



Comparison between double pulse and multipulse differential techniques

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ABSTRACT

The most common differential pulse techniques are analyzed and their responses are compared. Depending on whether or not the initial conditions are re-established before the application of each double pulse we distinguish between double pulse and multipulse differential techniques. The nomenclature employed in the literature is clarified to avoid future confusion.

The differences and similarities between the double pulse and multipulse responses are studied for electrode processes of any degree of reversibility, analysing the advantages and disadvantages of each method. The effect of the electrode size is also discussed, establishing the conditions under which the voltammograms obtained by different techniques are coincident or not.

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1. Introduction

Differential Pulse Voltammetry (DPV) is a very popular pulse technique due to its high sensitivity, the high resolution of the peak-shaped response and the minimization of double layer and background effects [1–3]. These properties partially come from the subtractive nature of the technique where the signal is given by the difference between currents recorded at the end of consecutive potential pulses, resulting in a peak-shaped voltammogram. In addition, given that it is a pulse technique and the value of the applied potential remains constant during each pulse, the effect of the charging current is greatly reduced since this sharply decays after the application of the pulse. As a consequence, the DPV technique is widely used in electroanalysis for determination of trace elements as well as for the study of electrode processes and identification of reaction mechanisms [1–5].

Currently, two types of waveforms are usually considered when studying or employing the DPV technique: successive double potential pulses recovering the initial equilibrium conditions after each one (“double pulse” mode, see Fig. 1a) [1,4–8], and a train of pulses superimposed on a staircase waveform (“multipulse”

mode, see Fig. 1d) [2,9–13]. Thus, in the double pulse technique the theoretical treatment and the interpretation of experimental results are easier, whereas the multipulse variant reduces the duration of the experiments. In general, for both cases in each pair of potential pulses the length of the first pulse is much longer than the second one.

As will be discussed in this paper, the voltammograms obtained with these two potential waveforms are not equivalent and so it becomes necessary to clearly distinguish between them in order to avoid misinterpretation of experimental data. Unfortunately, there is some disagreement in the literature about the terminology employed with the DPV technique. Thus, the term “Differential Pulse Voltammetry” (DPV) referring to the “double pulse” program has been used in the literature [1,4–8], whereas other authors and most of the commercial software available in electrochemistry employ the term DPV for the “multipulse” variant [2,9–13]. Some authors [9,14] have used the term “Differential Pulse Polarography” (DPP) for the “double pulse” mode, in reminiscence of the use of mercury drop electrodes where the drop is dislodged after each double pulse [15–19]. Nevertheless, this technique is not restricted to mercury electrodes but it can be, and often is, carried out at stationary nonpolarographic electrodes so that, from our point of view, the term DPP is best avoided hereafter. Indeed, Osteryoung et al. recommended the use of the term “polarography” for the dropping mercury electrode and the term “voltammetry” for the static mercury drop and solid electrodes [20]. Therefore, in this work we suggest and employ the term

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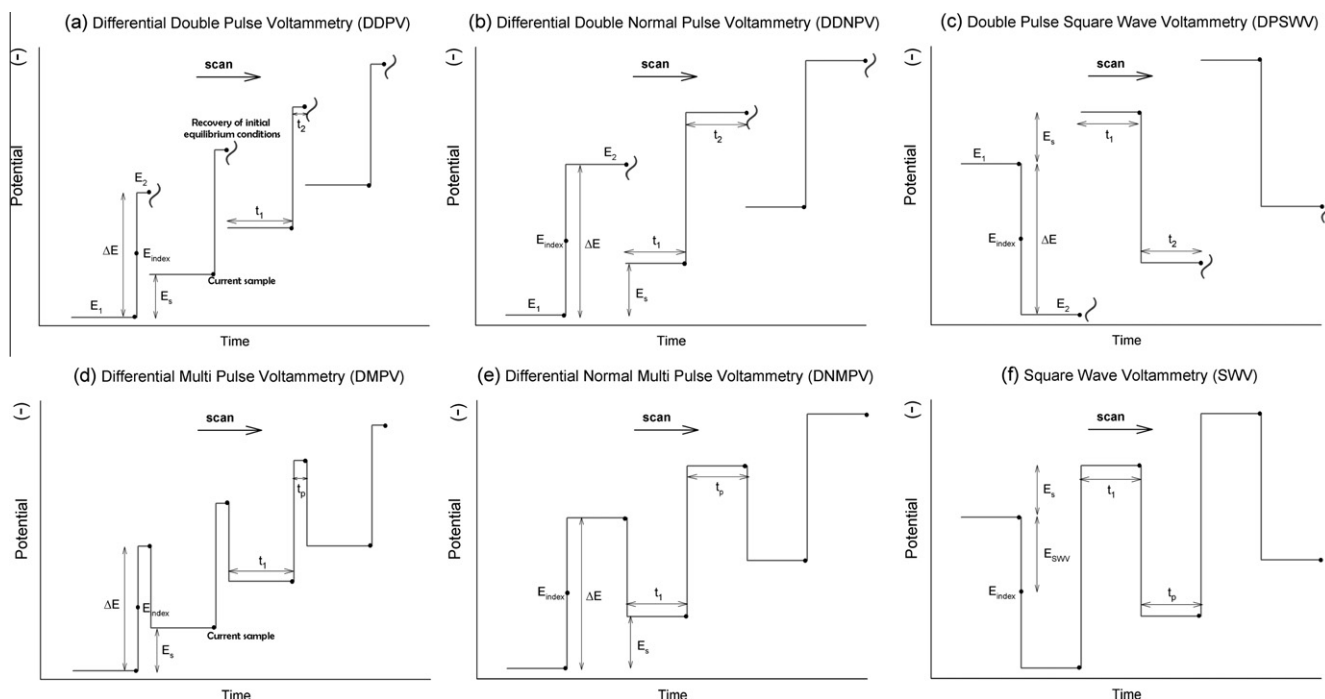


Fig. 1. Potential-time programs of the differential pulse techniques considered.

“Differential Double Pulse Voltammetry” (DDPV) [21] for the double pulse mode (Fig. 1a) and “Differential Multi Pulse Voltammetry” (DMPV) for the multipulse mode (Fig. 1d). With this convention both modes can be immediately distinguished and the generality of the electrochemical methods is not impaired.

A new problem arises when the durations of the two pulses in each pair of pulses are similar, which complicates the mathematical resolution of the problem with respect to DDPV. This situation has traditionally been referred as “normal” mode [3,6,7] and following this criterion we propose the term Differential Double Normal Pulse Voltammetry (DDNPV) and Differential Normal Multi Pulse Voltammetry (DNMPV) for these variants of the DDPV and DMPV methods, respectively, when $t_1 \approx t_2$ (Fig. 1b and e). Note that Square Wave Voltammetry can be viewed as a particular case of the DNMPV technique when $t_1 = t_2$ and the pulse height is opposite from the scan direction (Fig. 1f), and for the analogous double pulse technique we suggest the term Double Pulse Square Wave Voltammetry (Fig. 1c).

According to the above, the aim of this paper is to analyze the differences and similarities between differential double pulse techniques and differential multipulse techniques for different conditions of electrode kinetics, pointing out the sources of discrepancy or similarity. When the responses significantly differ, the advantages and disadvantages of each method are discussed.

The effect of the electrode size is also analyzed, showing that the differences between double pulse and multipulse techniques decrease with the electrode radius. The maximum value of the electrode radius to obtain equivalent $\Delta I - E$ responses is established.

2. Differential pulse techniques: potential-time program

The techniques considered in this work are all differential pulse techniques based on sampling the current at the end of consecutive potential pulses and plotting the current difference versus a potential axis, which gives rise to a peak-shaped response [1–3].

Depending on whether or not the initial conditions are regained before the application of each double pulse we can distinguish between double pulse and multipulse differential techniques.

2.1. Differential double pulse techniques

In double pulse techniques the initial, equilibrium conditions are re-established before the application of each double pulse (see Fig. 1a–c) so that there are no accumulative effects.

At stationary electrodes, the renewal of the initial conditions can be attained by open circuiting the working electrode [22,23] or by setting the applied potential at an adequate initial value [6] for a waiting period. Commercial instrumentation [24,25] enables to implement this potential-time program by designing a program of successive double potential step chronoamperometries with a delay time with cell off after each one. This fact greatly simplifies the theoretical treatment of the technique as well as the interpretation of the experimental results since each double pulse is independent of the previous ones such that analytical solutions are available for the direct study of the response (see Appendix A). On the other hand, the recording of a complete voltammogram is slower than with multipulse techniques.

2.1.1. Differential Double Pulse Voltammetry (DDPV)

In DDPV the length of the second pulse (t_2) is much shorter than the length of the first pulse (t_1), $t_1/t_2 = 50 - 100$ (Fig. 1a), which leads to very high sensitivity and further simplification of the mathematical treatment so that a very simple analytical expression is available for the analysis of the experimental results (see Appendix A).

2.1.2. Differential Double Normal Pulse Voltammetry (DDNPV)

In this case both pulses have similar durations $t_1 \approx t_2$ (Fig. 1b) which notably complicates the resolution of the problem and therefore the form of the analytical solution (see Appendix A). The shape of the response is also affected such that in DDNPV an

asymmetric peak is obtained with the signal tending to a non-null constant value for limiting current conditions.

2.1.3. Double Pulse Square Wave Voltammetry (DPSWV)

This is a particular case of DDNPV where the durations of both pulse are equal $t_1 = t_2$ and the pulse height ($\Delta E = E_2 - E_1$) is opposite from the scan direction (Fig. 1c). Because of its analogy with the potential-time program applied in Square Wave Voltammetry, we will refer to this technique as Double Pulse Square Wave Voltammetry.

2.2. Differential multipulse techniques

In multipulse techniques there is no renewal of the initial conditions during the experiment and so progressive depletion of the electroactive species and accumulation of the electrode product can take place near the electrode surface, consequently affecting the electrochemical response.

For these techniques, analytical solutions are not available except for reversible processes since for quasireversible and irreversible ones the superposition principle does not apply and therefore it has not been possible to deduce explicit general analytical expressions for multipulse techniques [26]. Accordingly, for such systems, we have employed numerical methods with procedures and conditions described in Appendix A.

2.2.1. Differential Multi Pulse Voltammetry (DMPV)

The DMPV technique can be viewed as a variant of DDPV where the initial conditions are not recovered during the experiment (Fig. 1d). Thus, the pulse length (t_p) is much shorter than the period between pulses (t_1), $t_1/t_p = 50 - 100$.

2.2.2. Differential Normal Multi Pulse Voltammetry (DNMPV)

The DNMPV is the multipulse variant of the DMPV technique such that the duration of the period between pulses and the duration of the pulses are similar: $t_1 \approx t_p$ (Fig. 1e).

2.2.3. Square Wave Voltammetry (SWV)

The well-known Square Wave Voltammetry can be considered as a particular situation of DNMPV where the length of both pulses are equal ($t_1 = t_p$) and the sign of the pulse height (ΔE) is opposite from the scan direction (Fig. 1f).

3. Results and discussion

The comparison of the double pulse techniques DDPV, DDNPV and DPSWV with respect to their corresponding multipulse variants DMPV, DNMPV and SWV was carried out for a wide range of conditions. In general, the similarity or difference between the responses reflects the significance of the accumulative effects that takes place in the multipulse techniques, in other words, the ability of the system to lose the “memory” of the previous pulses. This will obviously depend on the reversibility of the electrode process, the mass transport (i.e., on the electrode size) and the relative duration of the potential pulses.

For the results corresponding to double pulse techniques, Eqs. (A4), (A5), (A13), and (A14) presented in Appendix A are used, by making $r_0 \rightarrow \infty$ in the case of planar electrodes. For multipulse techniques, Eqs. (A8) and (A9) are employed for reversible processes, whereas for slow charge transfer processes we have used numerical methods as described in the same Appendix A.

3.1. Comparison of double pulse and multipulse differential techniques for different electrode kinetics

In Figs. 2–4 the responses of the three general cases: reversible, quasireversible and irreversible processes are considered in the different techniques. Note that t_2 refers to the length of the second pulse of each pair of pulses in double pulse techniques and t_p to the length of each pulse in multipulse techniques (see Fig. 1).

Fig. 2 shows the voltammograms corresponding to the double pulse and multipulse techniques where the duration of the pulses are such that $t_1 \gg t_2$ and $t_1 \gg t_p$, that is, DDPV and DMPV. As can be observed in Fig. 2a, the responses of reversible processes in both techniques are totally coincident as the electrode process is fast and the period between pulses (t_1) is much longer than the length of the pulse (t_p), since in DMPV the system is able to establish conditions equivalent to DDPV near the electrode surface during the first period as if previous pulses had not existed. Therefore, under these conditions (reversible processes and very short pulse period), we can take advantage of the simple analytical expression available for DDPV (Appendix A) together with the faster potential-time program of DMPV.

In Figs. 3 and 4 the voltammograms obtained considering similar durations of the potential pulses ($t_1 = t_2$, $t_1 = t_p$) are shown. In this case, the difference between the responses for reversible processes (Figs. 3a and 4a) is significant since the distortion of the previous pulses cannot be removed during the first period and, as a consequence, the double pulse and multipulse voltammograms are not coincident.

The results shown in Figs. 2a and 3a are in line with those previously reported for the case of reversible processes [9,27] according to which the period between pulses must be at least five times longer than the pulse so that the agreement between the DDPV and DMPV voltammograms when $t_1/t_p = 50 - 100$ is excellent whereas when $t_1 = t_p$ important differences are found. Nevertheless, as we indicated at the beginning of this section, the electrode kinetics will have a major effect on the relationship between double pulse and multipulse responses and so the conclusions inferred for reversible processes cannot be extended to slow charge transfer processes.

In Figs. 2b, 2c, 3b, 3c, 4b and 4c the comparison between double pulse and multipulse techniques for quasireversible and irreversible processes is analyzed. Unlike reversible processes, for sluggish electrode reactions the disagreement between the curves is apparent whatever the length of the pulses, the slower the charge transfer, the greater the discrepancy of the curves. This affects not only to the value of the peak current but also to the position of the peak such that the curves corresponding to the multipulse methods (DMPV, DNMPV and SWV) appear at less negative potentials.

As was mentioned above, the discrepancy or similarity between the response in double pulse and multipulse techniques is related to the ability of the system to compensate the accumulative effects taking place in the latter. In the case of irreversible charge transfer processes these effects are more significant since the electrode reaction does not regenerate the electroactive species and so there is a depletion of the reactant during the scan that gives rise to smaller signals (see Figs. 2c, 3c and 4c). Thus, for example, the comparison of the responses in DDPV and DMPV techniques provides a simple diagnosis test for the reversibility of the electrode process (Fig. 2).

According to the above, the electrochemical response in the different differential pulse techniques can be very different and it is worth analyzing the advantages and disadvantages of each method. With this aim, in Fig. 5 the voltammograms of the six techniques considered in this paper are plotted on the same graph for reversible and irreversible systems.

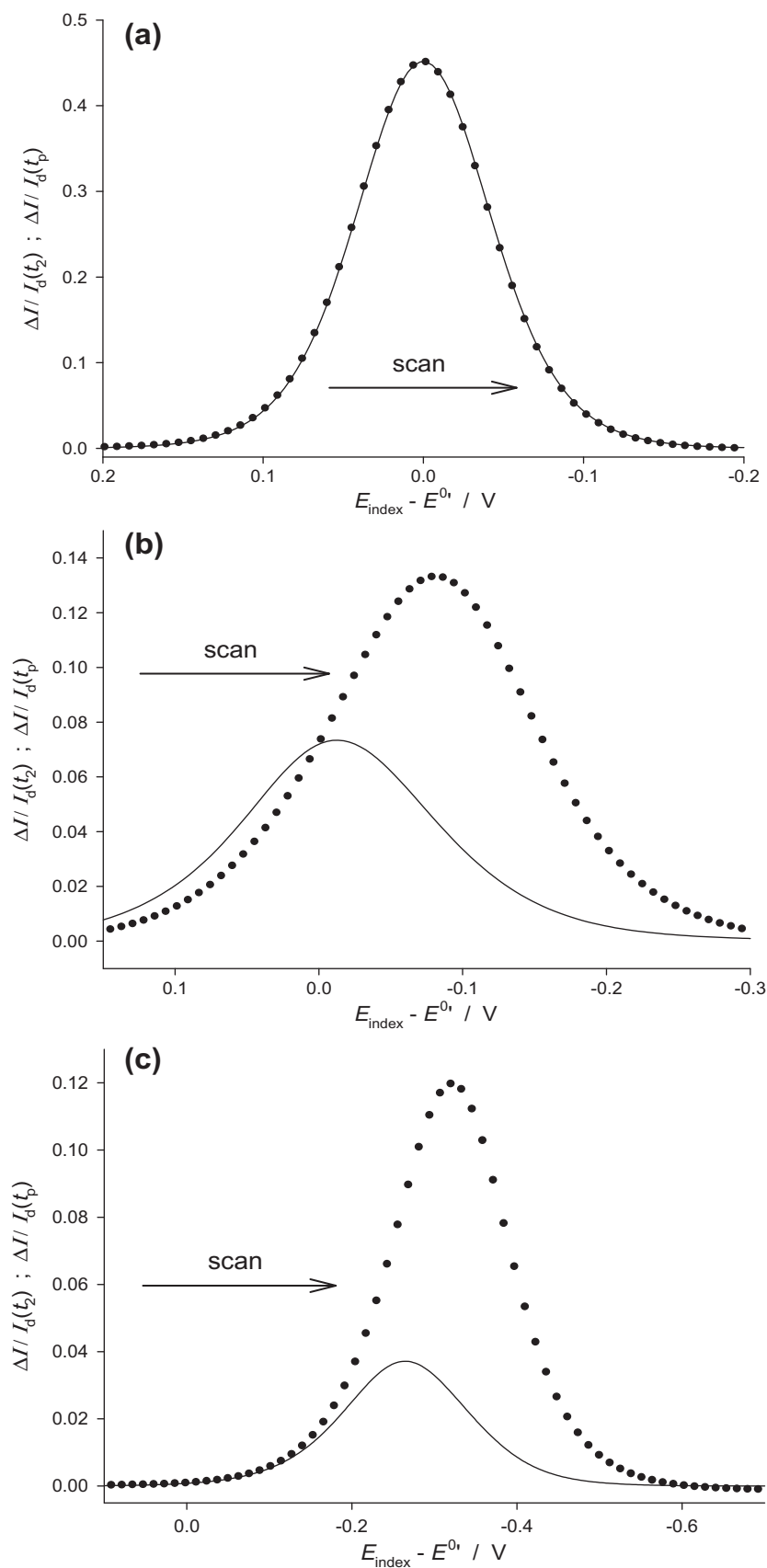


Fig. 2. Comparison between DDPV (●) and DMPV (—) curves for different electrode kinetics: (a) reversible, (b) quasireversible ($k^0 = 10^{-3}$ cm/s, $\alpha = 0.5$) and (c) irreversible ($k^0 = 10^{-5}$ cm/s, $\alpha = 0.5$) processes. Planar electrode, $t_1 = 1$ s, $t_1/t_2 = t_1/t_p = 50$, $\Delta E = -50$ mV, $E_s = 5$ mV.

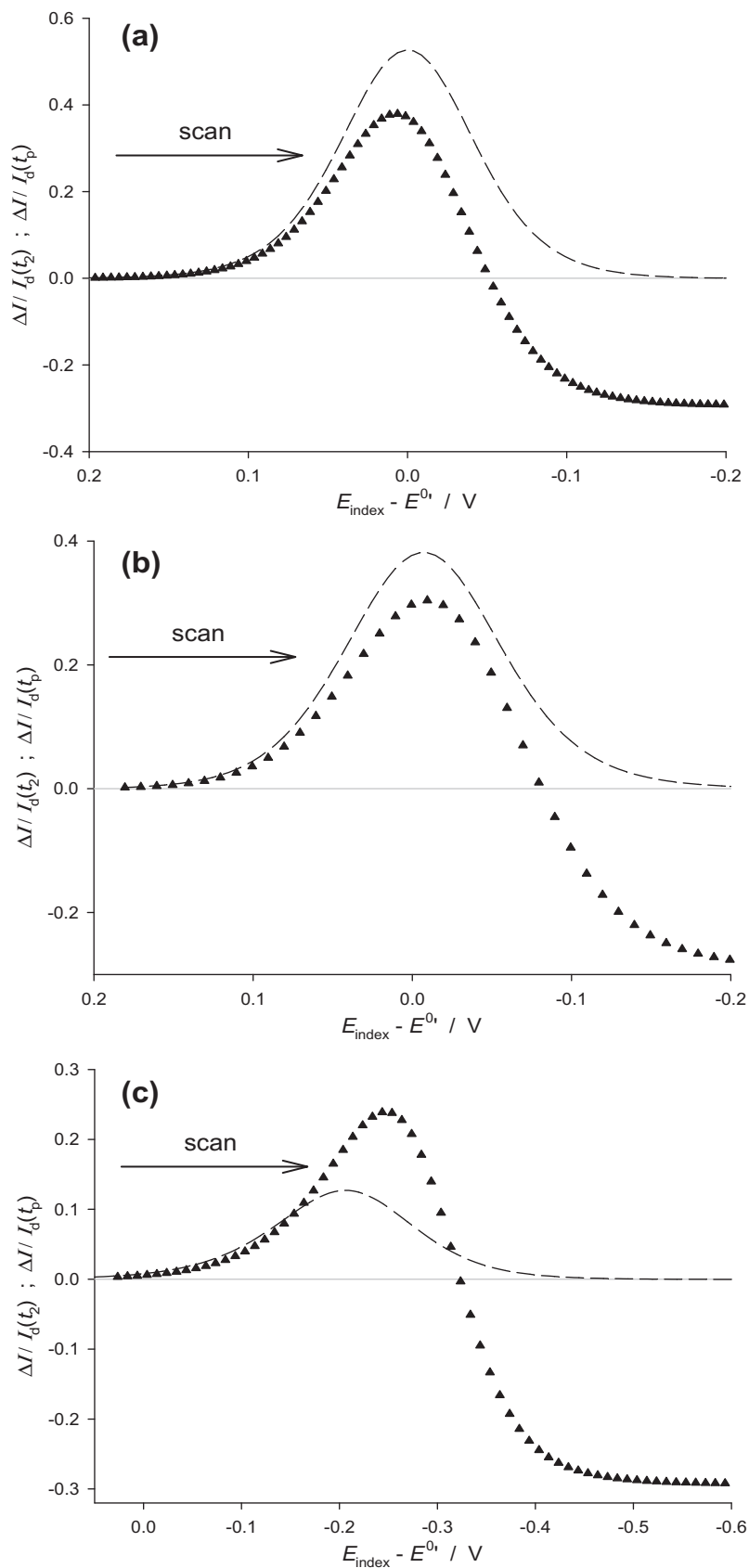


Fig. 3. Comparison between DDNPV (▲) and DNMPV (---) curves for different electrode kinetics: (a) reversible, (b) quasireversible ($k^0 = 10^{-2} \text{ cm/s}$, $\alpha = 0.5$) and (c) irreversible ($k^0 = 10^{-4} \text{ cm/s}$, $\alpha = 0.5$) processes. $t_1 = 0.02 \text{ s}$, $t_1/t_2 = t_1/t_p = 1$. Other conditions as in Fig. 2.

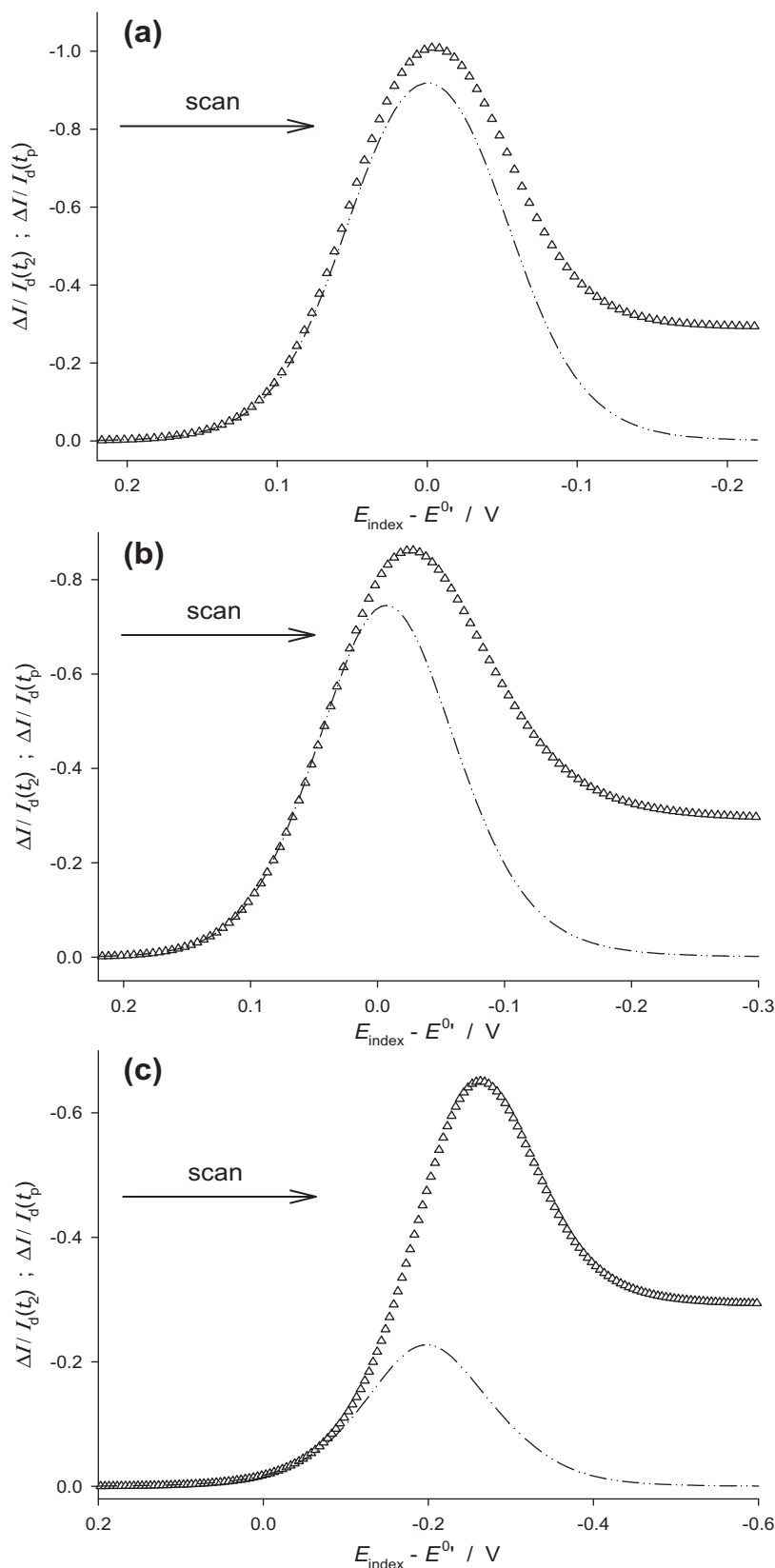


Fig. 4. Comparison between DPSWV (Δ) and SWV (— · — · —) curves for different electrode kinetics: (a) reversible, (b) quasireversible ($k^0 = 10^{-2}$ cm/s, $\alpha = 0.5$) and (c) irreversible ($k^0 = 10^{-4}$ cm/s, $\alpha = 0.5$) processes. Planar electrode, $t_1 = 0.02$ s, $t_1/t_2 = t_1/t_p = 1$, $\Delta E_{\text{DPSWV}} = 2 \times E_{\text{SWV}} = +100$ mV. Other conditions as in Fig. 2.

Regarding the double pulse methods in normal mode, DDNPV and DPSWV, these have the inconvenience of presenting asymmetrical peaks that can make difficult the experimental determination

of the peak current. In addition, the peak potential for a reversible process (Fig. 5a) is shifted from the half-wave potential. On the other hand, the other four techniques (DDPV, DMPV, DNMPV and

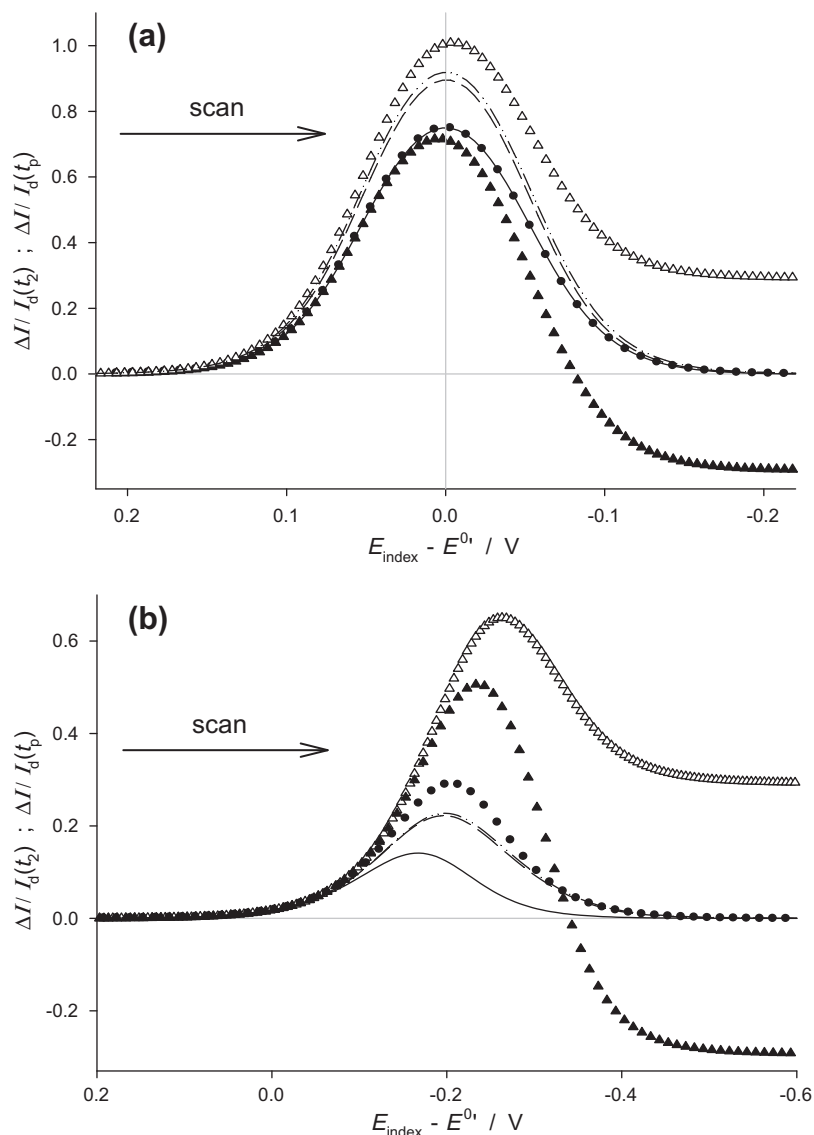


Fig. 5. Comparison of all the differential pulse techniques for (a) reversible and (b) irreversible ($k^0 = 10^{-4}$ cm/s, $\alpha = 0.5$) processes: DDPV (\bullet , $t_1/t_2 = 50$), DDNPV (\blacktriangle , $t_1 = t_2$), DPSWV (Δ , $t_1 = t_2$), DMPV ($-$, $t_1/t_p = 50$), DNMPV ($- \cdot -$, $t_1 = t_p$) and SWV (\cdots , $t_1 = t_p$). In the cases of the DPSWV and SWV techniques the absolute value of the signal ($|\Delta I|$) is plotted. Planar electrode, $t_2 = t_p = 0.02$ s, $|\Delta E| = 2 \times E_{SWV} = 100$ mV, $E_s = 5$ mV.

SWV) have well-defined peaks, all of them centered around the half-wave potential in the case of reversible charge transfer processes.

As can be observed, the choice of the method will depend on the electrode kinetics of the system under study. Thus, for reversible systems the multipulse SWV and DNMPV techniques show greater sensitivity than DDPV and DMPV. For totally irreversible processes, the height of the signal is notably greater in double pulse techniques than in multipulse ones, and therefore we can infer that DDPV is the better method for analyzing slow electrode processes because of its higher sensitivity and well-defined curves. Nevertheless, if the aim is to remove the interference of background irreversible signals when studying a reversible process the multipulse techniques (SWV, DNMPV and DMPV) provides a greater discriminatory power. Note that whatever the reversibility degree of the electrochemical process the responses in SWV and DNMPV are in absolute value very similar. Therefore, the sign of the pulse height (opposite or parallel to the scan direction) does not have a significant influence on the electrochemical response.

In previous papers [4,28,29], the striking splitting of the peak-shaped curves for quasireversible processes with small or large values of the transfer coefficient (α) has been described for DDPV and Additive Differential Pulse Voltammetry. In Fig. 6 the appearance of this phenomenon in the different differential pulse techniques is confirmed, which can lead to misinterpretation of experimental data by the unwary electrochemist. This effect is more evident in DDPV and multipulse techniques (Fig. 6a) and it is characteristic of sluggish charge transfer processes with a heterogeneous rate constant of the order $k^0 \sim 10^{-3} - 10^{-4}$ cm/s and $\alpha < 0.3$ for a reduction process and $\alpha > 0.7$ for an oxidation process.

3.2. Equivalence of the differential techniques at microelectrodes

The electrode size is another important factor since it affects the magnitude of the diffusive transport and it is considered in Figs. 7 and 8 for totally irreversible processes. At spherical microelectrodes significant differences are found between double pulse and multipulse modes, the discrepancy diminishing when the electrode radius decreases since the system loses the “memory” of the

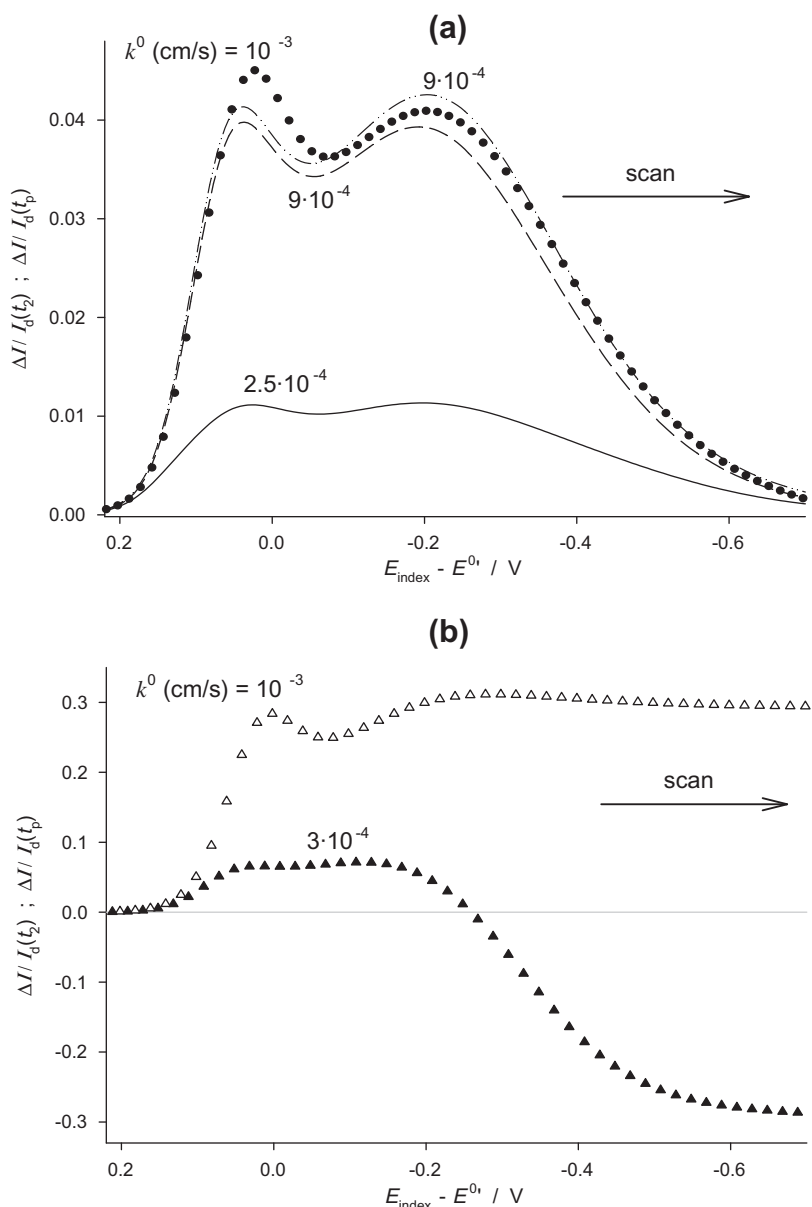


Fig. 6. Splitting of the peak in double pulse and multipulse differential techniques: DDPV (\bullet , $t_1/t_2 = 50$), DDNPV (\blacktriangle , $t_1 = t_2$), DPSWV (\triangle , $t_1 = t_2$), DMPV ($-$, $t_1/t_p = 50$), DNMPV ($- \cdot -$, $t_1 = t_p$) and SWV (\cdots , $t_1 = t_p$). $D \alpha = 0.2$, k^0 values marked on the curves. Planar electrode, $t_2 = t_p = 0.02$ s, $|\Delta E| = 2 \times E_{\text{SWV}} = 50$ mV, $E_s = 5$ mV.

previous pulses while approaching the stationary response. Thus, it is found that the relative difference in the peak current of a given double pulse technique and the corresponding multipulse variant is always smaller than 2% when $r_0 < 0.1\sqrt{\pi D t_1}$. Note that this implies that the attainment of equivalent responses requires the use of smaller electrodes when both pulses are short with similar lengths as in DDNPV and DNMPV (see Fig. 8c) than when the length of the pulse (t_2 , t_p) is much shorter than t_1 as in DDPV and DMPV (see Fig. 7c).

Regarding the splitting of the voltammograms described in Fig. 6, it is found that this is more apparent at planar electrodes, decreasing when diminishing the electrode radius such that it is not observed at microelectrodes.

4. Conclusions

A complete analysis of the most usual differential pulse techniques has been carried out under very different conditions of the electrode kinetics and the electrode size.

Firstly, the disagreement existing about the nomenclature for these techniques has been pointed out, and a new terminology has been proposed in accordance with the pioneering works on this matter.

Two main variants of the differential methods are distinguished in function of that the initial conditions are regained before the application of each double pulse (double pulse techniques) or not (multipulse techniques). The first alternative enables to simplify the theoretical treatment of the problem and to avoid accumulative effects whereas the second one reduces the time of the experiments. It has been found that, in general, the responses of the double pulse and multipulse techniques differ significantly at planar electrodes and conventional spherical electrodes, except in the case of reversible processes with very short pulse durations ($t_1 \gg t_p, t_2$). On the other hand, when microelectrodes are employed with $r_0 < 0.1\sqrt{\pi D t_1}$ the voltammograms are coincident whatever the electrochemical reversibility of the process.

Regarding the sensitivity of the different techniques, it has been shown that the multipulse techniques are more adequate when

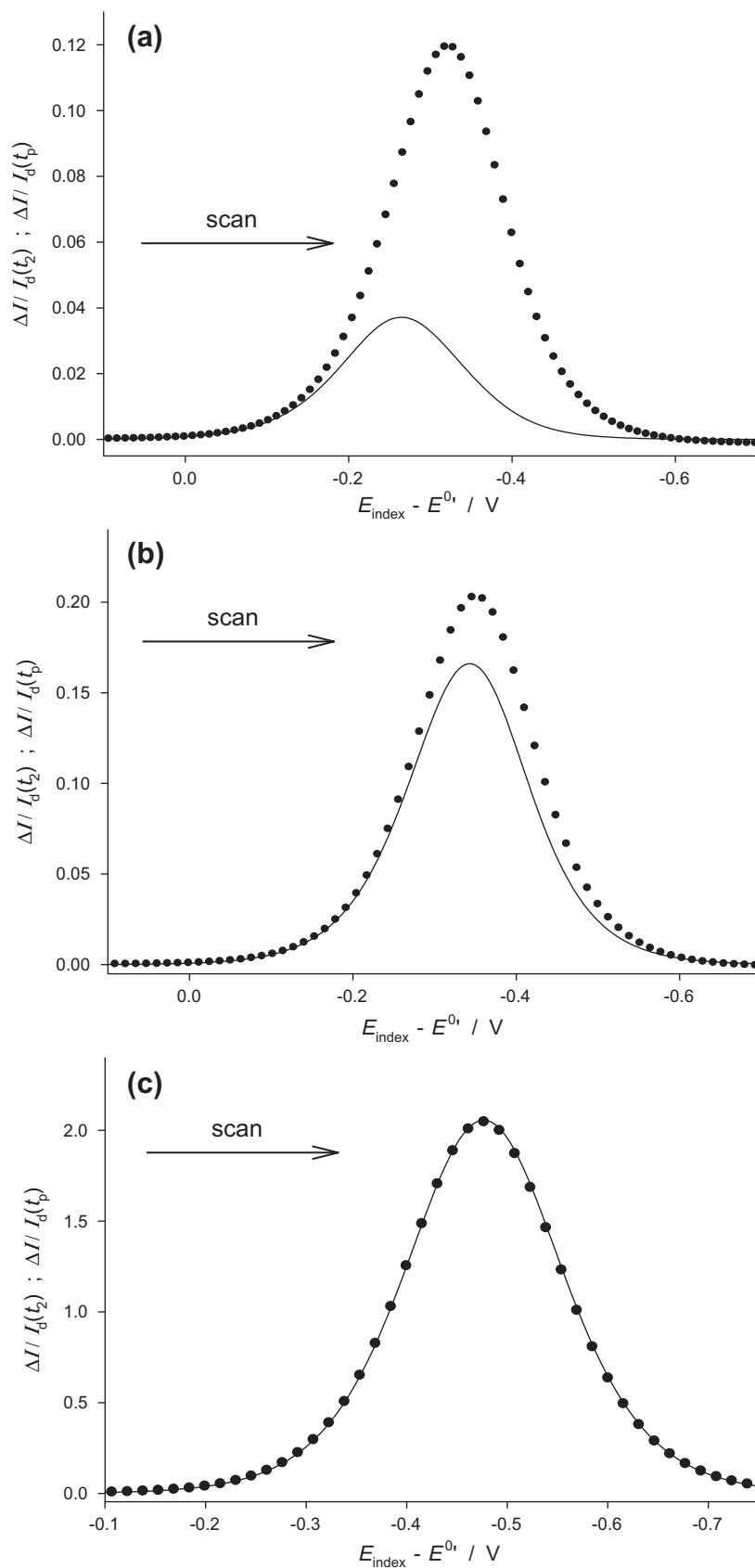


Fig. 7. Comparison between DDPV (●) and DMPV (—) curves for a totally irreversible process ($k^0 = 10^{-5} \text{ cm/s}$, $\alpha = 0.5$) at different electrode sizes: (a) planar electrode, (b) spherical electrode with $r_0 = 30 \mu\text{m}$ and (c) microelectrode with $r_0 = 1 \mu\text{m}$. Other conditions as in Fig. 2.

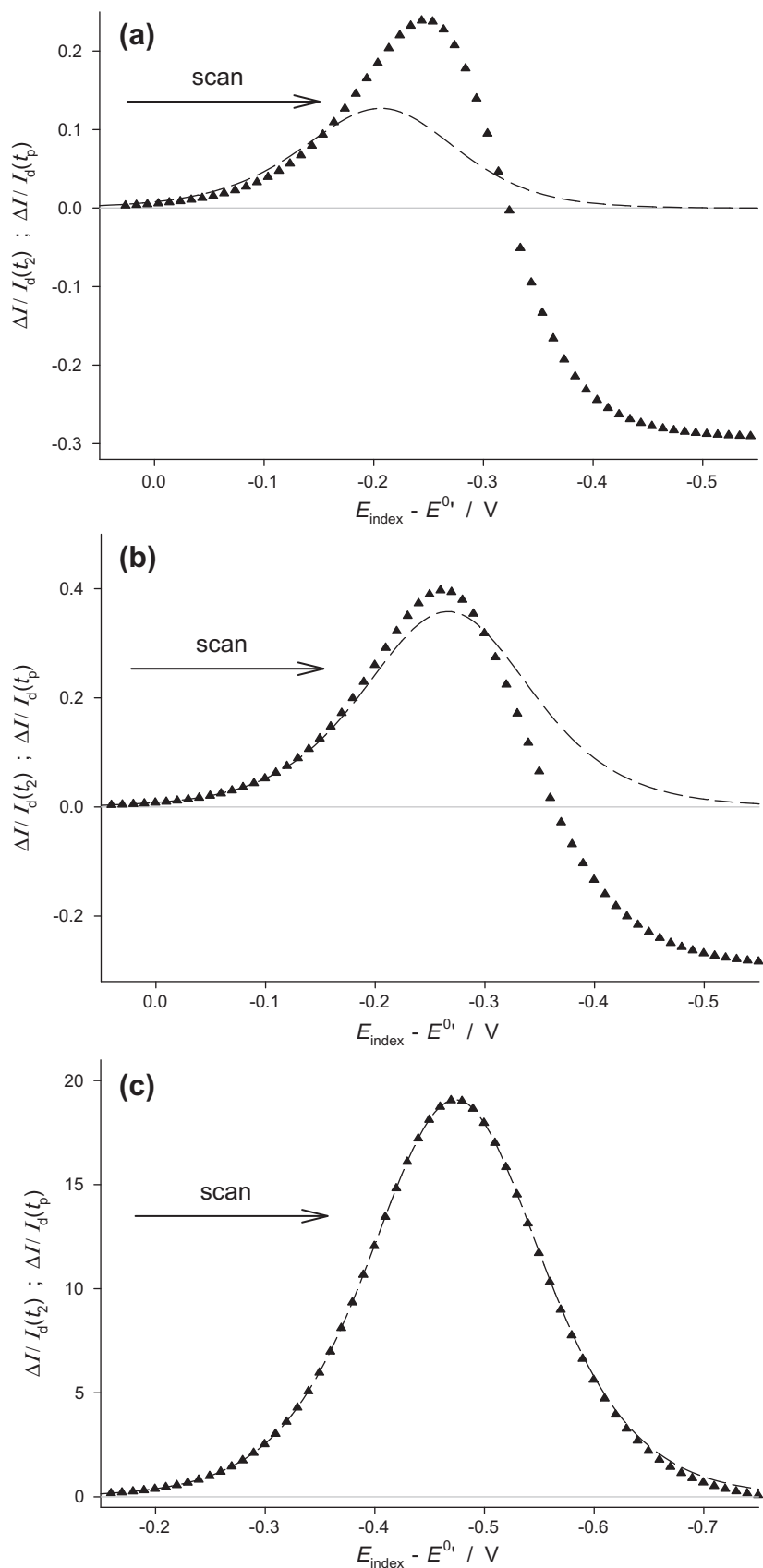


Fig. 8. Comparison of DDNPV (▲) and DNMPV (---) for a totally irreversible process ($k^0 = 10^{-4} \text{ cm/s}$, $\alpha = 0.5$) at different electrode sizes: (a) planar electrode, (b) spherical electrode with $r_0 = 10 \mu\text{m}$ and (c) microelectrode with $r_0 = 0.1 \mu\text{m}$. Other conditions as in Fig. 3.

studying fast charge transfer processes whereas Differential Double Pulse Voltammetry has a greater sensitivity for irreversible ones.

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Appendix A

A.1. Reversible charge transfer processes

A.1.1. Double pulse techniques

Let us consider a reversible electrode process taking place at a stationary spherical electrode:



When a double pulse is applied, the potential is set at a value E_1 during the first interval $0 \leq \tau_1 \leq t_1$, and then ($t \geq t_1$) it is stepped from E_1 to E_2 . The analytical expressions for the current in each pulse are given by [1–3,30]:

$$\frac{I_1^{\text{rev}}}{FADc_0^*} = (1 + c_R^*/c_0^*)Z_1 \left\{ \frac{1}{r_0} + \frac{1}{\sqrt{\pi Dt_1}} \right\} \quad (A2)$$

$$\frac{I_2^{\text{rev}}}{FADc_0^*} = (1 + c_R^*/c_0^*) \left\{ \sum_{n=1}^2 Z_n \left(\frac{1}{\sqrt{\pi Dt_{n2}}} \right) + \left(\frac{1}{1+K_2} - \frac{1}{1+K_0} \right) \frac{1}{r_0} \right\} \quad (A3)$$

where $t_{12} = t_1 + t_2$ and $t_{22} = t_2$ and all the variables and functions are given in Table 1 and Appendix B.

Hence, according to the definition of the double pulse techniques, the signal is obtained from the difference of the currents at the end of each potential pulse ($\Delta I^{\text{rev}} = I_2^{\text{rev}} - I_1^{\text{rev}}$):

$$\frac{\Delta I_{\text{DNPV}}^{\text{rev}}}{FADc_0^*} = (1 + c_R^*/c_0^*) \left\{ Z_2 \left(\frac{1}{r_0} + \frac{1}{\sqrt{\pi Dt_2}} \right) + \frac{1}{\sqrt{\pi D}} Z_1 \left(\frac{1}{\sqrt{t_1 + t_2}} - \frac{1}{\sqrt{t_1}} \right) \right\} \quad (A4)$$

When the second pulse is much shorter than the first one (i.e., in DDPV), the above equation simplifies since it is fulfilled that $t_1 + t_2 \approx t_1$ such that:

$$\frac{\Delta I_{\text{DDPV}}^{\text{rev}}}{FADc_0^*} = (1 + c_R^*/c_0^*) Z_2 \left(\frac{1}{r_0} + \frac{1}{\sqrt{\pi Dt_2}} \right) \quad (A5)$$

A.1.2. Multipulse techniques

Due to the fact that in this case (reversible processes) the surface concentrations are independent of time, the superposition principle applies and from Eq. (A3) we can write the following general expression for the current of the p th pulse [22,31]:

$$\frac{I_p^{\text{rev}}}{FADc_0^*} = (1 + c_R^*/c_0^*) \left\{ \sum_{n=1}^p Z_n \left(\frac{1}{\sqrt{\pi Dt_{np}}} \right) + \left(\frac{1}{1+K_p} - \frac{1}{1+K_0} \right) \frac{1}{r_0} \right\} \quad (A6)$$

where:

$$\left. \begin{aligned} t &= t_{1p} = t_1 + t_2 + \dots + t_{p-1} + t_p \\ t_{np} &= t_p + \sum_{m=n}^{p-1} t_m \\ t_{pp} &\equiv t_p \end{aligned} \right\} \quad (A7)$$

From this general solution, the expressions for the responses in DNMPV and SWV ($\Delta I^{\text{rev}} = I_p^{\text{rev}} - I_{p-1}^{\text{rev}}$) can be immediately obtained:

$$\frac{\Delta I_{\text{DNMPV}}^{\text{rev}}}{FADc_0^*} = (1 + c_R^*/c_0^*) \left\{ Z_p \left(\frac{1}{r_0} + \frac{1}{\sqrt{\pi Dt_p}} \right) + \frac{1}{\sqrt{\pi D}} \sum_{n=1}^{p-1} Z_n \left(\frac{1}{\sqrt{t_{np}}} - \frac{1}{\sqrt{t_{np-1}}} \right) \right\} \quad (A8)$$

In DMPV where the duration of the pulse is much shorter than the period between pulses, $t_1 \gg t_p$, the solution simplifies since it is fulfilled that $t_{np} \approx t_{np-1}$ for $p \gg 1$:

$$\frac{\Delta I_{\text{DMPV}}^{\text{rev}}}{FADc_0^*} = (1 + c_R^*/c_0^*) Z_p \left(\frac{1}{r_0} + \frac{1}{\sqrt{\pi Dt_p}} \right) \quad (A9)$$

Table 1
Definitions.

D	Diffusion coefficient of the electroactive species
$c_i^*, i \equiv O, R$	Bulk concentration of species i
r_0	Radius of the electrode
t_1	– Duration of the first pulse in double pulse techniques – Duration of the period between pulses in multipulse techniques
t_2	Duration of the second pulse in double pulse techniques
t_p	Duration of the pulses in multipulse techniques
k_f, k_b	Heterogeneous rate constants of reduction, oxidation processes
k^0	Standard heterogeneous rate constant
α	Transfer coefficient
$E^{0'}$	Formal potential of the electroactive couple
$E_{\text{eq}} = E^{0'} + \frac{RT}{F} \ln \left(\frac{c_O^*}{c_R^*} \right)$	Equilibrium potential
E_p	Potential applied during the p th pulse
ΔE	Pulse height in DDPV, DDNPV, DPSWV, DMPV and DNMPV
E_{SWV}	Pulse height in SWV
E_s	Staircase step height
$E_{\text{index}} = \frac{E_1 + E_2}{2}$	Index potential of the voltammogram in double pulse techniques: DDPV, DDNPV, DPSWV
$E_{\text{index}} = E_{\text{initial}} - [\text{Int}(\frac{p+1}{2}) - 1]E_s \quad (p \geq 1)$	Index potential of the voltammogram in multipulse techniques:
with: $E_{\text{initial}} = \frac{E_1 + E_2}{2}$	DMPV, DNMPV and SWV (where $\text{Int}(x)$ is the integer part of the argument, x)

A.2. Slow charge transfer processes

A.2.1. Double pulse techniques

In this case we consider a slow charge transfer process at a stationary spherical electrode:



By means of a modification of Koutecký's dimensionless parameter method [4,32], this problem has been solved and the expressions for the currents of the first and second pulses deduced:

$$\frac{I_1^{\text{slow}}}{FADc_0^*} = \frac{(\theta_1 - 1)(1 - c_R^*/c_0^*K_1)}{r_0\theta_1(1 + K_1)} \left[1 + (\theta_1 - 1) \cdot \frac{2F(\chi_1')}{\sqrt{\pi}\chi_1'} \right] \quad (\text{A11})$$

$$\frac{I_2^{\text{slow}}}{FADc_0^*} = \frac{I_1^{\text{slow}}(t_1 + t_2)}{FADc_0^*} + \frac{1}{\sqrt{\pi Dt_2}} \left\{ \left(1 - \frac{1}{\theta_2} \right) S_{\text{irre}}(\chi_1, \chi_2) + \chi_2 \left[\Omega + \frac{\varphi}{\theta_2} \left(\frac{F(\chi_1)}{\chi_1} - \frac{\sqrt{\pi}}{2} \right) \right] \right\} \quad (\text{A12})$$

where all the variables and functions are given in Table 1 and Appendix B. From the above equations, the expressions for the responses in DDNPV and DPSWV are derived:

$$\frac{\Delta_{\text{DDNPV}}^{\text{slow}}}{\Delta_{\text{DPSWV}}^{\text{slow}}} = \frac{1}{\sqrt{\pi Dt_2}} \left\{ \left(1 - \frac{1}{\theta_2} \right) S_{\text{irre}}(\chi_1, \chi_2) + \chi_2 \left[\Omega + \frac{\varphi}{\theta_2} \left(\frac{F(\chi_1)}{\chi_1} - \frac{\sqrt{\pi}}{2} \right) \right] \right\} + \frac{2(\theta_1 - 1)^2(1 - c_R^*/c_0^*K_1)}{\sqrt{\pi r_0\theta_1(1 + K_1)}} \left[\frac{F(\chi_1)}{\chi_1} - \frac{F(\chi_1')}{\chi_1'} \right] \quad (\text{A13})$$

When the second pulse is much shorter than the first one the resolution of the problem greatly simplifies since it can be assumed that the mathematical form of the solutions for the first pulse ($c_0^{(1)}(r, t)$ and $c_R^{(1)}(r, t)$) does not change with the application of the second pulse [4]. Thus, for the DDNPV technique the following simple expression is obtained:

$$\frac{\Delta_{\text{DDNPV}}^{\text{slow}}}{FADc_0^*} = \frac{(\theta_2 - 1)f(\chi_1)}{r_0\theta_2(1 + K_2)} \left[1 + (\theta_2 - 1) \frac{2F(\chi_2)}{\sqrt{\pi}\chi_2} \right] \quad (\text{A14})$$

A.2.2. Multipulse techniques

For charge transfer processes with finite kinetics, the time dependence of the surface concentrations does not allow to apply the superposition principle and therefore it has not been possible to deduce explicit analytical solutions for multipulse techniques.

For this case, we have resorted to numerical methods for the simulation of the response with a homemade program. In this program we have used an exponentially expanding grid with high expansion factors and four-point formulae for the discretisation of the spatial derivatives, which warrants very accurate results (four-figure accuracy) with only eight points in the grid for planar electrodes and 26 points for spherical microelectrodes [33]. Regarding time-integration, we have used the EXTRAP4 algorithm with 5-time intervals in each potential step that has proven to be very adequate for pulse techniques where we are only interested in the response at the end of each potential pulse [34].

According to the above, the method employed gives rise to very accurate results with very fast calculation calculations. In addition, it has the great advantage that a Thomas-like algorithm [35] and the $u-v$ procedure [35,36] for the calculation of surface concentrations can be used, which notably simplifies the resolution of the problem.

Appendix B

Functions and variables.

$$I_d(t) = FAc_0^* \sqrt{\frac{D}{\pi t}} \quad (\text{B1})$$

$$\left. \begin{aligned} K_0 &= \exp\left(\frac{F}{RT}(E_{\text{eq}} - E^{0'})\right) = \frac{c_0^*}{c_R^*} \\ K_p &= \exp\left(\frac{F}{RT}(E_p - E^{0'})\right) \quad (p \geq 1) \end{aligned} \right\} \quad (\text{B2})$$

$$k_s^{\text{micro}} = \frac{k^0 r_0}{D} \quad (\text{B3})$$

$$\theta_1 = 1 + k_s^{\text{micro}} K_1^{-\alpha} (1 + K_1) \quad (\text{B4})$$

$$\theta_2 = 1 + k_s^{\text{micro}} K_2^{-\alpha} (1 + K_2) \quad (\text{B5})$$

$$\chi_2 = \frac{2\sqrt{Dt_2}}{r_0} + 2\sqrt{\frac{t_2}{D}} k^0 K_2^{-\alpha} (1 + K_2) \quad (\text{B6})$$

$$\chi_1 = \frac{2\sqrt{D(t_1 + t_2)}}{r_0} + 2\sqrt{\frac{t_1 + t_2}{D}} k^0 K_1^{-\alpha} (1 + K_1) \quad (\text{B7})$$

$$\chi_1' = \frac{2\sqrt{Dt_1}}{r_0} + 2\sqrt{\frac{t_1}{D}} k^0 K_1^{-\alpha} (1 + K_1) \quad (\text{B8})$$

$$Z_p = \frac{1}{1 + K_p} - \frac{1}{1 + K_{p-1}} \quad (p \geq 1) \quad (\text{B9})$$

$$F(x) = \sum_{i=0}^{\infty} \frac{(-1)^i x^{i+1}}{\prod_{l=0}^i p_l} = \frac{\sqrt{\pi}}{2} x \cdot \exp(x/2)^2 \cdot \text{erfc}(x/2) \quad (\text{B10})$$

$$f(x) = 1 - \frac{c_R^*}{c_0^*} K_2 - \left(1 - \frac{c_R^*}{c_0^*} K_1 \right) \left(\frac{K_2}{K_1} \right)^{\alpha} \left[\frac{\theta_2}{\theta_1} + \left(1 - \frac{\theta_2}{\theta_1} \right) \frac{2F(x)}{\sqrt{\pi}x} \right] \quad (\text{B11})$$

$$\Omega = \frac{r_0 k^0}{\theta_2} (K_2^{-\alpha} - K_1^{-\alpha}) \quad (\text{B12})$$

$$\varphi = r_0 k^0 K_1^{-\alpha} \left(\frac{1}{\theta_1} - \frac{1}{\theta_2} \right) \quad (\text{B13})$$

$$S_{\text{irre}}(\chi_1, \chi_2) = \varepsilon_0 - \frac{2}{\sqrt{\pi}} \frac{\varphi}{\chi_1} \sum_{n=1}^{\infty} \varepsilon_n \quad (\text{B14})$$

$$\varepsilon_0 = F(\chi_2) \left[\Omega - \varphi + \frac{2}{\sqrt{\pi}} \varphi \frac{F(\chi_1)}{\chi_1} \right] \quad (\text{B15})$$

$$\varepsilon_n = \frac{1}{2^n (2n)!!} \left(\frac{1 - \theta_1/\theta_2}{1 + K_1} \right) \left(\frac{\theta_1}{\theta_2} \right)^{2n} \times \left(1 - F(\chi_1) + \sum_{l=1}^{n-1} \frac{(-1)^l 2^l (2l-1)!!}{\chi_1^{2l}} \right) \frac{P_n(\chi_2)}{\chi_1} \quad (\text{B16})$$

$$\left. \begin{aligned} P_1(\chi_2) &= 4\chi_2 \left(1 - \frac{2}{\sqrt{\pi}} \frac{F(\chi_2)}{\chi_2} \right) - \frac{2}{\sqrt{\pi}} \chi_2^2 [2 - F(\chi_2)] \\ P_n(\chi_2) &= 4nP_{n-1}(\chi_2) + \frac{2}{\sqrt{\pi}} \left(\frac{-1}{2n-1} \right) \chi_2^{2n} [2n - (2n-1)F(\chi_2)], \quad n \geq 2 \end{aligned} \right\} \quad (\text{B17})$$

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