

Differential Square-Wave Voltammetry

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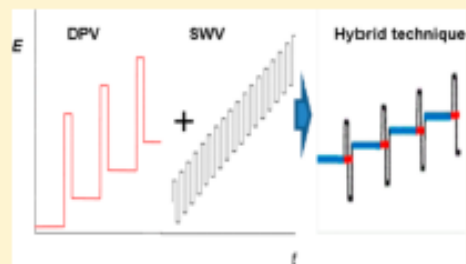
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ABSTRACT: A new voltammetric technique designed as a hybrid between differential pulse and square-wave voltammetry is proposed for the purpose of unifying the advantages of both techniques, i.e., the ability to provide mechanistic information, studying electrode kinetics of both sluggish and very fast electrode reactions, and the ability to suppress effectively residual background current. Voltammetric modulation of the hybrid technique consists of a staircase potential combined with square-wave potential modulation superimposed at the end of each potential step. By measuring the current at the end of each potential step and pulse, differential forward and backward voltammetric components can be composed, which is a unique ability of the hybrid technique. In addition, by analogy to square-wave voltammetry, a net differential component can be contracted with improved analytical performances compared to square-wave voltammetry. The proposed technique opens a new avenue for an advanced analysis of electrochemical processes and analytical application.



Square-wave voltammetry (SWV), as a special form of the popular differential pulse voltammetry,^{1,2} is one of the most advanced members in the family of pulse voltammetric techniques,^{3–6} being primarily designed to provide high sensitivity and speed of the analytical measurement.^{7,8} The popularity of the technique has been permanently progressing since the seminal work of Ramaley and Krause,⁹ contributions of Osteryoungs and O'Dea,⁴ Lovric et al.,^{10–12} and others.^{13–18} Methodological development and application of the technique have been reviewed recently.^{19,20} In the past 2 decades the application for studying mechanism^{21–25} and kinetics^{26,27} of electrochemical processes has been progressively increasing revealing the versatility and sophistication of the technique.

In a quest for further methodological development, several modifications have been recently proposed, including multi-sampling SWV²⁸ and square-wave chronoamperometry (or electrochemical faradaic spectroscopy).²⁹ Here also belongs a cyclic variant of SWV, known for a while as cyclic square-wave voltammetry^{30–32} and SWV in a reverse mode.^{33,34} Unique features of the technique for electrokinetic measurements are represented by a series of kinetic methods developed under conditions of constant scan rate.^{35–39}

Nevertheless, as any technique, SWV has its own drawbacks; it is relatively complex, and voltammetric data are less intuitively understandable compared to cyclic voltammetry. As a consequence, in most of the studies where SWV is utilized, only the net, voltammetric peak is analyzed, avoiding detail analysis of the forward and reverse voltammetric components. On the other hand, the forward and reverse components are experimentally measured curves, related

directly to the anodic and cathodic reactions of a given redox couple, while the net component is a differential curve.⁶ Moreover, for most of diffusion affected electrode mechanisms, both forward and reverse components are asymmetric peak-like curves; they are not real peaks, nor sigmoid curves, making the precise measurement of the peak current and potential frequently ambiguous. Surprisingly, the latter issue remains almost unaddressed in the literature so far.

In the context of electrode kinetics one recognizes that SWV is superior for studying fast quasireversible and reversible electrode processes, whereas, when a large overpotential separates the anodic and cathodic electrode reactions of a given redox couple, the overall system frequently appears totally irreversible in SWV at moderate pulse heights (i.e., SW amplitudes).⁶ For such a process the net component can be less intensive than the forward one, which compromises even the analytical application of SWV. Hence, the technique is seriously limited when slow, quasireversible processes are considered. The latter drawback is partly overcome with cyclic square-wave voltammetry^{30,32,40} or SWV applied in a reverse mode;^{33,34} unfortunately, the two variants are more complex than conventional SWV and interpretation and understanding of the voltammetric experiment could be even more difficult.

In analytical context, SWV discriminates the charging current effectively, which is also typical for other pulse

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77 voltammetric techniques, e.g., differential pulse voltammetry.¹
 78 However, when solid electrodes are concerned, a more serious
 79 problem is the background current due to residual charge
 80 transfer processes rather than the charging current of the
 81 electric double layer. At solid electrodes differential pulse
 82 voltammetry can be even more analytically effective than SWV,
 83 due to the ability for providing lower background current by
 84 adjusting the ratio between the potential step and pulse
 85 duration.¹ Parveen and Kant studied extensively the properties
 86 of arbitrary pulse voltammeters,^{41–45} considering in particular
 87 the role of the solid electrode roughness and unequal
 88 diffusivity. On the other hand differential pulse voltammetry
 89 is inferior in providing mechanistic information on the
 90 electrode reaction compared to SWV. Hence, it seems that a
 91 hybrid form of the two techniques is required to unify their
 92 advantages.

93 Three general questions serve as a motivation for the current
 94 study: *Whether SWV can be modified in a way to be more*
 95 *appropriate for analysis of slow electrode processes in order to*
 96 *expand the scope of the technique in a general context?*
 97 *Whether both the forward and backward component of the*
 98 *voltammetric response can be transformed into differential curves,*
 99 *which will enable precise estimation of the peak parameters, for*
 100 *the purpose of more advanced mechanistic and electrokinetic*
 101 *analysis? And, finally, whether analytical performances of SWV*
 102 *can be improved with respect to background current*
 103 *discrimination, as in the case of differential pulse voltammetry?*
 104 To these goals, the SW potential modulation is modified as
 105 shown in Figure 1. First it is recalled that the potential

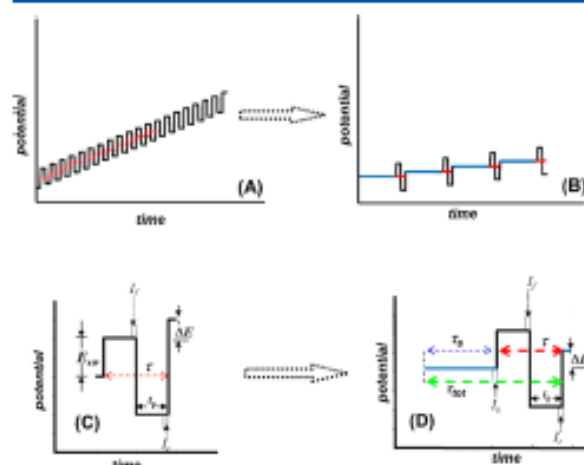


Figure 1. Potential modulation in (A) conventional SWV and (B) new, hybrid differential square-wave voltammetry. One potential cycle in (C) conventional SWV and (D) the new technique.

106 waveform in SWV (Figure 1A) can be envisaged as consisting
 107 of a staircase potential (Figure 1A, red points) with a step
 108 duration τ (Figure 1C, red line), modified with two opposite,
 109 equal in height pulses with duration t_p , such as $\tau = 2t_p$ (Figure
 110 1C). Consequently, the final potential form is a train of
 111 oppositely oriented pulses (black line in Figure 1A). The
 112 inverse value of τ is known as SW frequency f ($f = 1/\tau = 1/(2t_p)$).⁶ Commonly t_p ranges from 0.5 to 100 ms.

114 In the proposed new potential modulation the potential step
 115 is only extended for an additional value τ_1 (blue line in Figure
 116 1D), while the duration of pulses t_p remains as in the

conventional SWV (red line in Figure 1D). As a consequence,
 the overall potential modulation presented in Figure 1B
 consists of steps (blue lines) and pulses (black line). In the
 new technique the total duration of a single potential cycle
 presented in Figure 1D (green line) is $\tau_{\text{tot}} = \tau_1 + \tau$, while the
 period τ again consists of two, oppositely oriented pulses. In
 the present study, τ_1 ranges from $\tau_1 = 2t_p$ to $\tau_1 = 20t_p$, i.e., it
 spans a time interval from 1 ms to 2 s. By analogy with
 conventional SWV, the pulse duration t_p of the new technique
 can be expressed in terms of frequency $f = 1/(2t_p)$. The new
 potential modulation can be understood as being obtained by
 inserting a step potential with a duration τ_1 between each
 potential cycle in conventional SWV; as a consequence, instead
 of having a train of potential pulses (Figure 1A), one gets a
 combination of steps and pulses (Figure 1B).

The latter simple modification affects voltammetric features
 profoundly, as elaborated in the following discussion,
 addressing simple quasireversible electrode reaction of a
 dissolved redox couple.⁴⁶ More importantly, by measuring
 the current before the application of pulses (I_f in Figure 1D),
 as well as at the end of each pulse (I_r and I_p in Figure 1D),
 both forward and reverse voltammetric components can be
 transformed into differential curves. Thus, the new technique
 can be provisionally termed as *differential square-wave*
voltammetry. In addition, by analogy to SWV, net, differential
 voltammetric component can be constructed as well. Thus, the
 voltammetric response can be represented by three differential
 components, which is a unique feature of the proposed
 technique.

The proposed voltammetric technique bears some similarities
 with the technique of Zlatev et al.,^{47–49} termed as
 differential alternative pulses voltammetry, introduced for the
 purpose of improved voltammetric resolution. The present
 technique keeps the ability typical for SWV to access the
 kinetics of very fast charge transfer processes by adjusting the
 frequency of the pulses, as well as to provide an insight into the
 mechanism of the electrochemical reaction. On the other hand,
 as in differential pulse voltammetry, discrimination against the
 background current, as well as accession to the kinetics of
 sluggish electrode reactions, can be achieved by adjusting the
 step-to-pulse duration ratio $r = \tau_1/t_p$.

The new voltammetric technique is tested by the electrode
 reaction of the redox couple $\text{Eu}^{3+}(\text{aq})/\text{Eu}^{2+}(\text{aq})$ at hanging
 mercury drop electrode²⁹ and hexacyanoferrate(III)/
 hexacyanoferrate(II) at glassy carbon electrode.³⁶

EXPERIMENTAL SECTION

All chemicals used were of analytical grade purity (Sigma-
 Aldrich, ChemLab, or POCh). Aqueous solutions were
 prepared with purified water with Millipore Direct Q-3
 (Merck) purification system. Stock solutions of 0.01 mol L⁻¹
 europium(III) chloride and 0.1 mol L⁻¹ potassium
 hexacyanoferrate(II) were prepared in water. Accordingly
 supporting electrolyte solutions used for electrochemical
 measurements were 0.1 mol L⁻¹ citrate buffer at pH 3 and
 phosphate-buffered saline pH 7.4 (consisting of 0.01 mol L⁻¹
 phosphate buffer, 0.027 mol L⁻¹ potassium chloride, and 0.137
 mol L⁻¹ sodium chloride), respectively.

Experimental analyses have been performed with multi-
 Autolab potentiostat model M101 (MetrohmAutolab B.V.)
 controlled by the NOVA (v. 1.10.3) software. Hanging
 mercury drop electrode (HMDE, mtm-anko instruments,
 Poland, surface area 0.00102 cm²) served as a working

nents the following values for the formal rate constant have been found: $3.5 \times 10^{-4} \text{ cm s}^{-1}$ ($r = 1$) and $3.3 \times 10^{-4} \text{ cm s}^{-1}$ ($r = 10$), for $\alpha = 0.45$ and $D = 1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which are in agreement with previous data.

Finally, in order to illustrate that the new technique exhibits the ability to improve the residual background response (i.e., suppressing the background current) at solid electrodes compared to SWV, a set of experiments have been conducted at glassy carbon electrode with hexacyanoferrate(II) as a redox probe. Even at minimal step-to-pulse duration ratio $r = 1$, the background of net SW voltammogram is obviously diminished with the new technique, as depicted in Figure S4. As a consequence, the net peak current measured with a tangent method is $26.58 \mu\text{A}$ for the new technique vs $26.1 \mu\text{A}$ for the conventional SWV. In addition, the inset clearly reveals that the background response of the blank sample is significantly improved under conditions of the new technique, implying promising analytical applications. The ratio between the absolute net peak current and the blank current measured at the peak potential value is 18.76 for the new technique and 12.54 for SWV, indicating promising analytical performances of the proposed new hybrid technique.

CONCLUSIONS

The new differential square-wave voltammetry, designed as a hybrid form between conventional differential pulse (DPV) and square-wave voltammetry (SWV), aims to unify the advantages of both techniques and to provide a new means for advanced mechanistic and kinetic study of electrochemical processes, as well as for improved analytical application compared to both techniques. It has been demonstrated that the new technique, encompassing potential steps and square-wave potential modulation (i), enables mechanistic analysis of electrode processes, which is unlikely in conventional DPV; (ii) enables measurement of electrode kinetics of both fast and slow electrode processes, which is less probable with conventional SWV; and (iii) improves the electrochemical reversibility of sluggish electrochemical processes, which is highly advantageous in both mechanistic and electrokinetic contexts. Moreover, in analytical context, it is plausible to expect that the new technique will exhibit better analytical performances compared to conventional SWV, as already experimentally implied.

The technique is associated with two critical time parameters, i.e., the frequency of pulses, as in conventional SWV, and the step-to-pulse duration ratio, as typical in conventional DPV. The latter parameter is of critical importance for improving electrochemical reversibility and thus analytical performances, as well as enables estimation of electrode kinetics of sluggish processes.

Voltammetric response of the technique can consist of forward, reverse, and differential net component, identical as in conventional SWV. However, by virtue of current sampling at the end of each potential step (i.e., prior to the application of SW potential pulses), both forward and reverse currents can be transformed into differential components, providing a new voltammetric profile, different than conventional forms of both DPV and SWV, opening a new perspective for advanced analysis of electrochemical processes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.9b03035.

(Figures S1–S4) Comparison of conventional SWV and the new technique for different step potentials, typical response of a sluggish electrode reaction, effect of the electron transfer coefficient on the additive differential net component and hexacyanoferrate redox system at glassy carbon electrode (PDF)

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Notes

The authors declare no competing financial interest.

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