Double differential pulse voltammetry

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Abstract

From the solution obtained in previous work for the faradaic response to a triple pulse of potentials, the double differential pulse technique can be defined through the equation \( I_{DP} = i_2 - 2i_1 + i_3 \), where \( i_j \) (\( j = 1, 2, 3 \)) is the current corresponding to the potential \( E_j \). The solution to this equation, which is valid both for a static mercury drop electrode and for a dropping mercury electrode, was studied, and experimental conditions for the analysis of the corresponding curves are proposed. Likewise, approximate solutions and analysis criteria for completely reversible and irreversible processes are reported. The solutions were checked against experimental examples of well-known processes.

The analytical and kinetic advantages of this technique are discussed.

1. Introduction

Double-pulse electrochemical techniques allow specific current responses for different electrode processes to be determined as shown by some authors using the differential pulse (DP) polarographic technique [1–6].

Birke et al. [1] proposed the obtention of two recordings as an analysis criterion for this technique; one of the recordings is obtained by applying a negative potential pulse (\( \Delta E < 0 \)) (cathodic recording) and the other by a positive pulse (\( \Delta E > 0 \)) (anodic recording) of the same absolute magnitude \( |\Delta E| \). The relation between the maximum current of the two recordings depends markedly on the reaction mechanism involved [1–6]. Thus, for a reduction process, involving a reversible electron transfer, the anodic and cathodic peaks will be of same height in absolute value, whereas if the electron transfer is completely irreversible, the anodic peak will be shorter than the cathodic peak [1].

The results provided by the differential normal pulse (DNP) technique in the alternating pulse mode reported in the literature [7,8] seemingly point to a peak current relationship similar to that established in the DP technique.

Birke's criterion has been used to develop analytical methods for other reaction mechanisms in the DP technique [2–6], on the basis that their current responses vary in symmetry depending on whether negative or positive pulses are applied. The present work originated in the idea that these effects can be directly observed by using a triple pulse of potentials.

In a previous work [9] we studied the Faradaic response of a slow electron transfer to a triple pulse by applying the planar approximation to the static mercury drop electrode (SMDE) and dropping mercury electrode (DME). The theoretical treatment is also valid for a solid electrode provided that the boundary conditions are renewed, either by stirring or by employing a sufficiently long delay time \( t_d \) at an initial potential \( E_1 \) at zero Faradaic current. The analytical solution obtained can be used to develop new electrochemical techniques. In this work we analyse one of the aforementioned applications for kinetic and analytical purposes.

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We shall denote by $E_1$, $E_2$ and $E_3$, and $t_1$, $t_2$ and $t_3$, the potential and the time durations of each pulse. Likewise, we shall assume these potentials to be superimposed to a linear ramp of potentials, which is only effective in successive drops of lifetime $t_d$ (Fig. 1). The corresponding currents sampled at the end of each pulse will be called $i_1$, $i_2$ and $i_3$ respectively.

We shall also assume that $\Delta E_1 = E_2 - E_1$ and $\Delta E_2 = E_3 - E_2$ are constants and with the same sign. Therefore, $\Delta i_1 = i_2 - i_1$ and $\Delta i_2 = i_3 - i_2$ have the same sign.

$\Delta i_1$ corresponds to the signal defined in the DP (if $t_2 \ll t_1$) or DNP technique. For a small $\Delta E_1$ value and $t_1 \gg t_2$, the curves obtained are morphologically similar to the derivative of the $i_1$ response for the first pulse with respect to $E_1$, although the properties of the DP peak are much more complex than those of a simple derivative [5]. Under the same conditions, $\Delta i_2$ is similar to $\Delta i_1$.

In this work we shall define the function $I_{dp_2} = \Delta i_2 = i_3 - 2i_2 + i_1$. Under given experimental conditions ($\Delta E_1 = 2E_2 \rightarrow 0$ and $t_1 \gg t_2 + t_3$), the form of function $I_{dp_2}$ will be similar to the second derivative of the signal of the first pulse. Moreover, the shape of the curves is specific to the electron transfer concerned for a given $t_2/t_3$ ratio.

The technique based on plotting $I_{dp_2}$ vs. $E_1$ will be called double differential pulse (DDP) voltammetry (SMDE) or polarography (DME). As stated by Lowric et al. [10], some researchers [11,12] have used a similar name to refer to what should be called derivative normal pulse voltammetry or polarography.

$I_{dp_2}$ was determined as follows: $i_1$ was calculated from the Cottrell (SMDE) or Ilkovic (DME) equation, while $i_2$ was obtained from an equation previously reported by the present authors (see eqn. (5) in ref. 9). Finally, the expression for $i_3$ is also given in ref. 9.

In previous work, Gálvez et al. [13] derived a different analytical expression for $i_2$ on the assumption that the concentrations on surface gradient for the first pulse were not perturbed on applying the second pulse. Such an approximation is equivalent to using the superposition principle in those situations where its application is not strictly correct, as is the case with slow electrode process (see for example refs. 1, 14 and 15).

In any case, such a solution is scarcely different from the numerical solution to the problem as obtained by using any double pulse technique [16]. However, it does result in large errors when employed to obtain the current $i_3$ corresponding to the third pulse.

Our expression for $i_3$ [9] introduces a major correction in the previous equation [13]. In addition, under certain condition (e.g. in reversed pulse techniques), our solution is quite rigorous [16].

In this work we analyse the general properties of the function $I_{dp_2}$ for a slow electron transfer. Simple analytical expressions for this function for completely reversible or irreversible electron transfers and different experimental conditions (mainly $t_2/t_3$ ratios) are reported. These allow one to distinguish clearly between the two types of mechanisms and to determine the kinetic parameters of the process. An experimental DDP study on the reductions of Cd(II) (reversible process) and Cr(III) (irreversible process) is also reported.

As noted later, the definition of $I_{dp_2}$ has some analytical advantages over other electrochemical techniques (e.g. better resolution between the different processes and greater accuracy in the determination of the formal reduction potential). Moreover, the combination of the currents involved in the definition of $I_{dp_2}$ results in a smaller charging current for a DME by one order of magnitude than in DP, and hence in lower limits of detection.

2. Experimental

Potential pulses were manually generated and $i-t$ curves were recorded on a PAR 273 potentiostat-galvanostat attached to a 303A PARC polarographic stand. A Prowler 105 digital-memory oscilloscope was used for data acquisition. Measurements were made by using a thermostatted PAR cell, the temperature of which was kept constant at $25 \pm 0.1^\circ C$.

An SMDE with an area of 0.0258 cm$^2$ was employed as the working electrode. A saturated calomel electrode and a platinum electrode were used as reference and auxiliary electrode respectively.

All reagents were Merck a.g. and were used without further purification. Mercury was purified with dilute nitric acid and distilled three times in vacuum. Nitrogen gas was used for de-aeration.

A potential at which no faradaic reaction takes place is applied for 2 s in order to allow the drop to grow and the SMDE to stabilize (delay time). Then,
potentials $E_1$, $E_2$ and $E_3$ are applied over the time intervals $t_1$, $t_2$ and $t_3$ respectively, and the currents $i_1$, $i_2$ and $i_3$ are digitally acquired and manipulated to obtain $I_{dp}$ by means of the corresponding software.

The numerical fitting involved in the calculations was done by the program SigmaPlot [17]. This program uses a non-linear least-squares regression method based on the Marquardt–Levenberg algorithm [18]. The observed deviations in the current never exceeded 5%.

3. Theoretical background

Consider the following electrode reduction process:

$$A + ne^- \rightleftharpoons B$$

The definition $I_{dp} = i_1 - 2i_2 + i_3$ can be obtained from eqns. (3), (5) and (30) in ref. 9 without constraints on either the potentials or the interval over which the different potentials are applied. However, in this work we shall impose the following conditions: $\Delta E = E_2 - E_1 = E_3 - E_2$ and $t_1 \gg t_2 + t_3$. Therefore, for an SMDE and/or a DME,

$$\frac{I_{dp}}{i_{dp}} = \left[ (Z_1 + \mu_1) \left[ F(0, y)\lambda^{1/2} - 2F(0, y_2) \left( \frac{\lambda}{1 - \lambda} \right)^{1/2} \right] \right.$$

$$+ Z_1 \mu_2 H_0(\lambda, \omega)$$

$$+ F(0, \omega) \left[ Z_2 + \mu_2 \left( \frac{\mu_2 + \eta_2}{\eta_2 - \eta_1} \right) \right]$$

$$\left. \right]$$

where

$$i_{dp} = nFq_0(t_1 + t_2 + t_3) \left( \frac{D_A}{\tau t_3} \right)^{1/2} e^x$$

$$K_i = \exp[\alpha F(E_i - E_0)/RT]$$

$$\rho = \exp(nF \Delta E/RT) = K_2/K_1 = K_3/K_2$$

$$Z_1 = \frac{1}{1 + \gamma K_2} - \frac{1}{1 + \gamma K_1}, \quad Z_2 = \frac{1}{1 + \gamma K_3} - \frac{1}{1 + \gamma K_2}$$

$$\lambda = \frac{t_3}{t_2 + t_3}, \quad \gamma = (D_A/D_B)^{1/2}$$

$$\chi = \left[ \frac{4(t_1 + t_2 + t_3)}{(2z + 1)D_A} \right]^{1/2} K_s \frac{1 + \gamma K_1}{K_1^a}$$

$$y = \left[ \frac{4(t_2 + t_3)}{D_A} \right]^{1/2} K_s \frac{1 + \gamma K_2}{K_2^a}$$

$$y_2 = \left[ \frac{4t_2}{D_A} \right]^{1/2} K_s \frac{1 + \gamma K_2}{K_2^a}$$

### Table 1. Notation and definition

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>$I_{dp}$</td>
<td>DDP function</td>
</tr>
<tr>
<td>$i_{dp}$</td>
<td>time duration of $E_i$ potential</td>
</tr>
<tr>
<td>$t_i$</td>
<td>drop life time</td>
</tr>
<tr>
<td>$q(t) = q_0 t^\gamma$</td>
<td>time-dependent electrode area</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>apparent heterogeneous rate constant for the charge transfer at $E_0$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>transfer coefficient</td>
</tr>
</tbody>
</table>

$$\omega = \left( \frac{4t_3}{D_A} \right)^{1/2} K_s \frac{1 + \gamma K_3}{K_3^a}$$

$$\eta_1 = 1 - \frac{1}{1 + \gamma K_1} \rho^a, \quad \eta_2 = 1 - \frac{1}{1 + \gamma K_2} \rho^a$$

$$\mu_1 = 2F(z, \chi), \quad \mu_2 = 2F(0, \gamma)$$

$$\pi_1^{1/2} \chi(1 + \gamma K_1) \eta_1, \quad \mu_2 = \pi_1^{1/2} \gamma \eta_1$$

Equation (1) has been derived for an electrode of area $q(t) = q_0 t^\gamma$, where $z = 0$ for the SMDE and $z = 2/3$ for the DME, and all other symbols were defined elsewhere [9]. Finally, $F(z, x)$ is the Koutecky equation of argument $z$ and $x$ [13] and $H_0(\lambda, \omega)$ is defined in [9]; see Appendix A and Table 1.

When the electron transfer is completely irreversible, the function $I_{dp}$ can be considerably simplified by imposing the condition $k_s \approx \infty$ in eqn. (1), which implies that $F(z, x) \approx 1$ and $\mu = \mu_2 = 0$. Hence

$$\frac{I_{dp}}{i_{dp}} = \frac{1}{1 + \gamma \rho^2 K_1} - \frac{1}{1 + \gamma \rho K_1} + \frac{2(\tau_3/t_3)^{1/2} - [\tau_3/(t_2 + t_3)]^{1/2}}{1 + \gamma K_1}$$

A special case of this equation is that at which $t_3 = 2t_2/3$. The implications of this relation are analysed in the following section. In this case, the function $I_{dp}$ can be written as

$$\frac{I_{dp}}{i_{dp}} = \frac{1}{1 + \gamma \rho^2 K_1} - \frac{2}{1 + \gamma \rho K_1} + \frac{1}{1 + \gamma K_1}$$

At $k_s \leq 5 \times 10^{-4}$ cm $s^{-1}$, the process can be considered to be completely irreversible, so $I_{dp}$ can be written as

$$\frac{I_{dp}}{i_{dp}} = \frac{2F(z, \chi)(1 - \rho^a)}{\pi_1^{1/2} \chi} \left[ \left( \frac{t_3}{t_2 + t_3} \right)^{1/2} F(0, y) \right]$$

$$+ F(0, \omega) \left[ \rho^a + 2F(0, \gamma) \pi_1^{1/2} \gamma (1 - \rho^a) \right]$$

$$- 2 \left( \frac{t_3}{t_2} \right)^{1/2} F(0, y_2)$$

(14)
Figure 2 shows several $I_{ddp}/i_{dp}$ vs. $E_1 - E^0$ plots for a reversible process (eqn. (12)) with $\Delta E = -50$ mV and different $t_2/t_3$ ratios. All other pertinent conditions are described in the figure caption. As can be seen, under these conditions, the function $I_{ddp}$ is similar to the second derivative of a classic $i-E$ d.c. polarogram.

Figure 3 shows a typical recording corresponding to curve a in Fig. 2. The nomenclature used to designate the characteristic parameters of the $I_{ddp}$ vs. $E$ curves is included in the figure. As can be seen, in the first portion, the current increases as $E$ decreases to a maximum $I_n$ at $E^0$. At more negative potentials, the current sharply decreases to zero at $E_c$, whereas, at more negative potentials, a minimal current $I_m$ is reached at $E_m$, and, finally, the current increases as $E$ increases to zero again.

Curve a in Fig. 2 corresponds to the condition $t_3 = 2t_2/3$, for which eqn. (13) was defined. In this case, if $D_A = D_B$, $I_n/I_m = 1$. In the following sections analytical criteria are established for reversible processes according to eqn. (13).

Figure 4 shows the plot of $I_{ddp}/i_{dp}$ vs. $E_1 - E^0$ at $k_+ = 5 \times 10^{-4}$ cm s$^{-1}$ (a completely irreversible process), with $z = 0$ (SMDE). All other conditions are identical with those of Fig. 2. As a rule, the shapes of these curves are similar to those of the previous curves; however, the absolute value of the $I_p/I_n$ ratio is always greater in this case than for the reversible process illustrated in Fig. 2. At $t_3 = 2t_2/3$ (curve a), $|I_p/I_n| = 3.1$, although this ratio depends on $\alpha n \Delta E$, $t_2$ and $z$, as shown later. The marked difference in $I_p/I_n$ between reversible and irreversible processes can be used as an analytical criterion.

Figure 5 shows the plots of $I_{ddp}/i_{dp}$ vs. $E_1 - E^0$ at $t_1 = 5$ s, $t_2 = 0.05$ s, $t_3 = 2t_2/3$, and $\alpha = 0.5$, and different $k_+$ values. All other conditions are identical with those of Fig. 4. As can be seen, the shapes of the
tive significance of the two processes is also dependent on $k_x$.

The separation of the electrode process at smaller $\alpha$ values must be regarded as a universal phenomenon, as it can be observed in any technique, including linear sweep voltammetry and square wave voltammetry [8, 19–21]. However, the effect is specially marked in pulse techniques [22].

A more detailed description of the behaviour of both reversible and irreversible electrode reactions is provided in the following sections.

4. Analytical criteria for a completely reversible electron transfer at $t_2 = 2t_3/3$

A comprehensive study of the properties of eqn. (13) with $\Delta E = E_2 - E_1 = E_3 - E_2$, $t_1 \gg t_2 + t_3$, $t_2 = 2t_3/3$ and $D_\alpha = D_\beta$ was performed. As noted earlier, under these experimental conditions $|I_p/I_n| = 1$. It is important to note that the shapes of the $I_{\text{dpp}}/i_{\text{dpp}}$ vs. $E_1 - E_0$ curves are independent of the $z$ value ($z = 0$ (SMDE) and $z = 2/3$ (DME)).

The potential at which $I_{\text{dpp}} = 0$ was called $E_c$ (see Fig. 3). From eqn. (13) it can be readily inferred that $E_c = E_1^{0'} - \Delta E$, where $E_1^{0'} = E_0^{0'} - (RT/nF) \ln \gamma$. Measurements of $E_c$ can be made highly accurate thanks to the steep slope of the $I_{\text{dpp}}$ plot in the vicinity of this potential.

We shall denote $E_p - E_n$ by $W$ (see Fig. 3). Curve a in Fig. 7 shows the plot of $nW/mV$ vs. $n|\Delta E|$ (for this curve, we take arbitrarily $\alpha = 1$). At $n|\Delta E| > 0$, $nW = 70$ mV, and, at $n|\Delta E| < 120$ mV, $nW = 20 - n \Delta E$.

Figure 8, curve a, shows the plot of $I_p/i_{\text{dpp}}$ vs. $n|\Delta E|$ (with $x = 1$). As can be seen, $I_p$ tends asymptotically to $i_{\text{dpp}}$ (eqn. (2)) at large $n|\Delta E|$ values.

For a reversible process, under the experimental conditions described above, $I_{\text{dpp}}/i_{\text{dpp}}$ is independent of $t_2$ and $t_3$ (see eqn. (13)). Therefore $t_3 = t_1 + t_2 + t_3$ and $t_3$ only influence $I_{\text{dpp}}/i_{\text{dpp}}$, i.e., $I_{\text{dpp}}$ is proportional to $t_3^{1/2}$, for any given $\Delta E$ value.

5. Analytical criteria for a completely irreversible electron transfer at $t_2 = 2t_3/3$

Equation (14) was analysed at $\Delta E = E_3 - E_1 = E_3 - E_2$, $t_1 \gg t_2 + t_3$, $t_2 = 2t_3/3$ and $z = 2/3$ or $z = 0$.

Figure 9 shows the variation in $|I_p/I_n|$ with $an|\Delta E|$ at $t_1 = 2$ s, $t_2 = 0.05$ s and $t_3 = 0.033$ s, with $z = 2/3$ (curve a) and $z = 0$ (curve b). At $z = 2/3$, the plots exhibit maxima close to 2.0 for $an|\Delta E| = -25$ mV. At $an|\Delta E| \to \infty$, $|I_p/I_n| \to 1$, as for the reversible process at any $\Delta E$ value. At $z = 0$, the behaviour is similar, except for the fact that the maximum value of $|I_p/I_n|$ is ca. 2.5. In addition, the ratio is strongly dependent on both $t_2$ and $t_3$ values. Thus, if $t_1 = 2$ s, $t_2 = 0.03$ s and $an|\Delta E| = -25$ mV, then $|I_p/I_n| = 3$ for $z = 0$ and $|I_p/I_n| = 2.3$ for $z = 2/3$.

Under the experimental conditions given in Fig. 9 and irrespective of the $z$ value, $E_c$ is approximately given by

$$E_c \approx E_0^{0'} - \Delta E + \frac{RT}{anF} \ln \left[ \frac{1.35t_3 \pi}{D_\alpha} \right]^{1/2}$$

(15)

This equation can be used to calculate $k_x$, provided that $D_\alpha$ and $E^I$ are known.

Figure 7, curve b, shows the plot of $anW$ vs. $an|\Delta E|$ at the same time values used in Fig. 9. The curve is virtually independent of the $z$ value; also, at $an|\Delta E| < 60$ mV, $anW = 66 \pm 5$ mV. Likewise, in all cases, $E_0 - E_n > E_0 - E_n$, unlike the reversible process, where the two differences are identical.

Figure 8, curve b, shows the plot of $I_p/i_{\text{dpp}}$ vs. $an|\Delta E|$ at the time values used in Fig. 9. Again, the shape of the curve is independent of the $z$ value.

The influence of $t_4$ on the peak current was ascertained at different $an|\Delta E$ values. Ratios $I_{\text{dpp}}(t_1 = 4)$/$I_{\text{dpp}}(t_1 = 1)$ between the peak currents at two different drop times, the remainder of experimental conditions being kept constant ($t_1 = t_3$), were studied. At large $an|\Delta E|$ values, all ratios tend to $4^z$, i.e., at $z = 2/3$ (DME) $4^z = 2.52$, and at $z = 0$, $4^z = 1$ (SMDE), which means that $I_p$ and $I_n$ are proportional to $t_3^{1/2}$. At $an|\Delta E| \to 0$, $I_p(t_1 = 4)/I_p(t_1 = 1)$ tends to 1.2 for $z = 2/3$ and to 0.5 for $z = 0$ (curve b), i.e., $I_p$ is proportional to $t_3^{-1/2}$. At low $an|\Delta E|$ values, $I_p$ exhibits a $t_d$ dependence intermediate between those described.
6. Experimental application. Use of instantaneous and mean currents

We carried out an experimental study on the shape of the \( I_{dclp} \) vs. \( E_1 \) curves for two types of processes: completely reversible and irreversible. Figure 10 shows the plot of \( I_{dclp} \) for the reversible reduction of \( 10^{-4} \) M Cd(II) in 0.1 M H$_2$SO$_4$ with \( \Delta E = -50 \) mV, \( t_1 = 2 \) s, \( t_2 = 0.05 \) s and \( t_3 = 2t_2/3 \). The full line in the figure corresponds to the predictions of eqn. (13), with \( n = 2 \), \( E^0 = -713 \) mV and \( i_{dclp} = 7.33 \mu A \). As can be seen, there is good correlation between experimental data and the theoretical predictions.

It can be seen that \( I_p \) is slightly greater than \( I_0 \), in absolute value (\( \mid I_p/I_0 \mid = 0.99 \)). This effect, which can be explained on the basis of eqn. (13), arises from the different values of the diffusion coefficients of Cd(II) (\( D_A = 1.2 \times 10^{-5} \) cm$^2$ s$^{-1}$) [4] and Cd(Hg) (\( D_B = 1.42 \times 10^{-5} \) cm$^2$ s$^{-1}$) [23]. However, the initial absence of amalgamated Cd makes this effect negligible.

\( I_{dclp} \) values were determined from instantaneous current measurements as described under Experimental.

The use of instantaneous currents in automated measurements may lead to experimental errors. It is usual in other techniques to average the currents over a short interval, so we made a theoretical study of the function \( I_{dclp} \) (eqn. (13)) determined from the mean currents \( i_{dclp} = i_3 - 2i_2 + i_1 \). For this purpose, we averaged \( i_3 \) from ten data obtained over the last 10 ms of \( t_1 \). At \( t_2 = 0.05 \) s we averaged \( i_2 \) from the data obtained at the times 0.041, 0.042, ..., 0.050 s. Finally, \( i_3 \) was averaged from the times 0.024, 0.025, ..., 0.033 s. We found no significant differences between \( i_{dclp} \) and the \( I_{dclp} \) value determined from the instantaneous currents.

In our opinion, a more correct approach relying on the computational speed to today's personal computers would be to carry out a linear regression on the plot \( \log(i_2) \) vs. \( \log(t_1) \) at \( j = 1, 2, 3 \) over the aforementioned intervals in order to obtain the instantaneous value corresponding to the desired time.

By way of example of a completely irreversible process, we studied the reduction of \( 10^{-3} \) M Cr(III) in 1 M Na$_2$SO$_4$ + 0.01 M HClO$_4$. Figure 11 shows the variation in \( I_{dclp} \) as a function of \( E_1 \), with \( \Delta E = -100 \) mV, \( t_1 = 2 \) s, \( t_2 = 0.03 \) s and \( t_3 = 0.02 \) s. As in the previous case, the full line corresponds to the predictions of eqn. (14), with \( \alpha = 0.57 \) [24], \( i_{dclp} = 1.915 \mu A \), and \( E^0 + (RT/\alpha nF) \ln[k/(4/D_A)^{1/2}] = -1010 \) mV. As can be seen, there is a good fit between the experimental data and the theoretical predictions.

7. The charging current and analytical advantages of the DDP technique

Consider a DME where the effects of the charge current are more significant than in an SMDE. The charge current for this type of electrode is given by [25]

\[ i_c = k \sigma / t^{1/3} \]

(16)
In addition, the DDP technique has some advantages over other electrochemical techniques. First, \( E_c \) can be obtained with a great accuracy since it corresponds to the potential at which the zero current baseline and the inflection point of \( I_{\text{dep}} \) intersect. This ensures more accurate calculation of the formal reduction potential or its apparent value. Second, the function \( I_{\text{dep}} \) is markedly curved, which results in better resolution in those cases where two electrode processes take place at very close discharge potentials.

Kinetically, the shape of the DDP curves obtained can be directly related to the degree of reversibility of the electrode process. Thus, a \( \frac{I_{\text{p}}}{I_{\text{n}}} \) ratio of ca. 1 will be indicative of a reversible process, whereas a ratio greater than unity will be suggestive of an irreversible process.

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**References**

Appendix A

The Koutecky function $F(z, x)$ is given by [13]

$$F(z, x) = \sum_{j=0}^{\infty} \frac{(-1)^j x^{j+1}}{\prod_{i=0}^{j} p_i(z)}$$  \hspace{1cm} (A1)

where

$$p_i(z) = \frac{2 \Gamma \left( \frac{1}{2} + \frac{i}{4z + 2} \right)}{\Gamma \left( \frac{1}{2} + \frac{i}{4z + 2} \right)}$$  \hspace{1cm} (A2)

$\Gamma$ being the Euler gamma function.

The $F(z, x)$ functions can be calculated with errors of less than 0.4% by using the approximate analytical functions [6,28]:

$$F(2/3, x) \approx 1.293 \left( \frac{3\pi}{7} \right)^{1/2} \left[ 1 + \frac{9x}{8} \left( \frac{7}{12} \right)^{1/2} \right] - \left[ \frac{7}{12} \left( \frac{9x}{8} \right)^2 + 1 + 0.75 \left( \frac{7}{12} \right)^{1/2} x \right]^{1/2}$$  \hspace{1cm} (A3)

$$F(0, x) = \pi^{1/2} (x/2) \exp(x^2/4) \text{erfc}(x/2)$$

$$= \frac{1}{m + \left[ (1 - m)^2 + 4/\pi x^2 \right]^{1/2}}$$  \hspace{1cm} (A4)

where $m = 0.658$.

The function $H_0(\lambda, y)$ is given by

$$H_0(\lambda, y) = \sum_{j=0}^{\infty} \frac{(-1)^j y^{(j+1)}}{\prod_{i=0}^{j} p_i(0)}$$

$$\times \left[ 1 + \sum_{k=1}^{\infty} \frac{(2k - 1)! j!}{2^{2k-1} k! (k-1)! (j + 2k)} \right]$$  \hspace{1cm} (A5)