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Small-Amplitude and Related Controlled-Potential Techniques

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I. INTRODUCTION

A. What Is a Small-Amplitude Technique?

All of the techniques described in the preceding two chapters involve an initial condition in which the concentration of the reacting solute is uniform as a function of distance from the electrode surface. The experiments begin by application of a relatively large amplitude potential or current excitation signal. The initial flat reactant concentration profile is thereby dramatically perturbed. The perturbation of the electrode-solution interphase in these techniques is sufficient to require use of the entire exponential rate expression introduced in

Chapter 2 (see Sec. IV). As was described in Chapter 2, when the applied signal is of relatively small magnitude, the fundamental exponential rate expression can be linearized. For example, in a controlled-potential experiment if the excitation signal has an amplitude of less than about 10 mV/n, then the linearized version of the rate equation is adequately precise for essentially all experimental purposes.

The definition of a "small-amplitude" technique is obviously not precise because depending on the experimental objective, one might get away with a somewhat larger excitation signal. For example, when small-amplitude techniques are used for analytical purposes, the definition can be stretched somewhat in comparison to when they are used for careful studies of the physical chemistry of the electrode-solution interphase region.

While the small-amplitude perturbation can be made from an initial condition identical to that used for the large-amplitude techniques, it is usual to combine the two experiments together. One can, for example, add a small-amplitude perturbation on top of a large-amplitude signal to provide more complete information about the chemical system. Under normal circumstances the large-amplitude signal is applied for a longer period of time and the small amplitude is added momentarily. Looking at this another way, we use the large-amplitude signal to establish a new surface concentration for the oxidized and reduced forms of a redox couple and then move away from this condition slightly by rapid application of a small potential or current change. The large-amplitude technique therefore sets the initial condition for the small-amplitude technique.

Let us consider the very simple situation following a step change in applied potential. Refer back to Chapter 3 (see Sec. II.A and II.B) for an introduction to chronoamperometry. Consider Figure 5.1A in which a potential-step excitation is illustrated. A large-amplitude step is applied at $E_{1/2}$ for a period of time and then an additional small-amplitude perturbation is added. The total current response signal would look as is given in Figure 5.1B. A current-time transient would result as the surface concentration of reactant and product achieve a value consistent with the Nernst equation ($C_O^s = C_R^s$). When the additional small step is applied later in the experiment, the current will again respond as a transient piggybacked on the original current-time signal. This small-amplitude response can be considered to have been initiated at a condition defined by the concentration profile as it existed just prior to application of the small step. The concentration profile from the initial experiment (and therefore the reactant flux) is "wiggled" a small amount near the surface. Sometimes the surface concentration which exists prior to a small-amplitude perturbation is referred to as the "dc surface concentration." The time scale of the small-amplitude experiment is so much shorter than that for the large-amplitude signal that the latter for practical purposes is not changing during the course of a given small-amplitude perturbation.

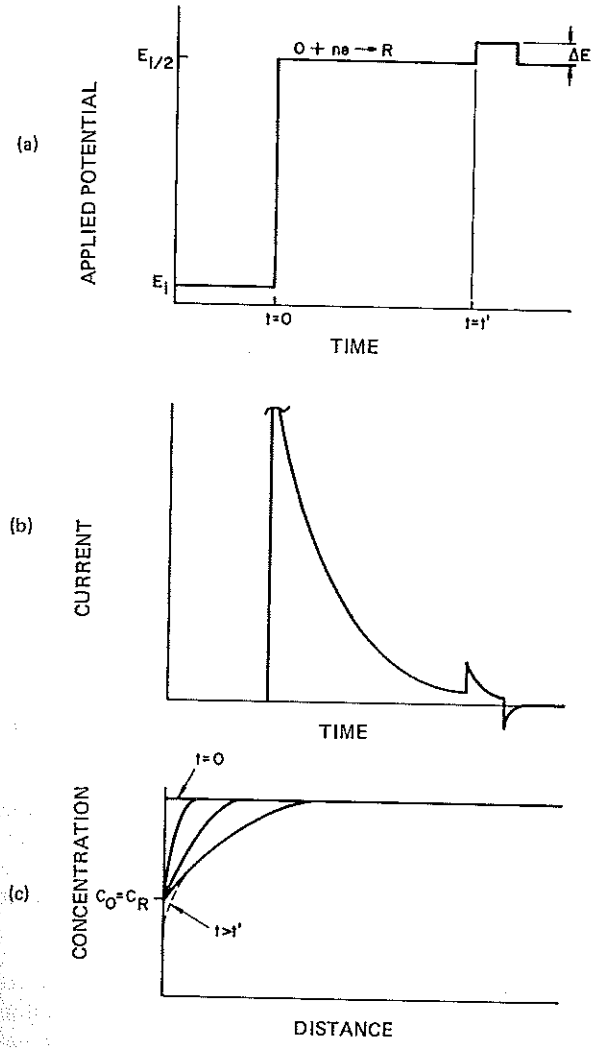

Figure 5.1 A small amplitude pulse applied following a large amplitude potential step. (a) excitation signal. (b) current response. (c) concentration-distance response.

B. Small-Amplitude Controlled-Potential Voltammetry

Over the years an extraordinarily large number of techniques have been explored based on the addition of a small-amplitude perturbation to a linear potential sweep. All sorts of different waveforms have been

used for the small-amplitude part of the excitation signal. Simple sine waves, square waves, triangular waves, and sawtooth waves are among those which have been considered. In the early forms of these techniques the small-amplitude (so-called ac part) was simply summed with a slowly moving ramp (so-called dc part). The excitation signal would look something like that given in Figure 5.2a. While this type of excitation signal can be applied to all types of electrodes in both stationary and moving solutions, let us consider the situation in which the dc current response would be sigmoidal in shape as illustrated in Figure 5.2b.

The variation in small-amplitude current around the dc response will depend very much on the relation between the dc excitation and the half-wave potential. This is illustrated in Figure 5.2c. Prior to initiation of significant dc reduction current, the small-amplitude excitation signal does not result in any significant faradaic process. Well beyond the half-wave potential (on the limiting current plateau), the small-amplitude perturbation will again contribute very little due to the fact that we are already at a point where the surface concentration of the reactant is zero for all practical purposes. On the rising part of the "dc" voltammogram we anticipate a significant variation in the current due to the small-amplitude perturbation. The amplitude of *this* current response would be maximum at the point where the dc surface concentration is the greatest function of the applied potential (i.e., at the half-wave point). As a result, when we plot the small-amplitude current response as a function of the dc applied potential we achieve a peak-shaped curve with a maximum value at $E_{1/2}$ (at which point the small-amplitude potential is varying symmetrically around the $E_{1/2}$ value). Whenever a time-variant signal is impressed across the interface a capacitive current will result regardless of the presence of a redox active substance. As with large-amplitude techniques, separation of faradaic from nonfaradaic events is a major experimental goal

Small-amplitude techniques can be conveniently divided into those which operate in the frequency domain and those which operate in the time domain. In principle, the information available from these different approaches is identical, but there are significant experimental factors which may make one or the other more desirable in a particular experiment. The frequency-domain techniques normally use analog instrumentation such as various impedance bridges and tuned amplifiers which can be made phase selective (such as the very popular "lock-in amplifier"). Phase selectivity provides discrimination against double-layer charging current.

The time-domain techniques in their present form are often instrumented by use of digital computers. They require the sampling of current signals at various times in response to the small-amplitude perturbation. Often the sampled currents are mathematically processed to minimize the inevitable charging current. By far the most popular technique of this type is so-called differential pulse voltammetry, but there are others on the horizon.

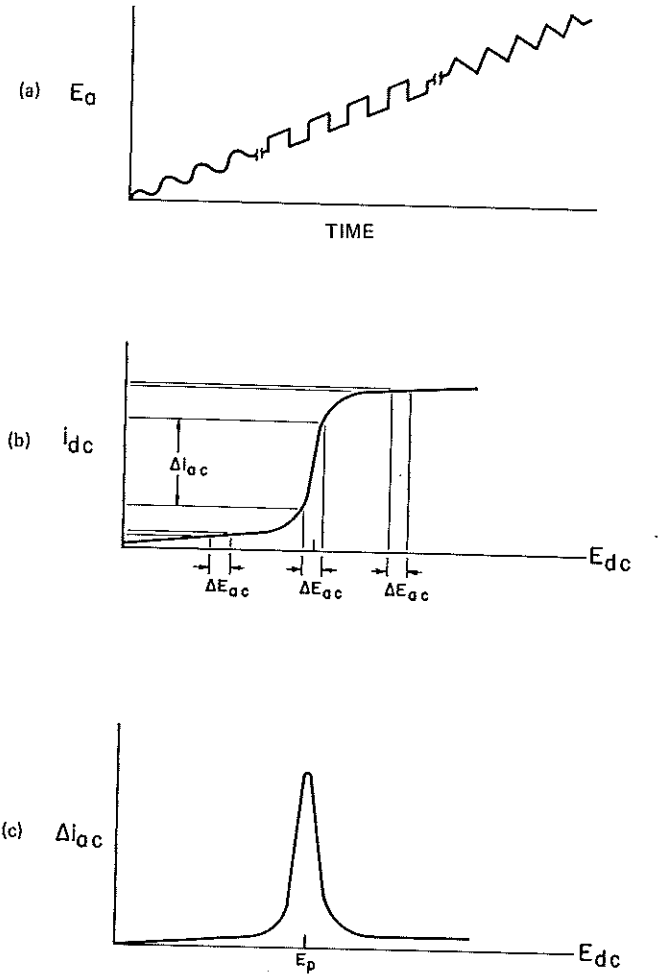

Figure 5.2 Small amplitude voltammetric techniques. (a) Various small amplitude waveforms are imposed on a "dc" ramp (normally only one waveform is used in a given experiment). (b) The sigmoidal shaped dc response is typical of dc polarography and hydrodynamic voltammetry. The greatest amplitudes for the small amplitude current (Δi_{ac}) are achieved on the rising part of the dc current, where the small amplitude voltage signal causes the greatest change in the surface concentrations. (c) Small amplitude current response vs. applied dc potential.

Small-amplitude voltammetry techniques do provide some advantag for both fundamental and analytical studies. Physical electrochemists like the mathematical simplification afforded by linearization. In addition, the small-amplitude frequency-domain experiments can be carried out in a steady-state mode which improves the precision of the measurements. Analytical chemists frequently like these methods because the format of the response is convenient and frequently both the detection limits and selectivity are improved somewhat in comparison to the corresponding "dc" technique. We will now introduce in a very qualitative fashion the most popular frequency-domain and time-domain variants. The literature on this subject is extremely vast and only a few leading reviews and recent key papers will be cited.

II. FREQUENCY-DOMAIN TECHNIQUES

A. Impedance Measurements

Any system that responds to an electrical excitation signal can, in principle, be represented by an equivalent circuit constructed from various resistors, capacitors, and inductors. An ideal equivalent circuit would behave exactly in the same manner as the system it represents. The extremely complex nature of the electrode-solution interface makes it very difficult to arrive at an equivalent circuit which fits under all circumstances. Nevertheless, very useful models are available. A very simple representation of a three-electrode cell is given in Figure 5.3. The reference electrode probe is represented as a battery in series with a resistance (there is also, of course, a capacitance associated with the reference electrode). The working and auxiliary electrodes are considered as a faradaic impedance (a resistance in simplest terms) which parallels a capacitor. The representation of an electrochemical reaction as an impedance and the ionic structure of the interface as a capacitor are introduced in Chapter 2 (Secs. III and IV). There is also a resistance associated with the solution contacting the auxiliary, reference, and working electrodes. The solution resistance between the reference probe and the working electrode is referred to as the uncompensated resistance and this is emphasized in Figure 5.3c, the equivalent circuit for the working electrode alone. For our purposes it can be assumed that resistance and capacitance associated with the external leads can be ignored. The magnitude of the uncompensated resistance R_u can be made very small in many circumstances, but can be an important factor in experiments which are either extremely fast or involve the use of nonaqueous solvents. The impact of R_u on the electronics and cell design for electrochemical experiments will be considered further in Chapters 6, 7, and 12.

The three-element equivalent circuit for the working electrode is clearly rather simplistic. The solution does not behave in the same

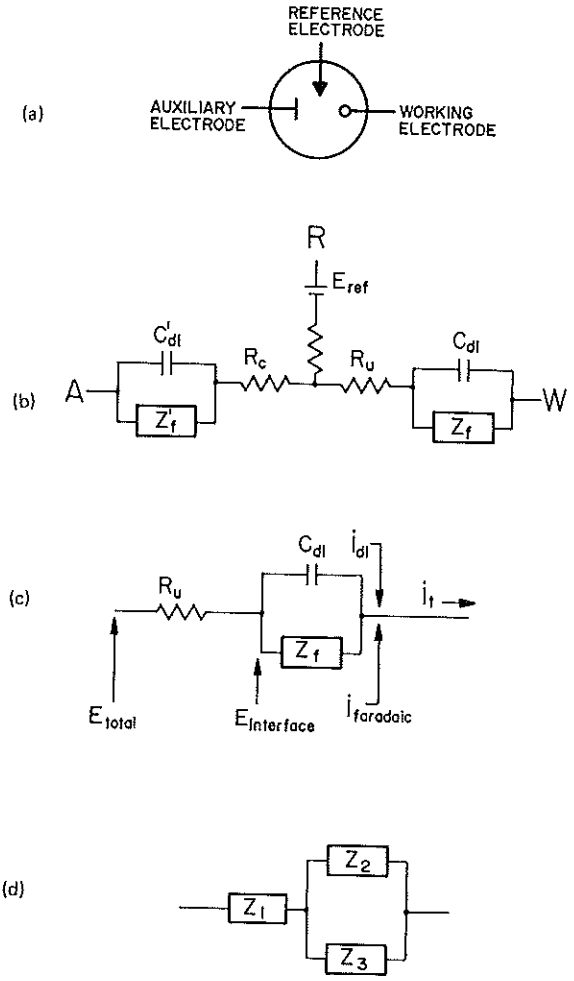

Figure 5.3 Schematic representation of an electrochemical cell. (a) three electrodes. (b) equivalent circuit for three electrode cell. (c) equivalent circuit for the working-electrode interphase. (d) a "solution" impedance in series with two parallel "surface" impedances.

manner as a simple resistor. The interface does not fit the properties of a simple physical capacitor (the capacitance here does depend on applied potential, so this element is, in actual fact, nonlinear). In spite of these limitations, the model works adequately well under many circumstances. The variation in the double-layer capacitance as a function of potential is one of the more serious problems. Often,

however, conditions are used here where the variation in the faradaic impedance with potential is much greater than that of the capacitance and a constant value for the latter can be assumed.

The three-element circuit can be represented as a generalized network as indicated in Figure 5.3d. The total impedance for the interface Z_t consists of a simple parallel network in series with Z_1. The total impedance may then be represented as follows:

$$Z_t = Z_1 + \frac{Z_2 Z_3}{Z_2 + Z_3}$$

The experimentalist and theoretician alike have as a goal to relate the values of these impedances to phenomena taking place at the electrode in particular experimental circumstances. In classical electrochemical experiments, measurements of interfacial impedances were carried out using an impedance bridge such as that illustrated in Figure 5.4. A variable-frequency ac potential is applied across the bridge and components in the bridge circuit are varied until a balance is achieved. One advantage of this kind of experiment is the fact that it is carried out under steady-state circumstances. The dc potential of the two electrode cell is varied by changing the ratio of the oxidized and reduced forms of the couple under study. By the combination of a change in frequency with a change in composition, a great deal of very precise data can be obtained about a given redox process. This method of measuring impedances, while still among the very best available with regard to precision, is very awkward and time consuming in practice. Analytical electrochemists have very little interest in such

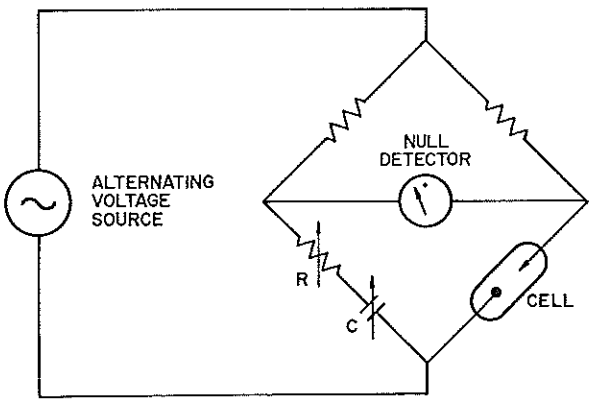

Figure 5.4 Classical impedance bridge for a two-electrode cell.

work and therefore we will not consider it in detail here (see Refs. 1 and 4).

B. Sinusoidal Alternating-Current Voltammetry

Alternating-current voltammetry requires an excitation signal based on adding a small-amplitude sinusoidal potential modulation to a ramp of very low slope. In a typical experiment, the ramp has a slope of 5 mV/s or less and the sinusoid is a few millivolts in amplitude at several hundred cycles per second. For all practical purposes, the ramp is at 0 Hz and does not vary significantly during any given cycle. As described in an earlier section, the ramp sets the "dc surface concentration" and the sinusoid "wiggles" it more or less, depending on the relationship between the ramp potential and the $E^{o\prime}$ of the electrochemical reaction. Near $E^{o\prime}$ the sinusoid will have its maximum impact on surface concentrations (and therefore on the current). Because the frequency of the sinusoid is so much faster than the ramp, it is a simple matter to isolate the small-amplitude (ac) current response from the large-amplitude (dc) current response. The ac signal is converted to a voltage and then full-wave rectified and plotted on a conventional XY recorder versus the ramp potential.

In this frequency-domain technique, it is a simple matter to vary the frequency to test the kinetics of the electrochemical events. This is equivalent to varying the scan rate in cyclic voltammetry, the pulse width in square-wave voltammetry (described below), or the time at which data is acquired during a chronoamperometry experiment. If one of these time-domain techniques must be carried out at high speed to "see" a given phenomenon, relatively high frequencies will be necessary for the corresponding frequency-domain techniques.

In time-domain "pulse" techniques, the influence of double-layer charging current is minimized by recording data at longer times. In ac techniques, there is a different phase relationship between the excitation and response signals for capacitive and faradaic currents. Considering a fast (reversible) electron transfer reaction, the faradaic current is phase shifted 45° and the capacitive current 90° relative to the applied sinusoidal potential. It is therefore possible to separate these two contributions to the total response with a phase-sensitive detection system. In the real world, it is not so simple. Slow kinetics, adsorption, coupled chemical reactions, and solution resistance can all contribute to the relative phase angle between the faradaic and capacitive currents. These influences can usually be dealt with effectively but the required mathematics are beyond the scope of this text.

There are excellent theoretical [1-4] and practical [1-5] treatments of ac voltammetry and polarography. Advanced topics include the use of higher harmonics and even Fourier transform techniques to study the response to multiple frequencies applied simultaneously.

The term "tensammetry" applies to the use of ac voltammetry to study adsorption/desorption phenomenon which influence double-layer capacitance. Tensammetric waves can be used to study surfactants which are not undergoing electron-transfer reactions.

We intentionally give these techniques short shrift because they currently are not nearly as attractive as they once were in competition with time-domain methods. The latter are now much easier to carry out than in the past due to the availability of low-cost computers which make precisely timed excitation-response measurements routine.

C. Cyclic Alternating-Current Voltammetry

Alternating-current voltammetry can be made more useful by cycling the direction of the potential ramp as in cyclic voltammetry (Chap. 3). As long as a large difference is maintained between the time scale of the CV scan (long) and the period of the sinusoid (short), it is possible to obtain the full information from both techniques in a single experiment. The CV part is most useful for diagnosing mechanisms and the ac part is ideal for quantitative work. For a rapid electron-transfer reaction where both forms of a redox couple are stable during the time scale of the dc scan, an identical forward and reverse ac response is obtained. This should make sense because the surface concentrations of O and R at any given potential are controlled only by the Nernst equation and not by the direction scanned to arrive at this potential. For slower electron-transfer kinetics, the relative positions of the peak maxima shift. For rapid electron transfers with a chemical reaction consuming the product, the peak height will be lower on the reverse scan. This relatively new technique is given more detailed coverage in Bard and Faulkner [1] and in a series of pioneering publications by Bond and co-workers [5-7].

III. TIME-DOMAIN TECHNIQUES

A. Differential Pulse Voltammetry

By the 1960s dc polarography was for all practical purposes a dying technique in American laboratories. The method suffered greatly from its slow speed, awkward apparatus, unusual data presentation, and poor detection limits. The latter two problems were largely corrected by the advent of differential pulse polarography (DPP), a technique that first became readily available in the late 1960s due to the efforts of Princeton Applied Research Corp. This technique overcame certain deficiencies of the dropping mercury electrode by (1) recording data only at the end of the drop life, (2) maximizing flux by using a potential pulse, (3) discriminating against charging current by using a timed sample-and-hold, and (4) by subtracting out the largest por-

tion of the dc background current. The results were a substantial improvement in the minimum detectable concentration and a data presentation (Fig. 5.2c) more acceptable to practicing analysts. Later, the same approach was found to be useful for solid electrodes and mercury film electrodes and thus differential pulse voltammetry (DPV) became one of the most popular electroanalytical techniques in the 1970s. Stripping voltammetry based on DPV is currently a favorite (Chap. 19).

All of these things are accomplished by using the waveform shown in Figure 5.5, which may be conveniently thought of as the sum of a staircase (step height ΔE_s) with a pulse train. The staircase potential establishes the dc surface concentrations (per Sec. I). Just prior to application of the small-amplitude pulse a current sample is taken at s_1, and a second sample, s_2, is taken at the end of the pulse. In the usual case, the sample is registered over a 16.7-ms window to nullify the impact of 60-Hz line interference (16.7-ms period). The pulse width t_p has traditionally been 50 ms (a fixed parameter in some commercial instruments).

When a dropping mercury electrode is used, the pulse is applied just prior to the end of the drop life ($t_d = T$ in Fig. 5.5). When a new drop is created the experiment is identical to dc polarography until the pulse is applied. The current prior to s_1 is not recorded (eliminating most of the charging current associated with the increase in electrode surface area). The pulse is applied only during the last 1-10% of drop life (typically 0.5-5.0 s). The charging current associated with the chronoamperometry response to the pulse is likewise not recorded. The second sample s_2 ideally consists only of faradaic current. A plot of $(i_{s_2} - i_{s_1})$ vs. applied potential (usually the potential at s_1 is plotted rather than the potential at s_2).

For analytical purposes, the pulse heights used in DPV frequently exceed the limits imposed by the small-amplitude restriction defined in Chapter 2 and the introduction to this chapter (e.g., 100-mV pulse amplitudes are quite common). Large amplitudes provide an increase in response which must be balanced against the loss in resolution and the increase in charging current, which ultimately limits the minimum

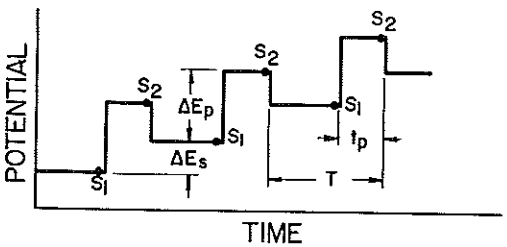

Figure 5.5 Excitation signal for differential pulse voltammetry.

detectable concentration. For most cases, a ΔEp of 50-100 mV is optimum. At greater amplitudes the relative increase in response falls off and performance is degraded.

A primary problem with DPV, which greatly limits its usefulness, is the very detrimental impact of slow electron-transfer kinetics (irreversibility). This lowers the response (peak current vs. sample concentration) and therefore raises the minimum detectable concentration. It also increases the peak width, making resolution a problem in some cases. Finally, slow electron-transfer kinetics (high activation energy) tends to make an electrochemical process very dependent on other substances present in the solution. When the samples under study are especially "dirty" (e.g., environmental samples), variation in the matrix can alter the DPV response for the analyte(s) of interest and make calibration of the procedure less reliable.

There are several good sources of more detailed information on differential pulse techniques [1,5,8]. As of this writing, instrumentation is available from Amel, Bioanalytical Systems, E. H. Sargent, IBM Instruments, Princeton Applied Research, and Tacussel. Application notes from these manufacturers can often provide invaluable practical information. Quality data can usually be obtained at 10^{-7} M for routine purposes and at lower concentrations under ideal circumstances.

B. Alternate Drop Differential Pulse Polarography

When differential pulse voltammetry is carried out at a conventional dropping mercury electrode a small error is created by the fact that the electrode surface area (and therefore the capacitance) is slightly different between each of the two current samples taken during the life of a single drop. This problem has been cleverly addressed by Osteryoung and co-workers by using one drop (no pulse applied) to establish a true dc current sample at the same time the chronoamperom-

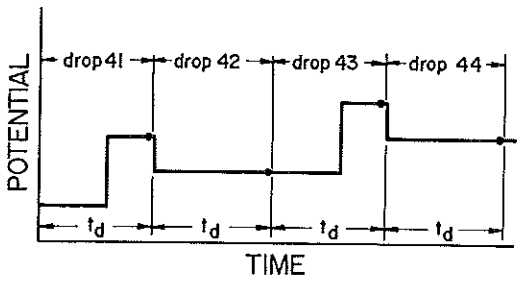

Figure 5.6 Excitation signal for alternate drop differential pulse polarography.

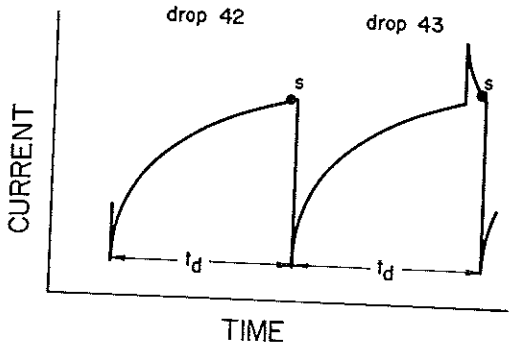

Figure 5.7 Total current response for alternate drop differential pulse polarography.

etry current is sampled when a pulse is applied (next drop) [5,9,10]. This is illustrated in Figures 5.6 and 5.7, where drop number 42 establishes the sampled background ("residual") current to be subtracted from the sampled chronoamperometry current recorded for drop number 43.

C. Differential "Normal Pulse" Voltammetry

Large-amplitude ("normal") pulse voltammetry techniques were introduced in Chapter 3. The differential "normal pulse" (DNP) method combines several features of both the small- and large-amplitude pulse techniques. The rather odd waveform depicted in Figure 5.8 is

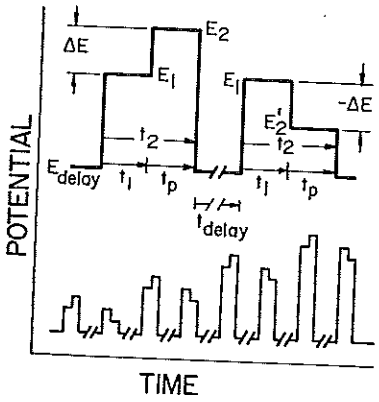

Figure 5.8 Excitation signal for differential "normal pulse" voltammetry (adapted from Ref. 12).

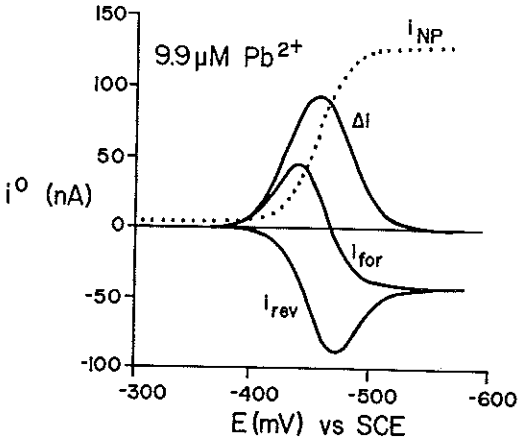

Figure 5.9 Forward, reverse, and difference current DNP voltammograms of 9.9 μm (2.05 ppm) Pb^{2+} in 0.5 M CH_3COOH/0.5 M CH_3 COONa Conventional NP voltammogram is also shown (dotted line): $t_1 = t_p =$ 50 ms; $t_s = 16.67$ ms; $t_{delay} = 0.4$ s; $E_{delay} = -300$ mV; $\Delta E = -25$ mV; T = 20°C. Solid lines are experimental curves. Dots (•••) are theoretical response. (From Ref. 12. Reprinted with permission. Copyright 1981, American Chemical Society.)

for DNP in the alternate pulse mode [11-13]. The pulses are initiated from a potential at which no faradaic reaction takes place. Each pair of large pulses rise first to E_1 and then is incremented either above (E_2) or below (E_2') E_1. E_1 is slowly increased for each subsequent pair of augmented pulses. A new mercury drop is initiated just after each large-amplitude pulse. If this is confusing, do not be alarmed, because this is one of the most complex electrochemical techniques and it will take time to master the details!

The current is sampled at t_1 and t_2. The forward current consists of that, $i(t_2) - i(t_1)$, monitored at E_2 on alternate pulses and the "reverse current" consists of that monitored at E_2', $i(t_2) - i(t_1)$, on the even pulses. A differential current, $i = i(t_2,E_2) - i(t_2,E_2')$, can also be plotted. All three responses are illustrated in Figure 5.9 for reduction of lead ion in an acetate buffer. There is a great deal of information in such a plot in which the forward and reverse currents combine to give a "cyclic voltammogram" and the differential current resembles a DPV curve with improved symmetry. The technique has the advantage of a relatively low duty cycle when compared to DPV since the action occurs during application of the large-amplitude pulse and not during the delay time between pulses. In DPV the potential applied between pulses is adequate to electrolyze the analyte continuously during most of the voltammogram. The DNP technique is

a combination of a large-amplitude and a small-amplitude technique. The large-amplitude pulse sets up the concentration profiles which are the initial condition for the small-amplitude pulse riding on top.

D. Square-Wave Voltammetry

The excitation signal for square-wave voltammetry (SWV) is illustrated in Figure 5.10 [14-17]. A symmetrical pulse train (the total amplitude is $2E_{sw}$) is added to a staircase (the step height is ΔE) with a period of τ. The response current is sampled at the end of both the forward and reverse half cycles (at 1 and 2 in Fig. 5.10). A difference current is determined by subtracting the current measured on the reverse cycle from that measured on the forward cycle. A dimensionless plot of the theoretical forward, reverse, and difference current is given in Figure 5.11 for a rapid electron transfer.

SWV is a very powerful technique. When a dropping mercury electrode is used one can apply the entire excitation waveform (Fig. 5.10) to a single mercury drop (allowing a delay time T_d for the drop to grow to a predetermined size). In the previously described polarographic techniques as many as 1000 drops might be used in a typical experiment. Besides being fast, the technique is somewhat more sensitive than the very popular differential pulse technique because both

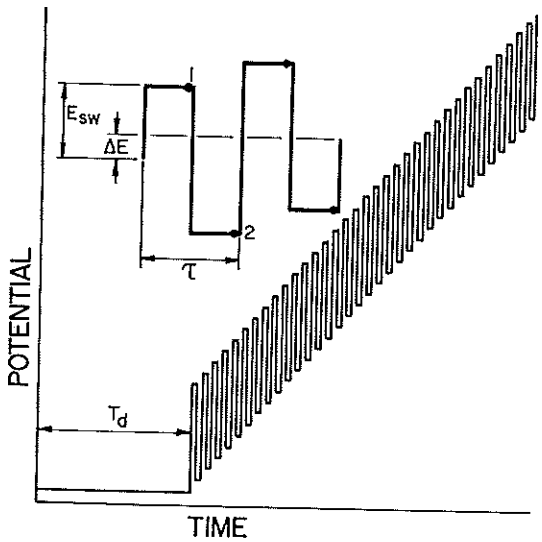

Figure 5.10 Excitation signal for square wave voltammetry (adapted from Ref. 16).

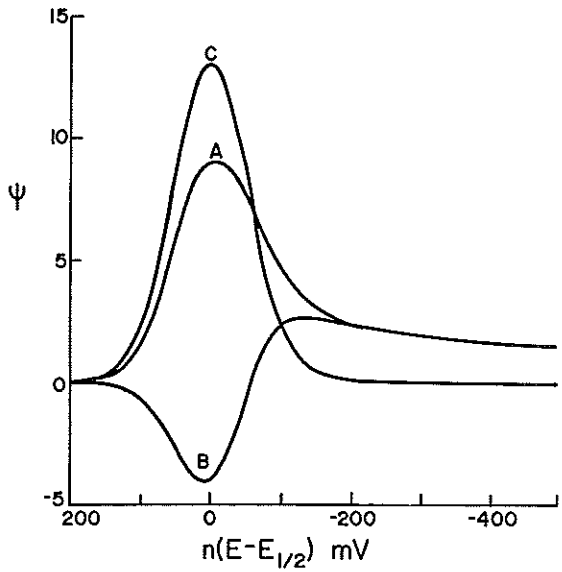

Figure 5.11 Calculated square wave voltammograms for reversible electron transfer: (A) forward current, (B) reverse current, and (C) net current, dimensionless units (adapted from Ref. 16).

forward and reverse currents are measured in SWV, whereas only forward currents are measured in DPV.

The speed of SWV makes it possible to monitor dynamic processes. For example, Osteryoung and co-workers have applied the technique as a detector for liquid chromatography [17]. Figure 5.12 illustrates a three-dimensional chromatogram obtained for two nitroso compounds.

E. Staircase Voltammetry

Staircase voltammetry is a small-amplitude variation on single-scan or cyclic voltammetry and the technique was described briefly in Chapter 3 (Sec. III.B). The excitation signal is a staircase which closely approximates a ramp since the step height is typically 10 mV or less (Fig. 5.13). The idea is quite simple. A sample is taken at the end of the step (typically 50 ms wide or less), where charging current has decayed and the faradaic current is still quite significant. With the large number of samples acquired over the width of a given voltammetric wave, the waveshape closely resembles a voltammogram operated with a single ramp excitation (Chapter 3). The benefit results from a much reduced charging current contribution even at quite high scan rates [18-20].

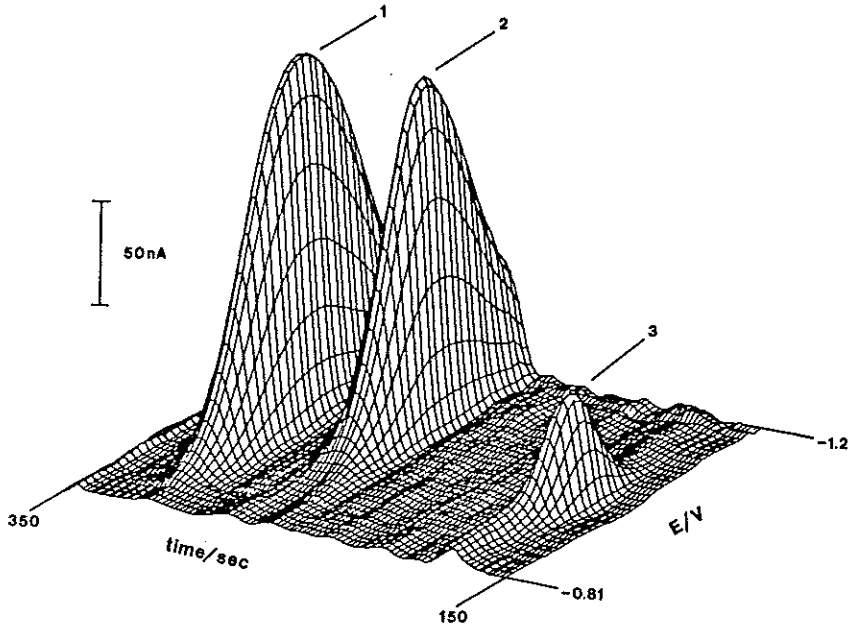

Figure 5.12 Three dimensional "chromatovoltammogram" for two nitrosamines (peaks 1 and 2) and an unknown impurity (peak 3). (From Ref. 17. Reproduced with permission. Copyright 1980, American Chemical Society.)

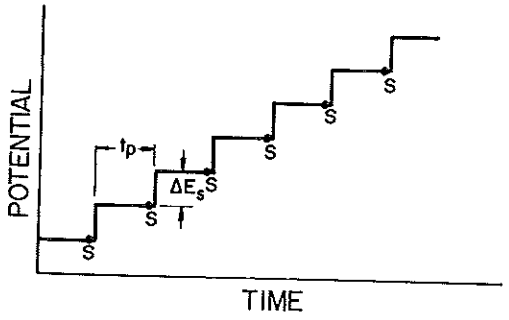

Figure 5.13 Excitation signal for staircase voltammetry.

IV. CONCLUSION

Frequency-domain and time-domain small-amplitude techniques provide unique advantages for both analytical and fundamental studies. They tend to be more sensitive than large-amplitude techniques and are often more precise. These advantages result from the ease with which the signal can be distinguished from the background, the ease of minimizing charging current influences, and the fact that steady-state measurements can be made. In most cases, small-amplitude techniques are coupled to large-amplitude techniques, with the latter setting the surface concentration as an initial condition for the former. Understanding how to properly use small-amplitude techniques for fundamental purposes (e.g., determination of rates and transfer coefficients) requires a mathematical appreciation beyond the interest of most chemists. There are excellent sources, and Bard and Faulkner is the best place to start [1].

If nothing else has been accomplished, it should be very clear from Chapters 3 to 5 that there are an extraordinary number of finite current electroanalytical techniques. There is no doubt that this can cause considerable confusion for novices. Fortunately, all of these methods are based on relatively few fundamental concepts. It must be understood (1) that electron transfer rates and equilibrium constants vary with potential, (2) that mass transport to an electrode surface is precisely defined and reproducible, and (3) that the charge required to establish an electrode potential can be temporally distinguished from that utilized by a redox couple. These concepts are addressed in Chapter 2. Now that we have covered the more important electrochemical techniques, it is strongly recommended that Chapter 2 be reviewed with these techniques in mind.

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