



## A New Accurate Equation for Estimating the Baseline for the Reversal Peak of a Cyclic Voltammogram

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### ABSTRACT

Here we propose a new equation by which we can estimate the baseline for measuring the peak current of the reverse curve in a cyclic voltammogram. A similar equation already exists, but it is a linear algebraic equation that over-simplifies the voltammetric curve and may cause unpredictable errors when calculating the baseline. In our study, we find a quadratic algebraic equation that acceptably reflects the complexity included in a voltammetric curve. The equation is obtained from a laborious numerical analysis of cyclic voltammetry simulations using the finite element method, and not from the closed form of the mathematical equation. This equation is utilized to provide a virtual baseline current for the reverse peak current. We compare the results obtained using the old linear and new quadratic equations with the theoretical values in terms of errors to ascertain the degree to which accuracy is improved by the new equation. Finally, the equations are applied to practical cyclic voltammograms of ferricyanide in order to confirm the improved accuracy.

**Keywords :** Cyclic voltammogram, Theoretical electrochemistry, Finite element simulation

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### 1. Introduction

Cyclic voltammetry is the most useful technique for electrochemical experiments because it can be carried out very easily and the cyclic voltammogram (CV) obtained therefrom includes rich information about the electrochemical reactions that are characterized by the relationship between the potential and the current. Even though the  $i$ - $E$  (current-potential) curve appears monotonic, several important parameters are involved, as shown in the following equation of a reversible faradaic reaction,

$$i_p = 0.4463 \left( \frac{F^3}{RT} \right)^{1/2} n^{3/2} A D_{ox}^{1/2} C_o^* \nu^{1/2} \quad (1)$$

where  $i_p$  is the peak current;  $F$ , the Faraday constant;  $R$ , the gas constant;  $T$ , the temperature;  $n$ , the number of electrons transferred;  $A$ , the electrode area;  $D_{ox}$ , the diffusion coefficient of an oxidized species;  $C_o^*$ , the

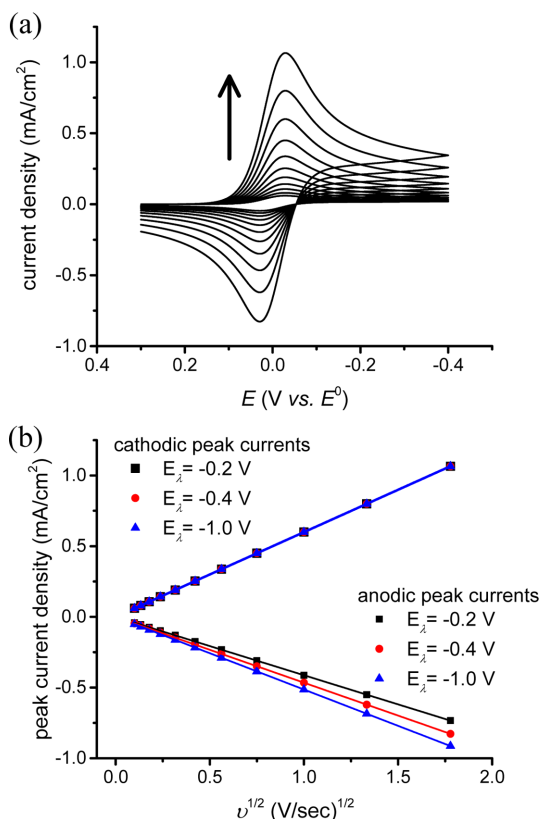
concentration of the oxidized species; and  $\nu$ , the scanrate as conventionally mentioned in a textbook [1].

However, the drawback of such an information-rich and easy to perform technique is the laborious analysis required to resolve the plots that appear simple but are complex in reality. One of the examples is performing the same experiments whilst varying only the scan rate. Fig. 1 shows a good example of finding the diffusion coefficient of an oxidized species ( $D_{ox}$ ) from the slope of the cathodic peak currents in Fig. 1(b) [2]. In the same way,  $\alpha$ ,  $n$ , and bulk concentrations can be evaluated as demonstrated in the literature [3-4].

It is interesting that while the CV comprises forward and reversed potential scans, there are only a few studies on the reverse currents, except for those examining the reversibility of the electrochemical reaction of interest [5]. One of the possible reasons for this is the effect of the switching potential ( $E_\lambda$ ) on the reverse current. Fig. 1(b) compares the anodic peak currents obtained with  $E_\lambda = -0.2$  V,  $-0.4$  V, and -

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**Figure 1.**(a) Simulated cyclic voltammograms with increasing potential scan rates (in the direction of the arrow). Simulation conditions:  $k^0=1.0$  cm/s,  $\alpha = 0.5$ ,  $n=1$ ,  $C_{Ox}=1$  mM,  $C_{Red}=0$  mM,  $D_{Ox}=5\times 10^{-6}$  cm<sup>2</sup>/s, scan rate = 10 mV/s - 3.2 V/s. (b) Plots of cathodic and anodic peak currents of CVs when the switching potentials ( $E_\lambda$ ) are -0.2, -0.4, and -1.0 V vs.  $E^0$ .

1.0 V vs.  $E^0$ , respectively. Even though the forward scans give the same peak current values, the reversal scans do not. Thus, we could speculate that all the plots have strong linear relationships with  $v^{1/2}$ , as seen in eq. (1); yet the exact values of parameters cannot be determined without information that would have to be obtained by conducting other experiments.

Nevertheless, an equation found in the literature [1,6] describes the ratios of the forward and reverse current peaks of a CV. When only the oxidized species (Ox) is present and its cathodic peak current ( $i_{pc}$ ) is generated during the forward linear potential sweep, the reversal anodic peak current ( $i_{pa}$ ) should be measured from the baseline of the decaying curve (refer to  $i_{pa}$  in Fig. 5). A Nernstian wave with stable

products will give  $i_{pa}/i_{pc} = 1$ , regardless of  $E_\lambda$ . However, obtaining a baseline for measuring  $i_{pa}$  is not always possible. In such cases, the baseline can be estimated by the following equation:

$$\frac{i_{pa}}{i_{pc}} = \frac{i_{pa,0}}{i_{pc}} + 0.485 \frac{i_{sp,0}}{i_{pc}} + 0.086 \quad (2)$$

Even though eq. (2) provides a good approximation for measuring the reversal peak current, the linear algebraic equation over-simplifies the voltammetric curve, even if the  $i$ - $E$  curve does not appear linear. This means that the tolerance of deviation should be taken into account.

Here, we propose a new equation that provides more accuracy by describing the current relationships through a quadratic algebraic equation. In order to acquire the equation, CV simulations were carried out by varying the parameters in eqs. (1) and (2), and by numerical analysis with varying currents.

## 2. Experimental Section

### 2.1 Simulation

The finite element method (FEM) was employed to conduct the digital simulation of CVs as has been described elsewhere [7-10]. To summarize, the molecular species Ox and Red and their concentrations  $C_{ox}$  and  $C_{red}$  were digitized as finite elements of distance ( $d$ ) and time ( $t$ ) to form  $C_O(d,t)$  and  $C_R(d,t)$ . For a convenient calculation in MATLAB, they were framed in a 2D-matrix, and re-defined as  $C_O(x,y)$  and  $C_R(x,y)$  [10]. Here,  $x$  and  $y$  are dimensionless parameters defined by  $x = d/\Delta d$ , and  $y = t/\Delta t$ , respectively, as is frequently done in electrochemistry simulations [1,7-10].

On the electrode surface, the balance between the rate of charge transfer and the flux of Ox and Red is calculated by the following equation with  $k_f$  and  $k_b$  as the rate constants of the forward and backward reactions, and  $D_M$ , a dimensionless diffusion coefficient calculated by  $D\Delta t/\Delta x^2$

$$-J(y) = \frac{[k_f C_O(1,y) - k_r C_R(1,y)]}{(1 + k_f/2D_M + k_r/2D_M)} \quad (3)$$

In the bulk solution, Ox and Red molecules diffuse in and out according to the concentration gradient. It is formulated by Fick's laws and calculated in the matrix as shown below:

$$C(x,y+1) = C(x,y) + D_M[C(x+1,y) - 2C(x,y) + C(x+1,y)] \quad (4)$$

Finally, the current was calculated by re-dimensionalizing the flux,  $J(y)$ .

## 2.2 Fitting procedure

The quadratic equation was obtained by fitting the calculated currents to a quadratic equation. The fitting was done by a pre-defined function in Matlab. The code is as follows:

$$P = \text{polyfit}(i_{sp,0}/i_{pc}, i_{pa,0}/i_{pc}, 2).$$

## 2.3 Cyclic voltammetry experiments

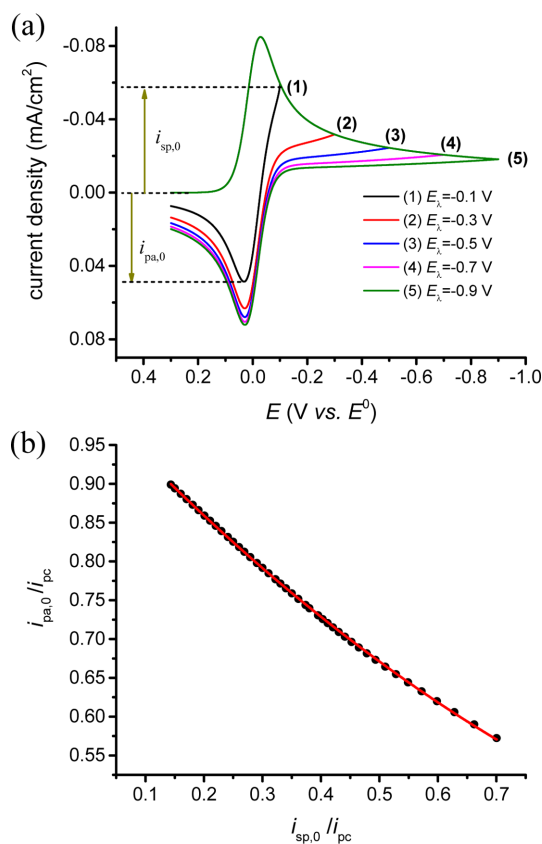
A conventional 3-electrode electrochemical cell was used. The working, counter, and reference electrodes were Au disk, Pt mesh, and Ag|AgCl, respectively. The electrolyte solution consisted of 5 mM ferricyanide (Sigma Aldrich), 100 mM KNO<sub>3</sub> (Sigma Aldrich) as the supporting electrolyte, and doubly distilled water as the solvent. Linear sweep and cyclic voltammetry experiments were carried out using SP200 (Bio-Logic). The voltammograms were recorded vs. a home-made Ag|AgCl reference electrode at a scan rate of 20 mV/sec.

## 3. Results and Discussion

Fig. 2(a) shows the change in the reverse current with switching potential ( $E_\lambda$ ). As  $E_\lambda$  increases (negatively), the currents at  $E_\lambda$  ( $i_{sp,0}$ ) decay downwards along the curve. Meanwhile, the uncorrected anodic peak current ( $i_{pa,0}$ ) increases in the anodic direction. Both  $i_{sp,0}$  and  $i_{pa,0}$  are normalized by the cathodic peak current ( $i_{pc}$ ) and are plotted in Fig. 2(b). Thus, fitting to a quadratic algebraic equation provides a good result.

$$\frac{i_{pa,0}}{i_{pc}} = 0.222\left(\frac{i_{sp,0}}{i_{pc}}\right)^2 - 0.775\left(\frac{i_{sp,0}}{i_{pc}}\right) + 1.005 \quad (5)$$

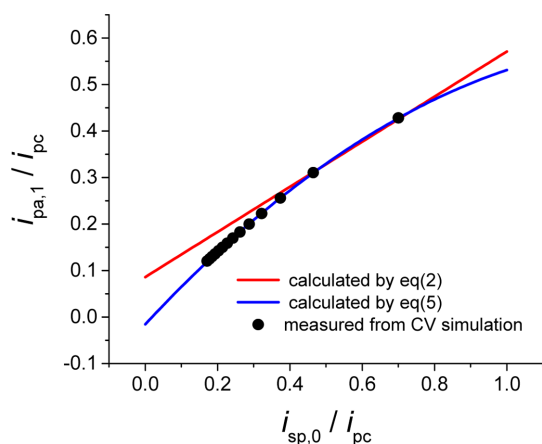
Additional simulations with different diffusion coefficients give the same results. If the baseline at the potential of the anodic peak for measuring  $i_{ap}$  is  $i_{ap,1}$ ,  $i_{ap} = i_{ap,0} + i_{ap,1}$ , then  $i_{ap,0}$  is replaced with  $i_{ap} - i_{ap,1}$  in eq. (5). If products are stable and no additional reaction is involved,  $i_{pa}/i_{pc} = 1$ , regardless of  $E_\lambda$ . Finally, we reach an equation that can calculate the virtual baseline current ( $i_{ap,1}$ ) from the current at the



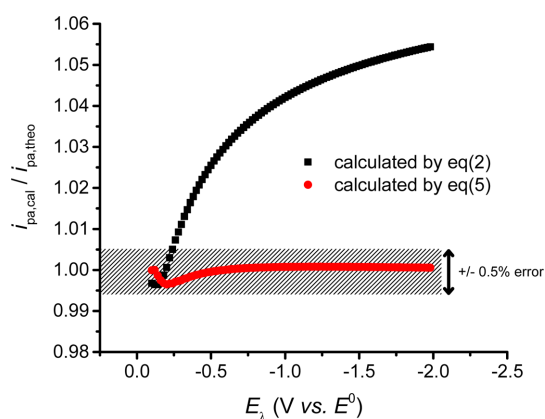
**Figure 2.**(a) Simulated cyclic voltammograms with increasing  $E_\lambda$  from -0.1 to -0.9 V vs.  $E^0$ . The definitions of  $i_{sp,0}$  and  $i_{pa,0}$  are graphically presented for easy understanding. (b) Plots of  $i_{sp,0}$  and  $i_{pa,0}$  (normalized by  $i_{pc}$ ) are fitted to a quadratic equation (red solid line) by eq. (5).

switching potential ( $i_{sp,0}$ ), irrespective of when the potential scan is reversed, as long as the current decays sufficiently, which is assumed to be around 70 % of the peak current of the forward sweep.

The new equation is compared with the existing one, eq. (2). Fig. 3 shows the baseline currents calculated according to  $i_{sp,0}/i_{pc}$  changing from 0.70 to 0.00. In a real system, the potential sweep can be applied within a range of -2 V to +2 V vs.  $E^0$  in order to avoid interfering with faradaic reactions such as electrolysis of the solvent. Thus, we can practically consider the variance of  $i_{sp,0}/i_{pc}$  from 0.14 to 0.70. In the figure, the calculated values by both equations are almost in agreement with each other for  $i_{sp,0}/i_{pc}$  from 0.45 to 0.70 which corresponds to 210 mV to 100 mV away from  $E^0$ . However, when the potential



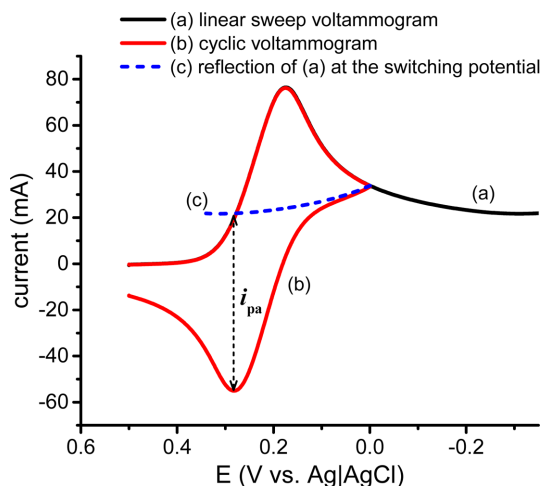
**Figure 3.** The red and blue lines are calculated by eq. (2) and (5), respectively, with  $i_{sp,0}$  changing from 0.0 to 1.0. The filled circles are obtained from the CV simulations by increasing  $E_{\lambda}$  from -0.1 to -2.0 V vs.  $E^0$ .



**Figure 4.**  $i_{pa,eq(2)}$  and  $i_{pa,eq(5)}$  are  $i_{pa}$  measured from the baseline currents calculated by eqs. (2) and (5) are normalized by  $i_{pa,theo}$ . They are plotted along the values of  $E_{\lambda}$ . The shaded zone covers  $\pm 0.5\%$  of relative error from the true value (1.00).

shifts further, the old formula deviates from the theoretical values while the new one does not. Therefore, the new equation is confirmed to provide more accurate virtual baseline currents for measuring the anodic peak current.

The anodic peak current estimated using the equations are compared with those measured using theoretically simulated cyclic voltammograms. Fig. 4 plots the values of  $i_{pa,eq(2)}/i_{pa}$  and  $i_{pa,eq(5)}/i_{pa}$ . Here,  $i_{pa,eq(2)}$  and  $i_{pa,eq(5)}$  are the estimated values using eqs.



**Figure 5.** (a) A linear sweeping voltammogram and (b) a cyclic voltammogram in an aqueous solution of 5.0 mM ferricyanide at a scan rate of 20 mV/s. (c) a baseline curve made by the mirror image of curve (a) around  $E_{\lambda}$  of curve (b).  $i_{pa}$  is measured from the baseline curve to the uncorrected peak current as shown by the arrow.

(2) and (5), respectively, and  $i_{pa}$  is the theoretical value. In other words, the estimated currents are normalized by the theoretical currents. Both equations provide good approximations, but when the overpotential increases, eq. (2) shows an increasing deviation from the theoretical values. Meanwhile, eq. (5) keeps  $i_{pa,eq(5)}/i_{pa} = 1$  even though the potential increases within the tolerance at less than  $\pm 0.5\%$ . This confirms that the new equation provides a more accurate baseline for measuring the peak current of the reverse scanning curve.

A practical application of this method is demonstrated with an aqueous solution of ferricyanide and the experimental results are shown in Fig. 5. Curve (a) is made by a linear sweep of potential from 0.30 to -0.35 V vs. Ag|AgCl and curve (b) is recorded with a cyclic potential scan switched at 0.00 V vs. Ag|AgCl. Curve (c) is the baseline current extracted from the current of curve (a) decaying continuously from the switching potential of curve (b). It is observed that until the potential reaches the switching potential (0.00 V), curves (a) and (c) are identical, which confirms the validity of curve (c) as a baseline for curve (b), though it is estimated from curve (a). Eventually, the value of  $i_{pa}/i_{pc}$  is measured to be 1.008 which is slightly higher than the ideal value of

1.000 for a reversible faradaic reaction. At the same time, the value of  $i_{pa}/i_{pc}$  is measured with the virtual baseline current to be 1.007 which is almost the same as the measured one. Both values have < 1% error and the error may be caused by the non-faradaic current such as the charging current for the electric double layer. On the other hand, the old equation calculates 1.014 which is very close to 1.007 but not as accurate as 1.008.

#### 4. Conclusion

We have explained how a new equation was developed from CV simulations and confirmed its validity with experimental results. The new equation describes that the currents at the scan-switching potential and the reversal peak potential are related to each other through a quadratic algebraic equation, providing a virtual baseline current for correcting the measured peak current to a true value. Both simulation and experimental results confirm that the correction is quite accurate; the error is less than  $\pm 0.5\%$ .

The proposed method will be successfully applied to cases where making a baseline is impossible because a high over-potential may activate interfering reactions such as the electrolysis of solvents or supporting electrolytes. In those cases, the potential sweep should be switched back to an appropriate potential; even then acquisition of the baseline current curve by the further potential may become experimentally impossible. At such moments, our

equation can provide a virtual baseline to approximate the *true* reversal peak current. Our proposed method is expected to be valuably utilized in such restricted experimental conditions.

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