avidin, a protein responsible for crop protection. The reaction between avidin (the glycosylated protein) and vitamin H (biotin) was utilized to develop a sensitive method for avidin quantification. The authors showed that the method was specific, while its sensitivity was comparable to the electrophoretic methods developed for avidin determination in transgenic plants. In another work [62], the authors developed an ultrasensitive procedure for streptoavidin determination (from *Streptomyces avidinii*) in the zeptomolar concentration range using carbon paste electrodes. Shu et al. developed a novel method for studying the ribonuclease activity of the dicer protein at an RNA-modified gold electrode [63].

Beyond methods for the quantification of proteins, SWV has been exploited for the detection of other important physiological organic compounds [64, 65]. Arevalo et al. [66] have recently reported on a sensitive adsorptive stripping method to detect the steroid progesterone on a glassy carbon electrode. The authors of this work also paid attention to the adsorption of progesterone on the working electrode surface, while evaluating the thermodynamic parameters of the adsorption strength. The same group [67] also published a comprehensive study of the determination of progesterone in acetonitrile at a glassy carbon electrode. Electrochemical reduction of progesterone in non-aqueous media is commonly accompanied by the formation of stable radical anions. In another work, Goyal et al. [68] developed a method for the simultaneous detection of adenosine and adenosine-5-triphosphate on an ITO electrode modified with gold nanoparticles. The specific catalytic effect of gold nanoparticles was a crucial factor that led to separating the voltammetric signals of adenosine and adenosine-5-triphosphate; thus, their simultaneous determination was achieved. In addition, a simple but efficient method was developed for the quantification of yeast RNA (yRNA) on a cetylpyridine bromide-cellulose modified ITO electrode [69], as yRNA strongly adsorbed to the cellulose-modified electrode while undergoing irreversible oxidation. The kinetic parameters of the electrochemical reaction of yRNA were evaluated from the SW voltammetric response. Fast Fourier transformed square-wave voltammetry has been applied to detecting the amino acid levodopa, the precursor for dopamine production in the brain [70]. With the help of this technique, L-dopamine was detected in urine and human serum in a micromolar concentration range using microelectrodes.

Nowadays, SWV finds applications in environmental analysis for trace metal monitoring [71, 72], as well as the detection of organic ecotoxic compounds [73, 74]. A highly promising, switchable and sophisticated sensor for Hg(II) monitoring was developed by Lai et al. [75]. The detection of organophosphorous pesticides was achieved by following the electrochemical activity of dichloroindophenol with thiocholine, a product created by the enzymatic reaction between acetylthiocholine and cholinesterase [76]. An SWV method for the detection of organophosphorous pesticides has been recently developed, based on inhibition of the enzyme cholinesterase in a biphasic system [77]. The activity of the enzyme cholinesterase toward indophenol acetate yielded indophenol, a redox active compound that is a subject of quantitative determination with SWV.

Remarkably, SWV is an effective technique for the analysis of some bacteria in real samples. Carpani et al. [78] recently reported on an SWV method to quantify the bacterial load of *Escherichia coli* and *Pseudomonas aeruginosa* in non-treated water samples. A microelectrode array was 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 was selective, simple and fast, and no water sample pretreatment was required. In addition, traces of *Escherichia coli* were detected by modifying a glassy carbon electrode with multi-walled carbon nanotubes [79]. The detection of these living microbial cultures is based on measuring the activity of oxidizable components present in *Escherichia coli*; the release of these molecules is catalyzed by the carbon nanotubes.

One of the advantages of SWV is also seen in its applications for the direct detection of some redox active compounds in complex organic matrixes or food products. Recently, detection of the antibiotic ceftiofur was achieved directly in milk samples following the hydrolysis of ceftiofur [80]. Owing to its performance in the 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 [81] and beverages [82]. Alkaloids are another class of natural compounds that have attracted considerable interest due to their wide range of applications in the pharmaceutical industry. The adsorptive stripping SW voltammetric quantification of protopine, an isoquinoline alkaloid, has been achieved in alkaline media, following its oxidation at a pyrolytic graphite electrode [83].

3. THEORY OF ELECTRODE MECHANISMS

In the last decade, significant contributions to the theory of SWV have been made by the research groups of Lovrić [84–93], Molina [94–100], Compton [101–104], Mirceski [105–108], Gulaboski [109–112], and others [113–115]. Considerable efforts have been made to develop the theoretical background for a variety of electrode mechanisms of a dissolved or immobilized redox couples at both macroscopic and microelectrodes, as well as electrode processes occurring in a restricted diffusion space. Worth mentioning are electrode processes including multistep, consecutive electron transfers [94, 87–89, 98, 109], and catalytic mechanisms [95, 96, 99, 110], due to their relevance to biochemical systems. In addition, a series of works has been dedicated to the study of electrode processes in the frame of the Marcus-Hush electron transfer kinetic model [101–104]. 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 [116, 117]. Works of merit are those where Fourier transformed SWV has been applied for the estimation of electrode kinetics [115, 118] and charge transfer kinetics across liquid/liquid (L/L) interfaces [113, 119]. In order to illustrate how a variable voltammetric response can be obtained in SWV, Figure 2 depicts the evolution of theoretical SW voltammograms for a few common electrode mechanisms at a macroscopic electrode [5]. The figure encompasses a quasireversible electrode reaction of a dissolved (Figure 2A) and immobilized (Figure 2B) redox couple, an electrode mechanism of a dissolved redox couple combined with a follow-up reversible chemical reaction, i.e., EC$_r$ mechanics (Figure 2C), an electrode reaction of two reversible redox couples bridged with an intermediary irreversible chemical reaction (E$_r$C$_i$E$_r$ (Figure 2D)), and a catalytic regenerative electrode mechanism, known as EC'$_i$ (Figure 2E).

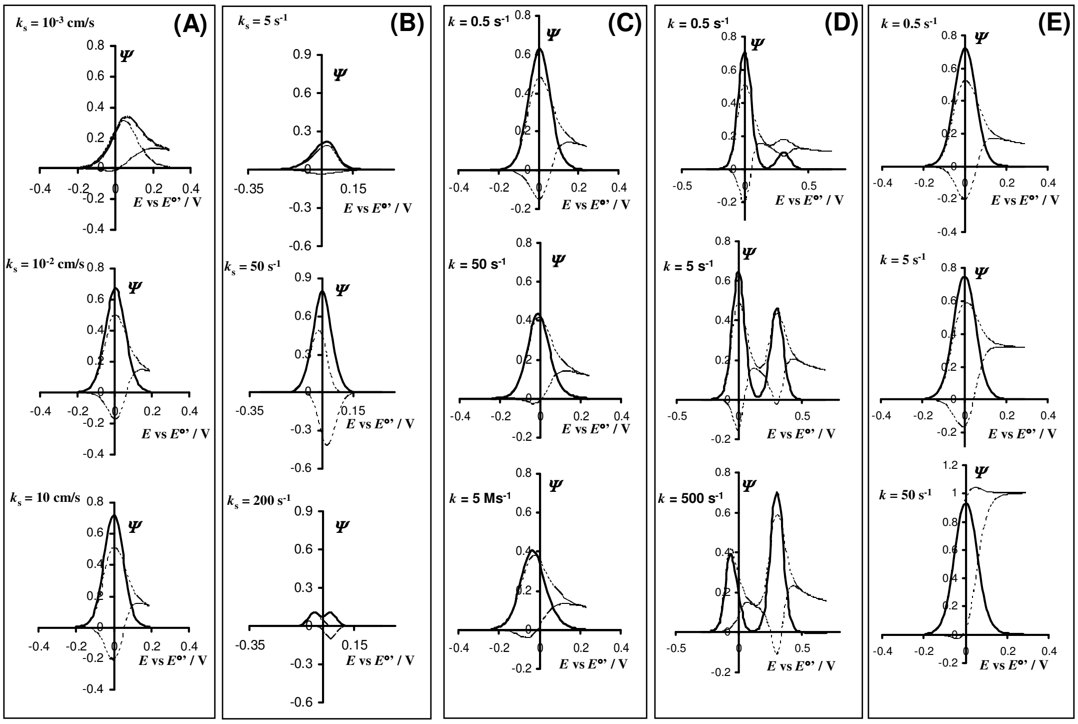

Fig. 2. Typical theoretical SW voltammograms of: **(A)** quasireversible electrode reaction of a dissolved redox couple; **(B)** quasireversible electrode reaction of a surface confined redox couple; **(C)** quasireversible electrode reaction of a dissolved redox couple followed by a reversible homogeneous chemical reaction (EC$_r$); **(D)** consecutive two-step reversible electrode reaction where the two electrochemical steps are linked with a homogeneous irreversible chemical reaction (E$_r$C$_i$E$_r$); and **(E)** quasireversible electrode reaction of a dissolved redox couple followed by a regenerative, irreversible, homogeneous chemical reaction (catalytic mechanism; EC$_i$'). Evolution of the response by varying the electrode reaction rate constant (A and B) and rate constant of the homogeneous chemical reaction (C, D, and E). The rate constant values are indicated on the panels. The conditions of the simulations are: $f = 50$ Hz, $E_{sw} = 50$ mV, $\Delta E = 10$ mV, $n = 1$ (n is the number of electrons), $\alpha = 0.5$ (α is the electron transfer coefficient). For panel C, the equilibrium constant is $K = 10$.

Lovrić et al. [87, 89] analyzed a two-step quasireversible consecutive electron transfer mechanism, as well as an EE mechanism [88], where both the initial reactant and the intermediary are stabilized with complexation reactions. Molina et al. developed the theory for an EE mechanism, consisting of two electrochemically reversible steps for a micro-disc electrode geometry [97] and for a spherical electrode [94]. A special case of the EE mechanism, where an overall transfer of three electrons is assumed, i.e., the first one-electron transfer step is followed by the second two-electron transfer step, has been also studied [91], which is important for processes at bismuth and antimony film electrodes used in modern anodic stripping voltammetry [108]. Gulaboski studied two specific surface mechanisms, designated ECE [109], where the two quasireversible electron transfer steps are linked with a kinetically controlled irreversible first order chemical reaction, and a catalytic EEC' system [110], where the second electron transfer step is coupled with a follow-up first order regenerative chemical reaction.

Molina et al. developed a theory for a series of catalytic mechanisms [95, 96, 99], including the EC' catalytic reaction scheme at a disc electrode, spherical microelectrode, and a simple surface catalytic mechanism, similar to the previous work of Mirceski and Gulaboski [120]. In addition to the theory of catalytic mechanisms, Mirceski et al. [105] performed a comparative analysis of the electrocatalytic mechanisms of the first and second kind at a planar electrode, considering quasireversible electrode reactions.

A few contributions to the theory of cathodic stripping processes of insoluble salts have been also published [107, 121]. In these specific mechanisms, one assumes the formation of an insoluble salt between the electrode materials, e.g. a mercury electrode, and an electroinactive reacting ligand present in the electrolyte solution. In this context, the contribution to the theory of anodic stripping processes at bismuth-film electrodes also has to be mentioned [108, 122], which, from the modeling point of view, follows the previous theory for cathodic stripping processes of insoluble slats.

Lovrić conducted particularly interesting theoretical work in which SWV was applied for the first time to analyze surface active, but redox inactive, species [93]. 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 look for the appearance of a tensammetric response under SWV conditions, in particular when complicated adsorption electrode mechanisms are considered.

In a separate group of studies, SWV was applied for mechanistic and electrokinetic purposes, invoking existing theoretical models [111, 112, 118, 119, 123–126]. A typical example is the work of Fernandez et al. [127], who applied 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 a glassy carbon electrode. Molina et al. [128] developed an important methodology for the determination of the partition constant of 1-naphthol between water and unilamellar phospholipid vesicles, based on the electrochemical response of the redox compound at macroscopic platinum and glassy carbon electrodes. Compton et al. studied the oxidation of nitrite anions at a variety of electrodes, addressing the mechanism and kinetics of the electrode reaction. They demonstrated the importance of knowledge regarding the electrode mechanism and kinetics for the optimization and development of advanced electroanalytical methodologies for quantitative determination [129].

The last decade has been also marked by important contributions of SWV in studying the charge transfer processes across L/L interfaces [100, 115, 119, 130–142], related to thin organic films and three-phase electrodes. The theoretical modeling relevant to film electrodes prompted the consideration of electrode processes in a restricted diffusion space [106], including the analysis of ion transfer kinetics across an L/L interface, as well as complex catalytic mechanisms in a thin film. As previously mentioned, FT-SWV has also been applied to estimate the kinetics of ion transfer across an L/L interface in thin film electrodes [119, 131]. Again, the feature of the quasireversible maximum was exploited, which was originally predicted for thin-film quasireversible electrode processes [143]. Molina et al. [100] studied, both theoretically and experimentally, the ion transfer processes at electrodes with two polarizable liquid interfaces, emphasizing the advantages of this system compared to conventional systems with a single liquid interface.

4. NEW METHODOLOGICAL CONCEPTS AND PERSPECTIVES

Several methodologically oriented contributions have recently appeared that are highly promising to expand the scope and application of SWV for mechanistic and electrokinetic studies [144–146]. So far, the SW frequency, which is the main parameter controlling the scan rate and the typical time of an SW voltammetric experiment, is the main tool in both mechanistic and electrokinetic studies. An exception is the work published by one of us almost two decades ago [147], referring to surface electrode processes where the kinetics were estimated based on the split-net SW peak under large SW amplitudes. The idea of further exploring the advantages of applying the SW amplitude as an alternative tool for electrokinetic analysis was recently developed [144, 145]. In the method, termed "amplitude-based quasirevesible maximum" [144], kinetic measurements are based on the analysis of the net SW peak current as a function of the varying amplitude, whereas in previous studies [145], the concept of potential-corrected SW voltammograms was introduced, which enables kinetic analysis by inspecting the peak potential separation of the forward and backward SW components as a function of the SW amplitude. In both methods, the kinetic analysis is conducted at a constant SW frequency, i.e. at a constant scan rate, which is particularly remarkable for any voltammetric methodology and seems to be a unique ability of SWV. Let us note that we are currently working on a new methodology to extract kinetic information from a single SW voltammogram by analyzing the current variation in the course of the entire duration of SW pulses.

Works of merit are also those where SWV is applied in the fashion of cyclic voltammetry, i.e., cyclic square-wave voltammetry (CSWV) [146]. This includes the work of Molina [94], as well as a series of studies in which SWV was applied in reverse mode [84–86, 148]. The basis of this highly promising technique is found in the previous works of Chen and Xinsheng [149]. Similar to the spectroscopic techniques, a typical CSW voltammetric pattern can be considered as a fingerprint of the studied experimental system.

In summary, SWV remains a superior electrochemical technique for analytical, mechanistic, and electrokinetic applications. While the first is fully confirmed, the wide application of the technique in analyzing the mechanism and kinetics of electrode processes remains a challenge. Yet, our hopes remain that the recent exhaustive development of the theory justifies expectations that staircase cyclic voltammetry could be soon be replaced by square-wave voltammetry in the investigation of electrode mechanisms. We hope that these novel methodological concepts might widen and facilitate the application of the technique 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. Cyclic square-wave voltammetry is particularly promising [146]. So, there is a necessity to analyze a variety of electrode mechanisms in order to establish diagnostic criteria under the 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 using a new and unique approach [144, 145].

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