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Theory of square-wave voltammetry of two-step electrode reaction using an inverse scan direction

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ABSTRACT

A theory of square-wave voltammetry of two-step electrode reaction with kinetically controlled electron transfers is developed and a special case of thermodynamically unstable intermediate is analyzed. If the first reaction step is reversible and the second one is quasireversible, the response splits into two peaks if the scan direction is inverted. The separation of these peaks increases with frequency.

KEYWORDS

Square-wave voltammetry;
Two-step electrode reaction;
Theory of quasireversible EE mechanism.

INTRODUCTION

In square-wave voltammetry (SWV) it is usual that only the reactant is initially present in the solution and that at the starting potential no electrode reaction occurs[1-3]. However, there is a variation of SWV in which the measurement starts at the potential at which the electrode reaction is controlled by the diffusion of reactant and the scan direction is reversed comparing to the classical SWV[4-6]. This inverse mode was used for the determination of kinetic parameters of electrode reactions[7-10]. In the present communication it is demonstrated that the inverse SWV can be used for the identification of quasireversible two-step electrode reaction with thermodynamically unstable intermediate. It is well known that the response of this type of mechanism depends on standard rate constants and transfer coefficients of both electrons[11-14]. If the second charge transfer is slower than the first one, the response may consist of a single two-electron voltammetric peak at the lowest square-wave frequency and of two peaks at the highest frequency. Nevertheless, there are only a limited number of reactions that can undergo such transformation within the available range of frequencies. It is shown here that in many of other cases the separation of the response into two peaks can be obtained by inverting the scan direction in SWV.

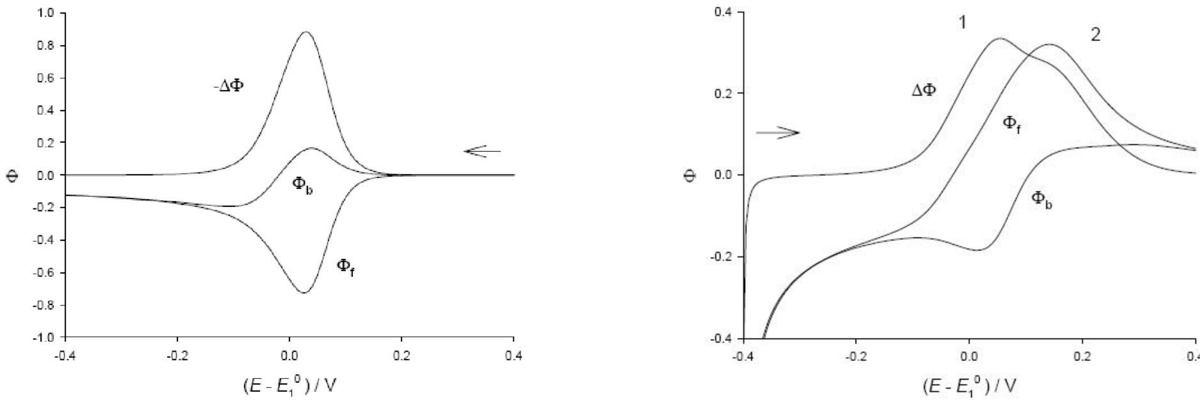
THE MODEL

An electrode reaction that occurs through two consecutive steps is analyzed:

$$\mathbf{OX^{(m+2)+} + e^- \leftrightarrows Int^{(m+1)+} \; (E^0_1, \alpha_1, k_{s1})} \quad \mathbf{(1)}$$

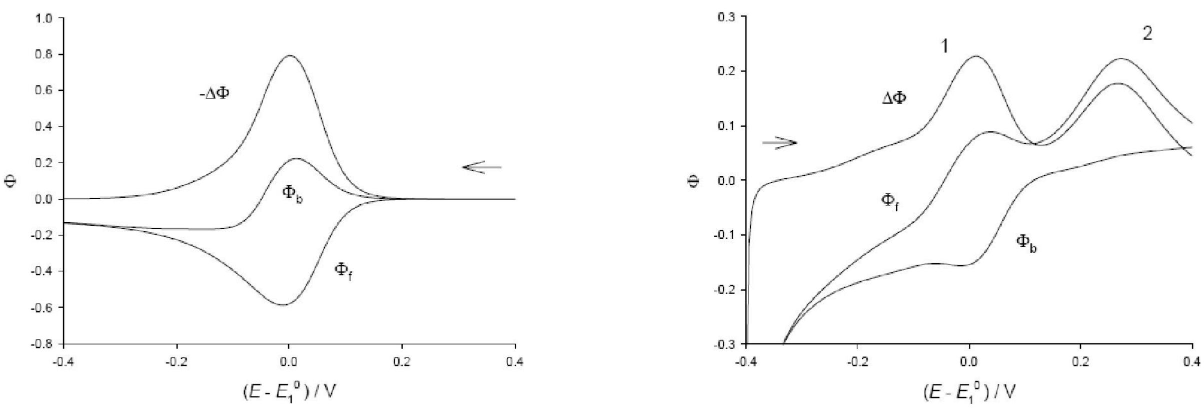
$$\mathbf{Int^{(m+1)+} + e^- \leftrightarrows Red^{m+} \; (E^0_2, \alpha_2, k_{s2})} \quad \mathbf{(2)}$$

The symbols E^0_i, a_i, and k_{si} stay for the standard



(1A) **(1B)**

Figure 1 : Theoretical square-wave voltammograms of two-step electrode reaction (1) and (2). E^0_2-E^0_1 = 0.1 V, c^*_{ox}/c^*_{tot} = 1, c^*_{Int} = 0, c^*_{Red} = 0, $ë_1$ = 100, l_2 = 0.1, a_1 = 0.5, a_2 = 0.5, E_{sw} = 50 mV, $|dE|$ = 5 mV and $E_{st} - E^0_1$ = 0.4 V (A) and -0.4 V (B). A dimensionless net current (DF) and its forward (F_f) and backward (F_b) components are shown



(2A) **(2B)**

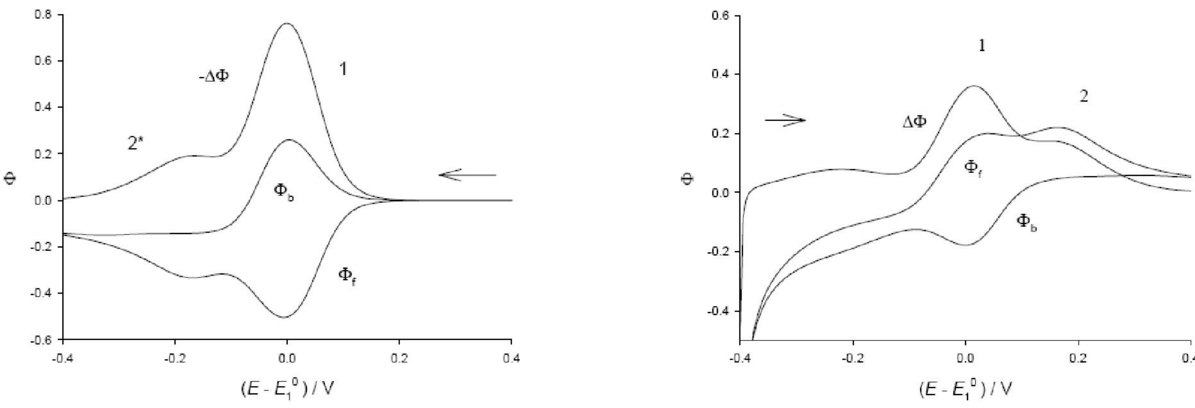
Figure 2 : SWV of electrode reactions (1) and (2); $ë_1$ = 10, $ë_2$ = 0.01 and E_{st} - E^0_1 = 0.4 V (A) and -0.4 V (B). All other data are as in figure 1

potential, the transfer coefficient and the standard rate constant of the first (i = 1) and the second (i = 2) electron transfer step, and m = 0, 1, 2 or 3. It is supposed that all three redox species may be initially present in the solution. For the mass transfer realized by the planar, semi-infinite diffusion, the system of differential equations and its solution are reported in the Appendix.

RESULTS AND DISCUSSION

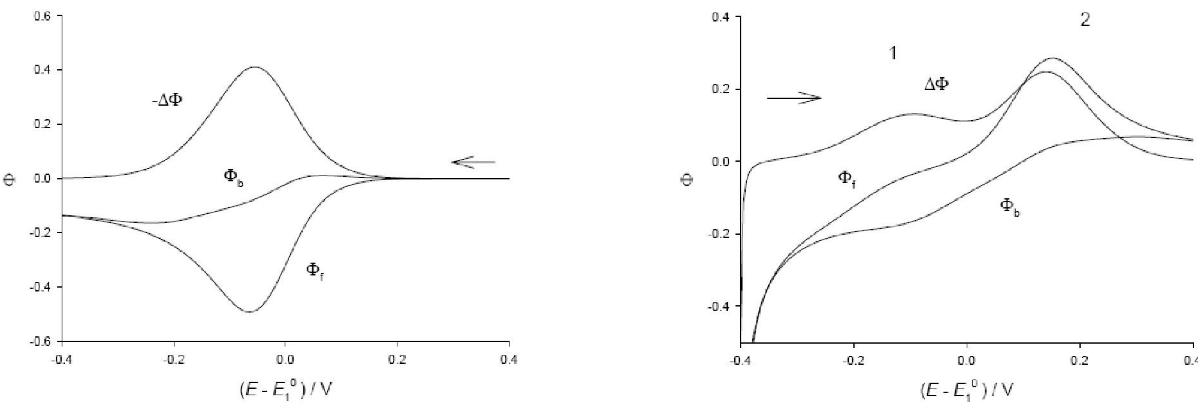
Square-wave voltammogram of fast and reversible two-step electrode reaction depends on standard potentials of individual electron transfers. If $E^0_2 - E^0_1$ ∆≥ 0.3 V, E_{st} - E^0_1 = 0.4 V, E_{sw} = 50 mV and dE = -5 mV, the response is a single peak appearing at the potential $(E^0_2 - E^0_1)/2$. Its dimensionless net peak current DF$\sqrt{_p}$ = $DI_p(FSC^*_{tot})^{-1}(Df)^{-1/2}$ is equal to 1.9115. The voltammograms start to split into two peaks if $E^0_2 - E^0_1$ < -0.1 V. For $E^0_2 - E^0_1$ < -0.3 V and the SWV parameters as above, the response consists of two peaks characterized by $DF_{p,1} = DF_{p,2}$ = 0.752, $E_{p,1} = E^0_1$ and $E_{p,2} = E^0_2$. The voltammograms of kinetically controlled electrode reactions are generally smaller and depend on the dimensionless kinetic parameter $l = k_s(Df)^{-1/2}$. The reaction appears quasireversible if 1 > l > 0.03[1].

Figure 1 shows SWV response of two-step electrode reaction in which the first charge transfer is reversible (l_1 = 100) and the second one is quasireversible (l_2 = 0.1). If the starting potential is 0.4 V and the scan is directed towards lower potentials, a negative value of dimensionless net current is in maximum at 0.030 V *vs*. E^0_1, which is close to the median potential $(E^0_1 - E^0_2)/2$ / 2 = 0.050 V. The potential of minimum of the forward, reductive component and the potential of maxi-



(3A) (3B)

Figure 3 : SWV of reactions (1) and (2). E^0_2-E^0_1, ë$_1$ = 10, ë$_2$ = 0.01 and E_{st} - E^0_1 = 0.4 V (A) and -0.4 V (B). All other data are as in figure 1



(4A) (4B)

Figure 4 : SWV of reactions (1) and (2). ë$_1$ = 0.1, ë$_2$ = 0.1 and E_{st} - E^0_1 = 0.4 V (A) and -0.4 V (B). All other data are as in figure 1

mum of the backward, oxidative component are 0.025 V and 0.040 V, respectively. If, however, the starting potential is -0.4 V and the scan direction is positive, the net current exhibits a shoulder at about 0.15 V and the potential of maximum of the forward, oxidative component is 0.140 V. The peak potentials of the net response and its backward component are 0.055 V and 0.015 V, respectively. The difference in voltammograms shown in figure 1A and 1B is the consequence of the kinetics of electrode reaction. If both electron transfers are reversible (l_1 = 1000 and l_2 = 1) the influence of the starting potential is negligible and the voltammograms are similar to the one in figure 1A: E_p = 0.055 V, $E_{p,f}$ = 0.060 V and $E_{p,b}$ = 0.045 V, for E_{st} = 0.4 V, and E_p = 0.065 V, $E_{p,f}$ = 0.065 V and $E_{p,b}$ = 0.060 V for E_{st} = -0.4 V. Furthermore, the response of two-step reaction consisting of reversible charge transfer (λ_1 = 10) and irreversible one (λ_2 = 0.01) is split into two peaks if E_{st} = -0.4 V, but not if E_{st} = 0.4 V. This is shown in figure 2. In the case of negative scan direction, a single peak appears with the following peak potentials: E_p = 0.000 V, $E_{p,f}$ = -0.010 V and $E_{p,b}$ = 0.015 V. The potentials of maxima of the split response are 0.015 V and 0.265 V. The forward component consists of two peaks, at 0.040 V and 0.275 V, but the backward component exhibits only one minimum at -0.015 V. There is a linear relationship between the second peak potential and the reciprocal of the transfer coefficient of the product oxidation: $E_{p,2}$ /$(1-\alpha_2)^{-1}$ = 0.09 V. Also, the second peak potential depends linearly on the logarithm of the second dimensionless kinetic parameter: $E_{p,2}$/log λ_2 = -2.3RT / $(1-\alpha_2)$F. These indicate that the second peak in figure 2B originates from totally irreversible oxidation of the product of the second step: $Red^{m+} \rightarrow Int^{(m+1)+} + e^-$. This product is created at potentials lower than -0.2 V by irreversible reduction of intermediate. The separation between reduction and oxidation processes in the second electrode reaction can be estimated from the difference between the second peak potential and the second standard potential: $E_{p,2}$ - E^0_2 = 0.165 V. So, the reduction peak can be expected at -0.065 V vs. E^0_1, where it is covered by the response of the first electrode reaction. This explanation was confirmed by the simulation for l_1 = 1 and l_2 = 0.001. If E_{st} = -0.4 V the second peak potential was 0.385 V, which meant that $E_{p,2}$ - E^0_2 = 0.285 V and that the reduction peak had to be expected at -0.185 V. Indeed, if E_{st} = 0.4 V, the response was split in two peaks with maxima at -0.005 V and -0.185 V. The second peak was ascribed to irreversible reduction of the intermediate. Additional support was obtained by the variation of the second standard potential. If the second reaction step was quasireversible (l_2 = 0.1 and l_1 = 100), and $E^0_2 – E^0_1$ ≥0.15 V, the shoulder shown in figure 1B was developed as a separate peak and its peak potential depended linearly on the difference between standard potentials: $E_{p,2}$ = E^0_2 + 0.040 V vs. E^0_1. Also, if E^0_2 – E^0_1 ≤ 0.05 V, the shoulder disappeared. In the case of irreversible second reaction ($ë_2$ = 0.01 and $ë_1$ = 10) the separation between cathodic and anodic peaks of the second electrode reaction was 0.230 V and they both appeared in voltammograms if $E^0_2 – E^0_1$. This is shown in figure 3. The peak potentials in this figure are the following: $E_{p,1}$ = 0.000 V and $E_{p,2*}$ = -0.165 V, for E_{st} = 0.4 V, and $E_{p,1}$ = 0.015 V and $E_{p,2}$ = 0.165 V for E_{st} = -0.4 V. If $E^0_2 – E^0_1$ = 0.05 V, the cathodic peak 2* merges with the peak 1 and appears as a shoulder at about -0.1 V. This is a transition to the response shown in figure 2. The change of responses shown in figure 1B and 2B can be achieved by the variation of square-wave frequency. The parameter l is diminished ten times if the frequency is increased hundred times.

The influence of the kinetics of the first electrode transfer is shown in figure 4. If both reaction steps are equally fast and quasireversible ($l_1 = l_2$ = 0.1) and E_{st} = 0.4 V, the SWV response is a single peak with the maximum at -0.055 V. The resolution of the reaction steps can be achieved by inverting the scan direction, as can be seen in figure 4B. Under this condition the voltammogram consists of two peaks with maxima at -0.093 V and 0.140 V, respectively. The second peak potential is equal to the potential of maximum of the forward component of the response shown in Fig. 1B. So, the second peak, originating from the second reaction step, is independent of the kinetics of the first reaction step, but the separation between two peaks is better in figure 4B than in Fig. 1B because of the quasireversible nature of the first reaction step in figuer 4B.

CONCLUSIONS

These results show that individual electron transfers of two-step electrode reaction with thermodynamically unstable intermediate can be resolved by square-wave voltammetry with inverse scan direction. The method applies to the combination of reversible and quasireversible, or two quasireversible steps. If the second charge transfer is irreversible, the second peak potential is a linear function of the logarithm of square-wave frequency, with the slope:

$E_{p,2}$ / log f = 2.3×RT / 2(1 – a_2)F.

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APPENDIX

For the electrode reactions (1) and (2), under the conditions of the planar, semi-infinite diffusion, the following system of differential equations has to be solved:

$$\frac{\partial cox}{\partial t} = D\frac{\partial^2 cox}{\partial x^2} \quad \text{(A1)}$$

$$\frac{\partial c\,Int}{\partial t} = D\frac{\partial^2 c\,Int}{\partial x^2} \quad \text{(A2)}$$

$$\frac{\partial c_{Red}}{\partial t} = D\frac{\partial c_{Red}}{\partial x^2} \quad \text{(A3)}$$

$$t=0,\ x\geq 0:\ c_{ox} = c^*_{ox},\ c_{Int} = c^*_{Int},\ c_{Red} = c^*_{Red},\ c^*_{ox} + c^*_{Int} + c^*_{Red} = c^*_{tot} \quad \text{(A4)}$$

$$t>0,\ x\to\infty:\ c_{ox} \to x^*_{ox},\ c_{Int} \to c^*_{Int},\ c_{Red} \to c^*_{Red} \quad \text{(A5)}$$

$$x = 0: D\left(\frac{\partial c_{ox}}{\partial x}\right)_{x=0} = -\frac{l_1}{FS} \quad \text{(A6)}$$

$$D\left(\frac{\partial c_{Int}}{\partial x}\right)_{x=0} = \frac{l_1 - l_2}{FS} \quad \text{(A7)}$$

$$D\left(\frac{\partial c_{Red}}{\partial x}\right)_{x=0} = \frac{I_2}{FS} \quad \text{(A8)}$$

$$I_1/FS = -k_{s1}\exp(-a_1 f_1)[(c_{ox})_{x=0} - (c_{Int})_{x=0}\exp(f_1)] \quad \text{(A9)}$$

$$I_2/FS = -k_{s2}\exp(-a_2 f_2)[(c_{Int})_{x=0} - (c_{Red})_{x=0}\exp(f_2)] \quad \text{(A10)}$$

$$f_1 = F/RT\,(E-E^0_1) \quad \text{(A11)}$$

$$f_2 = F/RT\,(E-E^0_2) \quad \text{(A12)}$$

The meanings of symbols are as follows: c_{ox}, c_{Int} and c_{Red} are concentrations of species $Ox^{(m+2)+}$, $Int^{(m+1)+}$ and Red^{m+}, respectively, c^*_{ox}, c^*_{Int} and c^*_{Red} are concentrations of these species in the bulk of solution, D is a common diffusion coefficient, I_1 and I_2 are currents, S is electrode surface area and t, x, T, R and F have their usual meanings. Differential equations (A1) – (A3) are solved by Laplace transformation and by the method of numerical integration proposed by Olmstead and Nicholson[15]. The solution is the system of recursive formulae for the dimensionless current $f_i = Ii(FSc^*_{tot})^{-1}(Df)^{-1/2}$, where i = 1 or 2 and f is square-wave frequency. Note that $F = F_1 + F_2$. Each square-wave half-period is divided into 25 time increments. It is assumed that within each time increment the function I_i can be replaced by the average value $I_{i,j}$.

$$\Phi_{1,m} = Z\left[\frac{-5c^*_{ox}\sqrt{\pi}}{\exp(\phi_{1,m})c^*_{tot}\sqrt{2}} + \frac{c^*_{Int}P}{c^*_{tot}} + \frac{c^*_{Red}Q}{c^*_{tot}} + V\sum_{j=1}^{m-1}\Phi_{1,j}S_{m-j+1} + W\sum_{j=1}^{m-1}\Phi_{2,j}S_{m-j+1}\right] \quad \text{(A13)}$$

$$\Phi_{2,m} = \Phi_{1,m}\left[\frac{5\sqrt{\pi}\exp(-(1-\alpha_1)\phi_{1,m})}{\lambda_1\sqrt{2}} + (1+\exp(-\phi_{1,m}))\right] + \frac{5c^*_{ox}\sqrt{\pi}}{\exp(\phi_{1,m})c^*_{tot}\sqrt{2}} - \frac{5c^*_{Int}\sqrt{\pi}}{c^*_{tot}\sqrt{2}} + (1+\exp(\phi_{1,m}))\exp(-\phi_{1,m})$$

$$\sum_{j=1}^{m-1}\phi_{1,j}S_{m-j+1} - \sum_{j=1}^{m-1}\phi_{2,j}S_{m-j+1} \quad \text{(A14)}$$

$$Z = N^{-1}l_1\exp((1-a_1)f_{1,m})\sqrt{2}[5\sqrt{p} + l_2\exp(-a_2 f_{2,m})(1+\exp(f_{2,m}))\sqrt{2} \quad \text{(A15)}$$

$$N = [5\sqrt{p} + l_1\exp(-a_1 f_{1,m})(1+\exp(f_{1,m}))\sqrt{2}][5\sqrt{p} + l_2\exp(-a_2 f_{2,m})(1+\exp(f_{2,m}))\sqrt{2}] - 2l_1 l_2\exp((1-a_1)f_{1,m})\exp(-a_2 f_{2,m}) \quad \text{(A16)}$$

$$P = \frac{25\pi + 5\lambda_2\sqrt{2\pi}\exp((1-\alpha_2)\phi_{2,m})}{5\sqrt{2\pi} + 2\lambda_2\exp(-\alpha_2\phi_{2,m})(1+\exp(\phi_{2,m}))} \quad \text{(A17)}$$

$$Q = \frac{5\sqrt{\pi}\lambda_2\exp((1-\alpha_2)\phi_{2,m})}{5\sqrt{\pi} + \lambda_2\sqrt{2}\exp(-\alpha_2\phi_{2,m})(1+\exp(\phi_{2,m}))} \quad \text{(A18)}$$

$$V = [-(1+\exp(f_{1,m}))5\sqrt{p} - l_2\sqrt{2}\exp(-a_2 f_{2,m}) - l_2\sqrt{2}(1+\exp(f_{1,m}))\exp((1-a_2)f_{2,m})][5\sqrt{p} + l_2\sqrt{2}\exp(-a_2 f_{2,m})(1+\exp(f_{2,m}))]^{-1}\exp(-f_{1,m}) \quad \text{(A19)}$$

$$W = \frac{5\sqrt{\pi}}{5\sqrt{\pi + \lambda_2\sqrt{2}\exp(-\alpha_2\phi_{2,m})(1+\exp(\phi_{2,m})}} \quad \text{(A20)}$$

$$l_i = k_{s,i}(Df)^{-1/2}\ (i = 1, 2) \quad \text{(A21)}$$

Here $Sk = \sqrt{k} - \sqrt{k-1}$, $1 \le m \le M$, $M = 50\,(E_{start} - E_{final}) / dE$ and dE = 5 mV is the step increment of square-wave signal. In all calculations the square-wave amplitude E_{sw} = 50 mV was used.

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