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Square-Wave Voltammetry

Theory and Application

Springer

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Preface

This is the first monograph in a series devoted to electrochemistry. Although the market is rich in books and series on electrochemical themes, it is surprising that a number of serious topics are not available. With the series "Monographs in Electrochemistry" an attempt will be made to fill these gaps. I am very thankful to the publishing house of Springer for agreeing to publish these books, and for the great freedom given to me in choosing the topics and the most competent authors, and generally for the fantastic cooperation with the publisher. I am especially thankful to Mr. Peter W. Enders.

Square-wave voltammetry is a technique that is readily available to anyone applying modern electrochemical measuring systems. Its use can be beneficial in analytical applications as well as in fundamental studies of electrode mechanisms. Upon first glance, it seems that the analytical application of square-wave voltammetry is rather simple and does not afford a deep knowledge of the background, however, this is certainly not the case. For an optimal exploitation of the potential of square-wave voltammetry, it is essential to know how the signal is generated and how its properties depend on the kinetics and thermodynamics of the electrode processes. For a detailed analysis of electrode mechanisms, this is indispensable, of course, in any case. I am very happy that three leading experts in the field of square-wave voltammetry have agreed to write the present monograph, which in fact is the first complete book on that technique ever published in English. All three authors have a long and distinguished publishing record in electroanalysis, and especially in the theory and application of square-wave voltammetry. I hope that this monograph will make it much easier for potential users in research, industrial, and environmental laboratories, etc., to apply square-wave voltammetry for their benefit.

Fritz Scholz
– Editor of the series "Monographs in Electrochemistry" –

Contents

Chapter 1
Introduction

1.1 From Square-Wave Polarography to Modern Square-Wave Voltammetry

Square-wave voltammetry (SWV) is a powerful electrochemical technique that can be applied in both electrokinetic and analytic measurements [1–5]. The technique originates from the Kalousek commutator [6] and Barker's square-wave polarography [7]. Kalousek constructed an instrument with a rotating commutator that switched the potential of the dropping mercury electrode between two voltage levels with the frequency of five cycles per second [8, 9]. Three methods for programming the voltages have been devised and designated as types I, II, and III, and these are shown in Fig. 1.1. Type I polarograms were recorded by superimposing a low-amplitude square-wave (20 – 50 mV peak-to-peak) onto the ramp voltage of conventional polarography. The current was recorded during the higher potential half-cycles only. Figure 1.2 shows the theoretical response of a simple and electrochemically reversible electrode reaction:

$$\mathrm{O}^{m+} + n\,\mathrm{e}^- \leftrightarrows \mathrm{R}^{(m-n)+} \tag{1.1}$$

obtained by the type I program. Only the reactant O^{m+} is initially present in the bulk of the solution. The starting potential is -0.25 V vs. $E_{1/2}$, where $E_{1/2}$ is a half-wave potential of dc polarogram of electrode reaction (1.1). The response is characterized by a maximum oxidation current appearing at 0.034 V vs. $E_{1/2}$. In the vicinity of the half-wave potential, the reactant is reduced during the lower potential half-cycle (which is not recorded) and the product is oxidized during the higher potential half-cycle, which is recorded. This is illustrated in Fig. 1.3, which shows theoretical concentrations of the reactant and product near the electrode surface at the end of the last cathodic (A) and anodic (B) half-cycles applied to the same drop. The method was improved by Ishibashi and Fujinaga, who introduced the differential polarography by measuring the difference in current between successive half-cycles of the square-wave signal [10–12]. The frequency of the signal was 14 Hz. It was superimposed on a rapidly changing potential ramp and applied to the single mercury

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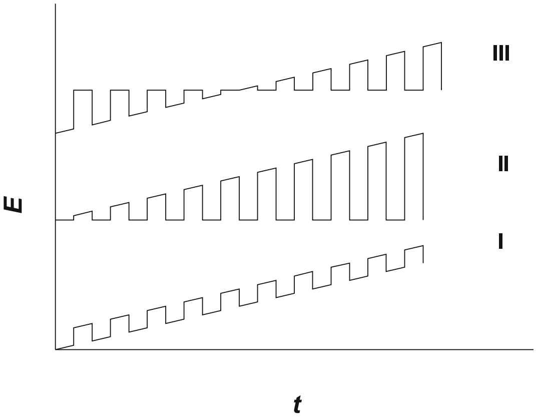

Fig. 1.1 Potential-time relationships realized by the Kalousek commutator

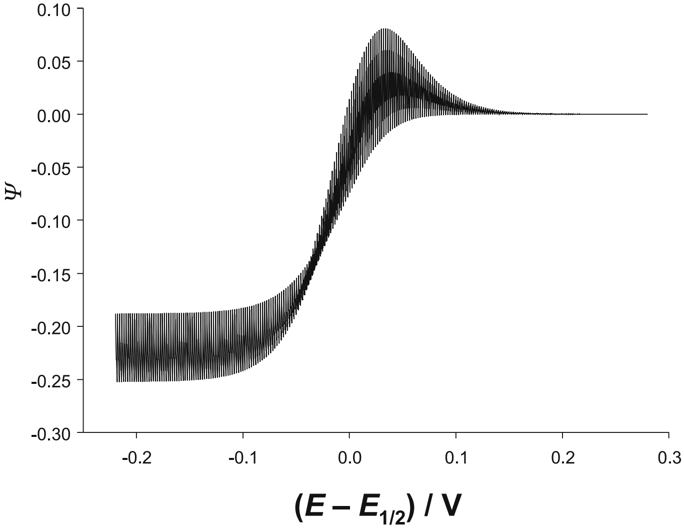

Fig. 1.2 Type I Kalousek polarogram of electrode reaction (1.1) on dropping mercury electrode. $\Psi = I/nFA_m c_{\mathrm{O}}^{*}(Df)^{1/2}$, frequency $= 5$ Hz, amplitude $= 30$ mV, drop life time $= 1$ s, $\mathrm{d}E/\mathrm{d}t = 2$ mV/s and $E_{\mathrm{st}} = -0.25$ V vs. $E_{1/2}$. For the meaning of symbols, see below (1.9) and (1.24)

drop. Barker and Jenkins introduced three important innovations: (i) the frequency of square-wave signal was 225 Hz, (ii) the current was measured during the last 280 µs of each half-cycle and the difference between two successive readings was recorded, and (iii) the measurement was performed only once in the life of each drop 250 ms before its end [13, 14]. Figure 1.5 shows the theoretical square-wave polarogram of the electrode reaction (1.1) under the same conditions as in Fig. 1.2. The response is a bell-shaped current-voltage curve with its maximum at -0.016 V vs. $E_{1/2}$. Each current-voltage step corresponds to a separate mercury drop. The objec-

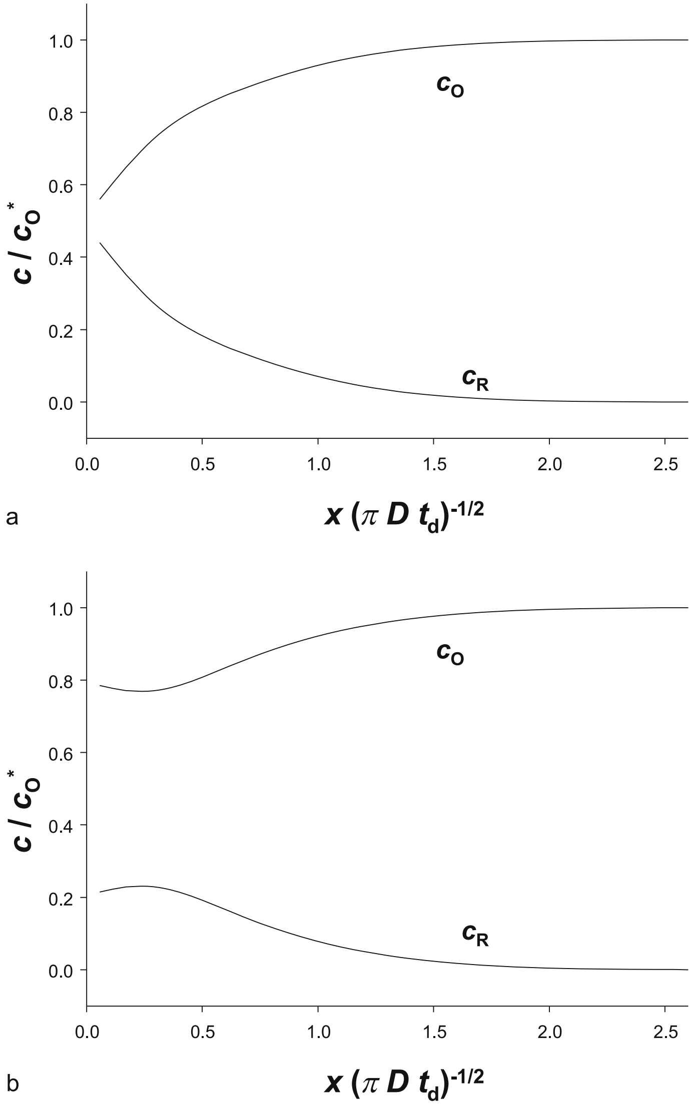

Fig. 1.3 Concentrations of the reactant and product of the electrode reaction (1.1) near the electrode surface at the end of the last cathodic (**a**) and anodic (**b**) Kalousek type I half-cycles applied to the same drop. $E = 0.004$ (**a**) and 0.034 V vs. $E_{1/2}$ (**b**). All other data are as in Fig. 1.2

tive of Barker's innovations was to minimize the influence of capacity current, i.e., to discriminate that current with respect to the faradaic current. During each half-cycle, the double layer charging current decreases exponentially with time, while the faradaic current is inversely proportional to the square-root of time. Under certain conditions, the charging current at the end of half-cycle may be smaller than the faradaic current. A theoretical example is shown in Fig. 1.6. Generally, the charg-

Fig. 1.4 Portraits of Mirko Kalousek (*left*) and Geoffrey Barker (*right*) (reprinted from [66] and [67] with permission)

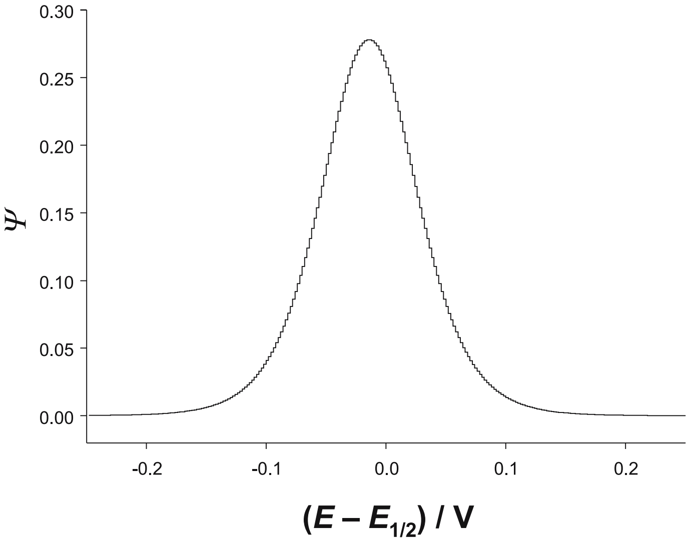

Fig. 1.5 Barker square-wave polarogram of electrode reaction (1.1) on dropping mercury electrode. $\Psi = I/nFA_m c_O^*(Df)^{1/2}$, frequency $= 225$ Hz, amplitude $= 30$ mV, drop life time $= 1$ s, $dE/dt = 2$ mV/s and $E_{st} = -0.25$ V vs. $E_{1/2}$

ing current is partly eliminated by the subtraction of currents measured at the end of two successive half-cycles. This is because the charging current depends on the difference between the electrode potential and its potential of zero charge. If the square-wave amplitude is small, the difference between the charging currents of the cathodic and anodic half-cycles is also small, and for this reason, square-wave

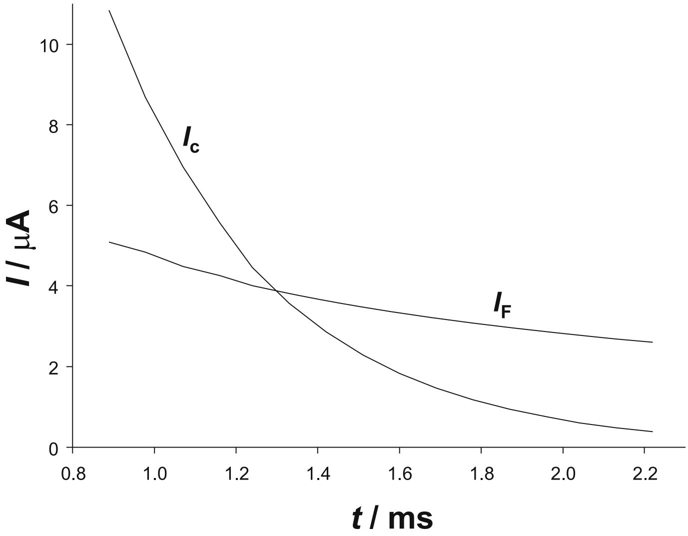

Fig. 1.6 A scheme of a double layer charging current (I_C) and the Faradaic current (I_F) during the second half of the last half-cycle of square-wave signal applied to the dropping mercury electrode. $E - E_{1/2} = -0.016$ V, $E - E_{\mathrm{pzc}} = 0.1$ V, $C = 40\ \mu\mathrm{F/cm}^2$, $R = 10\ \Omega$, $A_m = 0.01\ \mathrm{cm}^2$, $D = 9 \times 10^{-6}\ \mathrm{cm}^2/\mathrm{s}$, $n = 1$, $c_O^* = 5 \times 10^{-4}$ mol/L and $f = 225$ Hz

voltammetry and differential pulse polarography and voltammetry are discriminating against a capacitive current [1, 3, 15–19].

This method was developed further by superimposing the square-wave signal onto a staircase signal [20, 21]. Some of the possible potential-time waveforms are shown in Fig. 1.7. Usually, each square-wave cycle occurs during one stair-

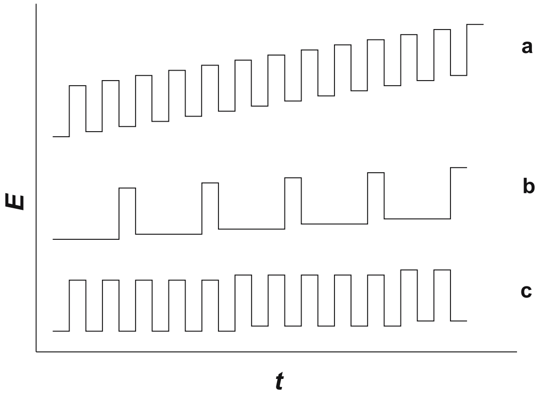

Fig. 1.7 Potential-time waveforms obtained by superimposing the square-wave signal onto a staircase signal: square-wave voltammetry (*a*), differential pulse voltammetry (*b*) and multiple square-wave voltammetry (*c*)

case period, which is sometimes called Osteryoung SWV [20–23], but in multiple square-wave voltammetry, several cycles are applied on the single tread [24,25]. The asymmetric signal (b) in Fig. 1.7 is a general form of differential pulse voltammetry [22, 23]. These complex excitation signals were applied to stationary electrodes, or a single mercury drop. More details can be found in several reviews [26–40].

1.2 Square-Wave Voltammetry: Calculations and Instrumentation

Figure 1.8 shows the potential-time waveform of the modern SWV [41]. Comparing to curve (a) in Fig. 1.7, the starting potential is a median of extreme potentials of the square-wave signal. To each tread of the staircase signal a single square-wave cycle is superimposed, so the waveform can be considered as a train of pulses towards higher and lower potentials added to the potential that changes in a stepwise manner. The magnitude of each pulse, E_{sw}, is one-half of the peak-to-peak amplitude of the square-wave signal. For historical reasons, the pulse height E_{sw} is called the square-wave amplitude [1]. The duration of each pulse is one-half the staircase period: $t_{\mathrm{p}} = \tau/2$. The frequency of the signal is the reciprocal of the staircase period: $f = 1/\tau$. The potential increment ΔE is the height of the staircase waveform. Relative to the scan direction, ΔE, forward and backward pulses can be distinguished. The currents are measured during the last few microseconds of each pulse and the difference between the current measured on two successive pulses of the same step

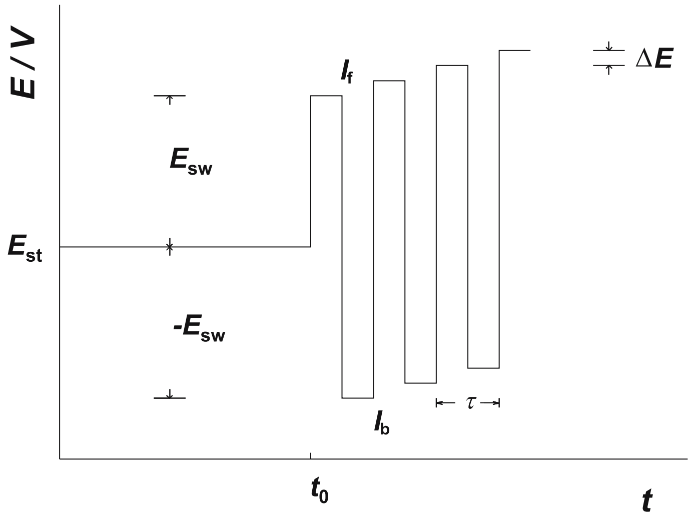

Fig. 1.8 Scheme of the square-wave voltammetric excitation signal. E_{st} starting potential, E_{sw} pulse height, ΔE potential increment, τ staircase period, t_0 delay time and I_{f} and I_{b} denote the points where the forward and backward currents are sampled, respectively

is recorded as a net response ($\Delta I = I_f - I_b$). For analytical purposes, several instantaneous currents can be sampled at certain intervals during the last third, or some other portion of the pulse, and then averaged. This is done because the response appears less noisy if the sampling window is wider [42,43]. The two components of the net response, I_f and I_b, i.e., the currents of the forward and the backward series of pulses, respectively, are also displayed. The currents are plotted as a function of the corresponding potential of the staircase waveform. The delay period, t_0, which may precede the signal, is used for the accumulation of the reactant on the working electrode surface in order to record the stripping process.

SWV experiments are usually performed on stationary solid electrodes or static mercury drop electrodes. The response consists of discrete current-potential points separated by the potential increment ΔE [1,20–23]. Hence, ΔE determines the apparent scan rate, which is defined as $\Delta E/\tau$, and the density of information in the response, which is a number of current-potential points within a certain potential range. The currents increase proportionally to the apparent scan rate. For better graphical presentation, the points can be interconnected, but the line between two points has no physical significance, as there is no theoretical reason to interpolate any mathematical function between two experimentally determined current-potential points. The currents measured with smaller ΔE are smaller than the values predicted by the interpolation between two points measured with bigger ΔE [3]. Frequently, the response is distorted by electronic noise and a smoothing procedure is necessary for its correct interpretation. In this case, it is better if ΔE is as small as possible. By smoothing, the set of discrete points is transformed into a continuous current-potential curve. Care should be taken that the smoothing procedure does not distort the square-wave response.

A solution of the diffusion equation for an electrode reaction for repetitive stepwise changes in potential can be obtained by numerical integration [44]. For a stationary planar diffusion model of a simple, fast, and reversible electrode reaction (1.1), the following differential equations and boundary conditions can be formulated:

$$\partial c_O/\partial t = D(\partial^2 c_O/\partial x^2) \tag{1.2}$$

$$\partial c_R/\partial t = D(\partial^2 c_R/\partial x^2) \tag{1.3}$$

Initially, only the reactant O^{m+} is present in the solution and its concentration is uniform:

$$t = 0: \quad c_O = c_O^* \, , \, c_R = 0 \tag{1.4}$$

At the infinite distance from the electrode surface, the concentrations of the reactant and product do not change:

$$t > 0 \, , \, x \to \infty: \quad c_O \to c_O^* \, , \, c_R \to 0 \tag{1.5}$$

The current is proportional to the gradient of concentration of product at the electrode surface:

$$x = 0: \quad D(\partial c_{\mathrm{O}}/\partial x)_{x=0} = -I/nFA \tag{1.6}$$

$$D(\partial c_{\mathrm{R}}/\partial x)_{x=0} = I/nFA \tag{1.7}$$

The concentrations of reactant and product at the electrode surface are connected by the Nernst equation:

$$(c_{\mathrm{O}})_{x=0} = (c_{\mathrm{R}})_{x=0} \exp(\varphi) \tag{1.8}$$

$$\varphi = (nF/RT)(E - E^{\theta}) \tag{1.9}$$

Here c_{O} and c_{R} are the concentrations of the reactant and product, respectively, D is a common diffusion coefficient, c^*_{O} is the bulk concentration of the reactant, I is the current, n is the number of electrons, F is the Faraday constant, A is the electrode surface area, E is electrode potential, E^{θ} is the standard potential, R is the gas constant, T is absolute temperature, x is the distance from the electrode surface and t is the time variable [45].

Using the Laplace transformations of the reactant concentration and its derivative on time [46]:

$$\mathscr{L}c_{\mathrm{O}} = \int_0^{\infty} c_{\mathrm{O}} \exp(-st)\, \mathrm{d}t \tag{1.10}$$

$$\mathscr{L}(\partial c_{\mathrm{O}}/\partial t) = s\mathscr{L}c_{\mathrm{O}} - (c_{\mathrm{O}})_{t=0} \tag{1.11}$$

the differential equation (1.2) can be transformed into:

$$\partial^2 u/\partial x^2 - (s/D)\, u = 0 \tag{1.12}$$

where $u = \mathscr{L}c_{\mathrm{O}} - c^*_{\mathrm{O}}/s$ and s is the transformation variable. The boundary conditions are:

$$x \to \infty: \quad u \to 0 \tag{1.13}$$

$$x = 0: \quad (\partial u/\partial x)_{x=0} = -\mathscr{L}I/nFAD \tag{1.14}$$

The general solution of (1.12) is:

$$u_{1,2} = K_1 \exp(-(s/D)^{1/2}x) + K_2 \exp((s/D)^{1/2}x) \tag{1.15}$$

A particular solution is obtained by using (1.13) and (1.14):

$$K_2 = 0 \tag{1.16}$$

$$K_1 = s^{-1/2}\mathscr{L}I/nFAD^{1/2} \tag{1.17}$$

$$(\mathscr{L}c_{\mathrm{O}})_{x=0} = c^*_{\mathrm{O}}/s + s^{-1/2}\mathscr{L}I/nFAD^{1/2} \tag{1.18}$$

By the inverse Laplace transformation of (1.18) an integral equation is obtained [46]:

$$(c_{\mathrm{O}})_{x=0} = c_{\mathrm{O}}^{*} + (nFA)^{-1}(D\pi)^{-1/2}\int_{0}^{t} I(\tau)(t-\tau)^{-1/2}\,\mathrm{d}\tau \tag{1.19}$$

Within each time interval from 0 to t, the current I depends on the variable τ. The integral $\int f(\tau)g(t-\tau)\,\mathrm{d}\tau$ is called the convolution of functions f and g.

The solution of (1.3) is obtained by the same procedure:

$$(c_{\mathrm{R}})_{x=0} = -(nFA)^{-1}(D\pi)^{-1/2}\int_{0}^{t} I(\tau)(t-\tau)^{-1/2}\,\mathrm{d}\tau \tag{1.20}$$

The convolution integral in (1.19) and (1.20) can be solved by the method of numerical integration proposed by Nicholson and Olmstead [47]. The time t is divided into m time increments: $t = md$. It is assumed that within each time increment the function I can be replaced by the average value I_j:

$$\int_{0}^{t} I(\tau)(t-\tau)^{-1/2}\,\mathrm{d}\tau = \sum_{j=1}^{m} I_j \int_{(j-1)d}^{jd} (md-\tau)^{-1/2}\,\mathrm{d}\tau \tag{1.21}$$

The integral in (1.21) is solved by the substitution $p = md - \tau$:

$$\int_{(j-1)d}^{jd} (md-\tau)^{-1/2}\,\mathrm{d}\tau = 2d^{1/2}[(m-j+1)^{1/2} - (m-j)^{1/2}] \tag{1.22}$$

Each square-wave half-period is divided into 25 time increments: $d = (50f)^{-1}$. By introducing (1.19) and (1.20) into (1.8), the following system of recursive formulae is obtained:

$$\Psi_1 = -5(\pi/2)^{1/2}(1+\exp(\varphi_1))^{-1} \tag{1.23}$$

$$\Psi_m = -5(\pi/2)^{1/2}(1+\exp(\varphi_m))^{-1} - \sum_{j=1}^{m-1} \Psi_j S_{m-j+1} \tag{1.24}$$

where $\Psi = I/nFAc_{\mathrm{O}}^{*}(Df)^{1/2}$, $S_1 = 1$, $S_k = k^{1/2} - (k-1)^{1/2}$, $\varphi_m = (nF/RT)(E_m - E^{\theta})$, $m = 2, 3, \ldots M$ and $M = -50\,(E_{\mathrm{fin}} - E_{\mathrm{st}})/\Delta E$. The potential E_m changes according to Fig. 1.8.

If the electrode reaction (1.1) is kinetically controlled, (1.8) must be substituted by the Butler–Volmer equation:

$$I/nFA = -k_{\mathrm{s}}\exp(-\alpha\varphi)[(c_{\mathrm{O}})_{x=0} - (c_{\mathrm{R}})_{x=0}\exp(\varphi)] \tag{1.25}$$

where k_s is the standard rate constant and α is the cathodic transfer coefficient. In this case, the following recursive formulae are obtained [44, 48–50]:

$$\Psi_1 = -\frac{\kappa \exp(-\alpha\varphi_1)}{1 + \kappa \exp(-\alpha\varphi_1)\frac{\sqrt{2}}{5\sqrt{\pi}}\left[1 + \exp(\varphi_1)\right]} \tag{1.26}$$

$$\Psi_m = -Z_1 - Z_2 \sum_{j=1}^{m-1} \Psi_j S_{m-j+1} \tag{1.27}$$

$$Z_1 = \frac{\kappa \exp(-\alpha\varphi_m)}{1 + \kappa \exp(-\alpha\varphi_m)\frac{\sqrt{2}}{5\sqrt{\pi}}\left[1 + \exp(\varphi_m)\right]} \tag{1.28}$$

$$Z_2 = \frac{\kappa \exp(-\alpha\varphi_m)\frac{\sqrt{2}}{5\sqrt{\pi}}\left[1 + \exp(\varphi_m)\right]}{1 + \kappa \exp(-\alpha\varphi_m)\frac{\sqrt{2}}{5\sqrt{\pi}}\left[1 + \exp(\varphi_m)\right]} \tag{1.29}$$

where $\kappa = k_s(Df)^{-1/2}$ is a dimensionless kinetic parameter and the meanings of other symbols are given below (1.24).

The developments of instrumentation for Kalousek [31, 51, 52] and square-wave polarography [53–58] and square-wave voltammetry [59–65] are mainly of historical interest. Today, many computer-controlled potentiostats/galvanostats providing SWV signal generation are available from numerous manufacturers, such as Eco-Chemie (models PGSTAT 10, 12, 20, 30, 100 and 302 and μAutolab I, II, and III), Metrohm (models VA 646 and 797 Computrace), Princeton Applied Research (models 263A, 273A, 283, 2263, 2273, and 384B), Bioanalytical Systems (models 100A, 100B/W and Epsilon), Cypress Systems (models CS 1090 and 1200 and CYSY-2), Amel Srl (models 433, 7050 and 7060), Gamry Instruments (models PCI 4/300 and 4/750), Analytical Instrument Systems (models LCP-200 and DLK-100), Uniscan Instruments (model PG 580), Palm Instruments (model Palmsens), Rudolph Instruments (model GATTEA 4000 AS) and IVA Company (model IVA-5).

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Chapter 2
Electrode Mechanisms

2.1 Electrode Reactions of Dissolved Species on Stationary Planar Electrodes

2.1.1 Reversible Electrode Reactions

Figure 2.1 shows computed square-wave voltammogram of the simple, fast and electrochemically reversible electrode reaction (1.1), i.e., $\mathrm{O}^{m+} + n\,\mathrm{e}^- \leftrightarrows \mathrm{R}^{(m-n)+}$. The response was calculated by using (1.23) and (1.24). The dimensionless net response ($\Delta\Psi = -\Delta I / nFAc_{\mathrm{O}}^{*}(Df)^{1/2}$), where $\Delta I = I_{\mathrm{f}} - I_{\mathrm{b}}$, and its forward (reductive) (Ψ_{f}), and backward (oxidative) (Ψ_{b}) components are shown. The meanings of other symbols are given below (1.9). The voltammogram is characterized by the maximum net response, which is also called the net peak current, ΔI_{p}. The corresponding staircase potential is the net peak potential E_{p}. Other characteristics are the minimum of the reductive component, the maximum of the oxidative component and their potentials. The net peak potential and the peak potentials of both components are independent of SW frequency. This is one of various indications that the electrode reaction is electrochemically reversible within the range of applied frequencies [1–6].

Both the dimensionless net peak current $\Delta\Psi_{\mathrm{p}}$ and the peak width at half-height, or the half-peak width, $\Delta E_{p/2}$ depend on the products “the number of electrons times the SW amplitude”, i.e., nE_{sw}, and "the number of electrons times the potential increment", i.e., $n\Delta E$. This is shown in Table 2.1 and Fig. 2.2 (curve 1), for the constant product $n\Delta E$. With increasing nE_{sw} the slope $\partial\Delta\Psi_{\mathrm{p}}/\partial nE_{\mathrm{sw}}$ continuously decreases, while the gradient $\partial\Delta E_{\mathrm{p}/2}/\partial nE_{\mathrm{sw}}$ increases. The maximum ratio $\Delta\Psi_{\mathrm{p}}/\Delta E_{p/2}$ appears for $nE_{\mathrm{sw}} = 50\,\mathrm{mV}$, as can be seen in Fig. 2.2. This is the optimum SW amplitude for analytical measurement [7]. At higher amplitudes the resolution of two peaks is diminished. The ratio of peak currents of the forward and backward components, and the peak potentials of the components are also listed in Table 2.1. If $nE_{\mathrm{sw}} > 10\,\mathrm{mV}$, the backward component indicates the reversibility of the electrode reaction, and if $nE_{\mathrm{sw}} > 5\,\mathrm{mV}$, the net peak potential E_{p} is equal to the half-wave potential of the reversible reaction (1.1). If $E_{\mathrm{sw}} = 0$, the square-wave sig-

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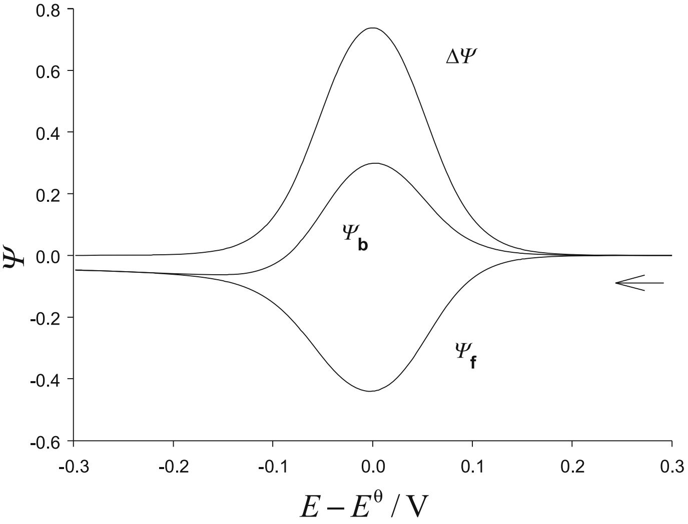

Fig. 2.1 Theoretical square-wave voltammogram of fast and reversible electrode reaction (1.1). $E_{sw} = 50\,\text{mV}$, $n = 1$, $E_{st} - E^{\theta} = 0.3\,\text{V}$, $t_0 = 0\,\text{s}$ and $\Delta E = -2\,\text{mV}$. The dimensionless net response ($\Delta\Psi$) and its forward (Ψ_f) and backward (Ψ_b) components

Table 2.1 Square-wave voltammetry of fast and reversible electrode reaction (1.1). The dimensionless net peak current, the ratio of peak currents of the forward and backward components, the peak potentials of the components and the half-peak width as functions of SW amplitude; $n\Delta E = -2\,\text{mV}$

nE_{sw}/mV	$\Delta\Psi_p$	$I_{p,f}/I_{p,b}$	$E_{p,f} - E_p/\text{mV}$	$E_{p,b} - E_p/\text{mV}$	$\Delta E_{p/2}/\text{mV}$
10	0.1961	−10.35	−12	26	92
20	0.3701	−2.78	−8	10	96
30	0.5206	−1.94	−6	6	104
40	0.6432	−1.63	−4	4	112
50	0.7383	−1.47	−2	2	124
60	0.8093	−1.37	−2	2	139
70	0.8608	−1.31	0	0	152
80	0.8975	−1.27	2	−2	168
90	0.9231	−1.23	4	−2	186
100	0.9409	−1.21	6	−4	204

nal turns into the signal of differential staircase voltammetry [8–10], and $\Delta\Psi_p$ does not vanish [4]. To establish an additional criterion of the reversibility of the reaction (1.1), the standard SW amplitudes $E_{sw} = 50$, 25 and 15 mV, for $n = 1$, 2 and 3, respectively, and the common potential increment $\Delta E = -2\,\text{mV}$ are proposed. The characteristic data of responses of simple and electrochemically reversible electrode reactions under standard conditions are listed in Table 2.2.

The net peak current depends linearly on the square root of the frequency [5,11]:

$$\Delta I_p = -nFAD^{1/2}\Delta\Psi_p f^{1/2} c_O^* \qquad (2.1)$$