

Trapezoidal Cyclic Voltammetry as a Baseline for Determining Reverse Peak Current from Cyclic Voltammograms

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Abstract

Several techniques for determining the reverse peak current from a cyclic voltammogram (CV) for a reversible system are described in the literature: CV itself as a baseline with long switching potential (E_λ) that serves as a baseline for other CVs, Nicholson equation that uses CV parameters to calculation reverse peak current and linear extrapolation of the current obtained at the switching potential. All methods either present experimental difficulties or large errors in the peak current determination. **The paper demonstrates, both theoretically and experimentally, that trapezoidal cyclic voltammetry (TCV) can be used as a baseline to determine anodic peak current (i_{ap}) with high accuracy and with a switching potential shorter than that used by CV, as long as E_λ is at least 130 mV away from the cathodic peak. Beyond this value of switching potential the electroactive specie is completely depleted from the electrode surface. Using TCV with $E_\lambda = 0.34 V$ and a switching time (t_λ) of 240 s as a baseline, the determination of the reverse peak current presents a deviation from the expected value of less than 1% for most of the CVs studied (except cases when E_λ is close to the direct potential peak). This result presents better accuracy than the Nicholson equation and the linear extrapolation of the current measured at the switching potential, in addition to presenting a smaller error than that obtained in the acquisition of the experimental current. Furthermore, determining the reverse peak current by extrapolating the linear fit of i_{ap} vs $\frac{1}{\sqrt{t_\lambda}}$ to infinite time gave a reasonable approximation to the expected value. **Experiments with aqueous potassium hexacyanoferrate (II) and ferrocene in acetonitrile confirmed the theoretical predictions.****

Keywords: Trapezoidal cyclic voltammetry, Reversible system, Baseline, Peak current.

1. Introduction

Cyclic voltammetry (CV) is a versatile technique widely applied in the study of reaction mechanisms, allowing determination of thermodynamic and kinetic parameters. Some applications are: corrosion analysis, determination of catalytic activities of electrodes, study of electrodeposition baths, study of the mechanism of electron transfer reactions, cycling of batteries and supercapacitors, *in vivo* determination of neurotransmitters, among countless other possibilities[1], [2], [3], [4].

There is so many examples about kinetic studies of electron transfer reactions using CV in the literature, because this approach is employed since 50's[5], [6], [7]. However, errors of interpretation and mistaken generalizations of the theory still persist. A relevant example is the determination of the reverse sweep peak current ($i_{p,rev}$), essential for reversibility analysis. Because the reverse sweep begins under transient conditions, the reverse peak current must be measured from the direct current decaying as a baseline. Assuming that the direct current becomes independent of the potential[8], a cyclic voltammetry with higher switching potential (E_λ) can be used as a baseline in a time-base representation of the voltammograms. However, by extending the switching potential until that CV can be used as baseline, secondary reactions can occur in the system under study, making this technique experimentally unfeasible. A practical method commonly used to obtain a baseline consists in graphically constructing a linear extrapolation of the current/potential curve at the beginning of the reverse wave[9]. In addition to the errors inherent to the graphical construction, this method is an oversimplification, as the diffusion limited current is expected to decay linearly with $t^{-1/2}$.

Another strategy proposed in the literature[10], [11], but not commonly adopted, is the use of current values from some regions of the voltammogram, like $(i_{p,rev})_0 -$

reverse peak current without no baseline – and $(i_{sp})_0$ – current measured in the switching potential –, to determine $i_{p,rev}$ using a linear equation. This equation proposed by Nicholson[10] was developed to reversible systems, but is frequently used in non-reversible cases.

The problem to determine the reverse peak current with as little error as possible is commonly studied. Oh and Chang[12] developed a quadratic equation to find the baseline for a reversible system instead of the traditional approaches discussed above.

Trapezoidal cyclic voltammetry (TCV) is a technique known in the literature[13], [14], but it is commonly used for the purpose of accumulating products at a determined potential after carrying out an anodic (or cathodic) scan, before inverting it.

The present paper uses TCV as an alternative for determining the reverse peak current ($i_{p,rev}$) in a simulated reversible one-electron transfer system. The technique was used both as a baseline for traditional cyclic voltammograms and also to evaluate the influence of the switching time on the reverse peak current. [Experimental tests were conducted with aqueous potassium hexacyanoferrate \(II\) and ferrocene in acetonitrile.](#)

2. Methodology

2.1 Computational modeling

Computational modeling of the voltammetric transients was done by solving the diffusion equation for the relevant species in a 1D domain, assuming a linear mass transport regime within a well-supported electrolyte. At the electrode/electrolyte interface, a reversible one-electron transfer was assumed. Consequently, the Nernst equation was used as a boundary condition (Dirichlet type). At the bulk of the electrolyte, the semi-infinite diffusion condition was used. The simulations were performed in COMSOL Multiphysics 5.6 combining two modules: Secondary Current Distribution and Dilute

Species Transport. By using a very high conductivity for the electrolyte, we ensured that the potential drop in the electrolyte was irrelevant. This approach was chosen instead of using the Electroanalytical module, foreseeing additional modifications to the model.

2.2 Experimental

The experimental study examined two distinct systems. The first system comprised 5 mM ferrocyanide in ultrapure water with 1 M KCl as the supporting electrolyte, while the second system consisted of 1 mM ferrocene in HPLC-grade acetonitrile with 0.1 M sodium perchlorate as the supporting electrolyte. All the reagents used are of analytical grade and used as received without further purification. Before the experiments, all solutions were degassed with analytical grade N₂. Background signal was recorded in experiments without the electroactive species.

For both systems, a one-compartment three-electrode cell was utilized, with a 3mm diameter platinum disk serving as the working electrode and a platinum wire as the counter electrode. In the aqueous system, a reference electrode of Ag|AgCl in saturated KCl solution was used, while in the non-aqueous system, a pseudo-reference electrode of Ag in 5mM Ag(NO)₃ solution was used in conjunction with a Luggin capillary. The surface of the working electrode was first degreased with ethanol and then with acetone. It was then polished with 1-micron alumina, rinsed with ultrapure water, and ultrasonicated in acetone and ultrapure water for 2 minutes each.

All voltammetric measurements were performed with a digital Gamry® 600 potentiostat using the surface mode for current acquisition, a 1 mV step potential and positive feedback compensation of ohmic drop. The laboratory temperature was controlled at 22 ± 1 °C. When conducting trapezoidal voltammetry, it is necessary to set a holding time at the switching potential of the triangular cyclic voltammetry. This is done

on Gamry® 600 by setting the hold time at the vertex delay option. To activate this option, the experiment script file was edited and specific lines were uncommented. Cyclic voltammetry was performed for both systems under study at different scan rates. For ferrocyanide, scan rates varied between 0.02 V/s and 0.25 V/s, while for ferrocene, scan rates varied between 0.02 V/s and 0.10 V/s. Then, cyclic voltammetry and trapezoidal voltammetry were performed with a fixed scan rate (0.1 V/s for ferrocyanide and 0.05 V/s for ferrocene), varying the switching potential and the holding time.

Results and Discussion

3.1 Comparison between *simulated CV* and TCV

Considering a one-electron transfer reversible system, being the process represented by $A_{(aq)}^z + e^- \rightleftharpoons B_{(aq)}^{z-1}$, with 1 mM A^z and no B^{z-1} initially present in the system, and considering a linear diffusion with $D_A = D_B = 1 \times 10^{-9} \text{ m}^2\text{s}^{-1}$, $E^0 = 0.5 \text{ V}$, and $T = 298.15 \text{ K}$, two different types of cyclic voltammetry were simulated as shown in Figure 1(a). In TCV, the forward scan is stopped at the switching potential (E_λ)[15] for a certain interval (switching time – t_λ) before the reverse scan begins. Appropriate values for E_λ and t_λ were chosen to make the TCV forward and reverse scans coincide with the CV, i.e., if v is the scan rate:

$$t_\lambda = 2 \frac{|E_{\lambda,CV} - E_{\lambda,TCV}|}{v} \quad (1)$$

Figure 1 (b) shows the equivalent behavior by the two superimposed current/time curves, which can also be demonstrated by the peak potentials and currents listed in Table 1. In both curves, the dimensionless peak current (i_{cp}) in the forward sweep is equal to 0.4463, as expected according to the well-known Randles-Ševčík equation. Furthermore,

the peak-to-peak separation is 57 mV, as expected for a reversible one-electron process, showing that the simulations fully reproduced the reversible behavior. Then, the expected value for the non-dimensional peak current (i_{ap}^*) in the reverse sweep after baseline correction is also 0.4463. This value was used as a reference to calculate the errors in the estimates of i_{ap} with the different baseline corrections discussed in this article.

3.1.1 Trapezoidal cyclic voltammetry as a baseline

Figure 1 and Table 1 demonstrate that there is no need to use a CV with a E_λ very far from the cathodic peak, because it is possible to obtain the same voltametric profile and with a similar value for peak currents and peak potentials using TCV with an E_λ closer to the forward peak potential[8].

Comparison between a CV with a long switching potential ($E_\lambda = -1.50 V$ – approximately 1.9 V away from E_{cp}) and a TCV with E_λ closer to cathodic peak potential can be seen in Figure 2.

Figure 2 demonstrates that using TCV with switching potentials closer to E_{cp} and sufficiently long t_λ values, all trapezoidal voltammograms are equivalent of CV with $E_\lambda = -1.50 V$. Therefore, using TCV is more advantageous because there is no need to extend the potential to very long values, which could make the technique experimentally feasible.

Insert 2(a) shows that TCV and CV are equivalent when $E_\lambda \leq 0.34 V$. For larger E_λ , small discrepancies are observed in the cathodic current decay, which makes unfeasible the use of these voltammograms as a baseline for traditional CVs. In insert 2(b) it can be seen that when the switching potentials are close to E_{cp} , the peak current presents a small decay in the intensity, proving that CV and TCV are not equivalent in these cases.

This different behavior at switching potentials close to E_{cp} can be explained by the consumption of the A^z species on the electrode surface (Figure 3). When the switching potential is very close to the peak, $E_\lambda = 0.44 V$ as example, Figure 3 shows that the species A^z has not yet been fully consumed on the electrode surface, i.e., its concentration has not fallen to zero when E_λ is reached. The same seems to happen to other switching potentials closer to the cathodic peak. This explains the behavior shown by the voltammograms in Figure 2, since the purely diffusional control of the cathodic process has not yet been completely achieved and consequently the anodic current depends on the potential. For $E_\lambda \leq 0.34 V$, the concentration of species A^z is close to zero when the scan reaches the switching potential, proving what was observed in voltammograms in Figure 2.

Thus, TCV with E_λ greater than $0.34 V$ do not fully reproduce the behavior of a traditional CV and, therefore, cannot be used as a baseline for measuring the reverse peak current. However, for switching potentials $130 mV$ beyond the peak potential, there is the possibility of using TCV as a baseline. Table 2 shows the difference between the expected peak current (i_{ap}^*) and the baseline corrected peak current obtained by five different strategies illustrated in Figure 4. In Figure 4a, a cyclic voltammetry with longer E_λ was used as a baseline[8] to obtain $i_{ap,CV}$. Figure 4b presents an equation proposed by Nicholson[10] which was used to calculate $i_{ap,eq}$. Figure 4c illustrate a graphical method, consisting in a linear extrapolation of the current measured at E_λ [9], used to obtain $i_{ap,lin}$. In Figures 4d and 4e two TCVs with different switching potentials, 0.30 and $0.34 V$, and the same switching time, $240 s$, were used as baseline to obtain $i_{ap,TCV0.30V}$ and $i_{ap,TCV0.34V}$, respectively.

Table 2 shows that CV with $E_\lambda = -1.50 V$ can be used as a baseline for higher E_λ values quite satisfactorily, reaching the expected current for the reverse peak, in most

cases. From $E_{\lambda} \geq 0.34 V$, near the cathodic peak current, the error starts to increase, but is still within the instrumental resolution (around 1% of the current scale). In other words, it is the most accurate technique described in the literature. However, as noted previously, it is impractical to extend the potential to such high values.

The errors are more pronounced when Nicholson's equation [10] is used to determine i_{ap} . For example, for the switching potential of $-1.50 V$, the relative error is approximately 5% of the expected value. The reverse peak current that worth highlighting occurs when $E_{\lambda} = 0.30 V$, which is exactly i_{ap}^* .

The limitations of the commonly used graphical method for determining peak reverse current are illustrated in Table 2. When the cyclic voltammetry presents a long switching potential, between -1.50 and $-0.30 V$, the $|i_{ap,lin} - i_{ap}^*|$ is in the third decimal place, the same precision found in experimental acquisition. However, as E_{λ} approaches E_{cp} , but still in a region of diffusional control, the relative error increases up to approximately 30% when compared to the expected value. Above the switching potential of $0.36 V$ is no longer possible to determine the $i_{ap,lin}$ using this method.

When TCV is used as a baseline for traditional cyclic voltammograms, it is worthwhile to note that the reverse peak current for cyclic voltammetry with $E_{\lambda} = -1.50 V$ can be determined, whereas when CV itself is the baseline, it is not possible to measure $i_{ap,CV}$ for this value of switching potential.

The difference of $i_{ap,TCV0.34V}$ from 0.4463 is smaller than that obtained using Nicholson's equation[10] and the extrapolation of a linear baseline[9]., However, using TCV with the switching potential of $0.34 V$ as a baseline technique, the longest CV with $E_{\lambda} = -1.50 V$ as a baseline still presents better results and small errors. When the switching potential of TCV is extended to slightly smaller values ($E_{\lambda} = 0.30 V$, for example), $i_{ap,TCV0.30V}$ obtained is equal to i_{ap}^* for cyclic voltammograms with $E_{\lambda} =$

–1.50 to 0.28 V. After 0.28 V, the difference between the expected and the simulated currents are still present, but smaller than the instrumental resolution.

Thereby, using TCV with $E_{\lambda} = 0.34$ V can be more advantageous, as it reaches a reverse peak current very close to 0.4463 with lower computational cost and with better results than that provided by Nicholson equation[10] or the extrapolation of the linear baseline[9], the most commonly used techniques.

The entire discussion carried out based on the information provided by Figures 2, 3 and 4 and Table 2 shows the need to reverse the scan approximately 130 mV after the cathodic peak potential ($E_{cp} = 0.47$ V). If the scan is reversed using a switching potential less than 130 mV away from E_{cp} , the concentration of the initial species on the electrode surface will not be equal to zero and, therefore, the system will not be governed by a purely diffusional process. The literature[10] shows that the value of E_{λ} adopted must be at least $\pm 60/n$ mV after the peak of the forward sweep to ensure that there is no interference on the reverse peak – the positive signal refers to an anodic sweep and the negative to a cathodic one. This criterion depends on the error considered acceptable. However, the analysis carried out shows that at least twice this value is necessary to guarantee the total consumption of the initial species.

3.1.2 Influence of the switching time in the reverse peak current

The anodic peak current was measured in function of the switching time for several switching potentials using TCV technique and it is represented in Figure 5(a). The relation between i_{ap} and the square root of the switching time is represented in Figure 5(b).

The longer one waits in the switching potential, regardless of the E_{λ} , the anodic peak current tends to approach the expected value of 0.4463, as illustrated by Figure 5(a).

However, when E_λ is closer to the potential peak, as represented by the curve with switching potential at 0.44 V, even with $t_\lambda = 20000$ s, i_{ap} barely approaches the value of 0.42.

Switching potentials lower than 0.34 V present a stabilization in the peak current close to 0.44, which is in the same region and it is consistent with the results presented by Figures 2 and 3, once again highlighting the importance of finishing the entire cathodic process before switching the scan.

According to Cottrell equation[11], the current drops as a function of the inverse square root of time in a system with potentiostatic control, describing the diffusional behavior of the system under these conditions. Then, i_{ap} vs $\frac{1}{\sqrt{t_\lambda}}$ curves were plotted for each E_λ and only the linear region was considered for fitting, as presented in Figure 5(b).

Fittings show that when the switching time tends to infinite, for switching potentials below 0.36 V, limit peak currents (i_{lim}) are close to 0.446. However, for $E_\lambda = 0.44$ and 0.40 V, the limit peak currents are close to 0.423 and 0.442, respectively.

Figure 6 shows the limit peak current (i_{lim}) determined using very long switching times (up to 20000 s), which are experimentally unfeasible, and also determined from smaller t_λ , up to 360 s.

Figure 6 shows that the limit peak current reached is below the expected value at switching potentials close to the peak. As E_λ moves away from the cathodic peak potential, a maximum i_{lim} is reached, 0.4412 at $E_\lambda = 0.34$ V when switching times of up to 360 s are used. For lower E_λ values, a smooth decrease in the limit peak current is observed. When t_λ tends to infinity (demonstrated by the black squares in Figure 6), a limit peak current plateau of approximately 0.4460 is observed in the same switching potential of 0.34 V, the one in which it was determined that all the initial species had already been consumed on the electrode surface.

Thus, it is clear that for infinite switching times, the limit peak current approaches to the expected value using TCV. For shorter switching times, up to 360 s, the difference between the limit current and the expected one is 0.0051 (around 1% difference), that is, smaller associated error than that presented when linear extrapolation is used as a baseline and of the same magnitude order as the equation proposed by Nicholson[10].

3.2 Experimental results

Background-subtracted voltammograms for ferrocyanide and ferrocene at various scan rates are shown in Figures 7a and 7c respectively. The peak current is plotted against the square root of the scan rate in the insets. Both systems show reversible behavior under diffusional control, as expected. For ferrocene, a minor displacement of potential with scan rate is observed, indicating a residual uncompensated resistance. Diffusion coefficients of $5.74 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$ for ferrocyanide and $1.62 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ for ferrocene were calculated using the Randles-Ševčík equation. Both values are in reasonable agreement with literature [16-17].

Figures 7b and 7d show, respectively for ferrocyanide and ferrocene, the background-subtracted current against time for several CV's varying the switching potential. Two TCV's equivalent to the longest CV is also plotted for each system. Holding times were calculated by equation (1) so that each TCV corresponds to the longest CV ($E_\lambda = 0.80 \text{ V}$ for ferrocyanide and $E_\lambda = 0.465 \text{ V}$ for ferrocene). We note the full equivalence between CV and TCV with E_λ at least 130 mV beyond the peak (0.43 V for ferrocyanide and 0.235 V for ferrocene), confirming the theoretical predictions. Then a baseline for all other CVs can be obtained with a lower switching potential. An even lower switching potential could be used depending on the accepted experimental

error. For example, for ferrocene system a TCV with $E_{\lambda} = 0.135 \text{ V}$, i.e. 110 mV beyond the peak, still leads to acceptable results.

In Table 3 we compare the dimensionless peak currents obtained with TCV's serving as a baseline ($i_{cp,TCV}$) with those obtained by linear extrapolation ($i_{cp,lin}$). In the 2nd and 7th columns, we see that $i_{ap} = 0.446 \pm 0.006$ for ferrocyanide and 0.446 ± 0.003 for ferrocene, showing that the measurement is quite reproducible. These values can be used to estimate the error of each method since the system is reversible.

It becomes clear that when employing the extrapolation method, the estimation deteriorates rapidly as the switching potential nears the peak potential.

Using the TCV method allowed estimates to be obtained with an error of around 5% for ferrocyanide and 2% for ferrocene. This shows the applicability of the proposed method. When employing the extrapolation method, to acquire a reliable estimate of the reverse current, the sweep needed to be extended to 0.47 V for ferrocyanide and 0.465 V for ferrocene. However, using the TCV method, more accurate estimates were achieved with switching potentials 60 mV and 330 mV less anodic, thereby circumventing any potential parallel reaction.

3. Conclusion

Trapezoidal cyclic voltammetry can be used as a baseline for traditional cyclic voltammograms for reversible one electron transfer system, as long as the switching potential of the scan is at least 130 mV away from the cathodic peak potential. At a switching potential closer to the cathodic peak, the initial species was not completely consumed before the inversion of the scan and this influences the analysis of the anodic peak current.

The difference between the expected current and that obtained using TCV with switching potential of 0.34 V as a baseline is in the same order of magnitude as the error associated with using CV as a baseline. Besides, TCV is a more accurate technique for the determination of the reverse peak current than the Nicholson equation and using a linear extrapolation starting on E_λ .

The relationship between the anodic peak current and the switching time shows that the longer the time stopped at the switching potential, the closer the current is to the expected value. The i_{lim} obtained when $t_\lambda \rightarrow \infty$ was 0.446 when $E_\lambda \leq 0.34$ V.

The experimental data confirmed the results obtained in the simulation, that is, i) at the switching potentials very close to the direct peak, the inverse peak current becomes a function of the potential because the concentration of the species did not fall to zero, i. e., it is not a completely diffusional system; ii) for ferrocyanide, TCV with $E_\lambda = 0.43$ V is similar to CV with long E_λ (0.80 V) and for ferrocene, TCV with $E_\lambda = 0.235$ V is similar to CV with $E_\lambda = 0.465$ V and both can be used as a baseline, and iii) TCV is more accurate than linear extrapolation for inversion potentials close to 130 mV away from the direct peak.

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