Effect of the chemical reaction rate to the features of square-wave voltammograms of a “CrevErev” mechanism

Rubin Gulaboski

Faculty of Medical Sciences, Goce Delcev University, Stip, Macedonia

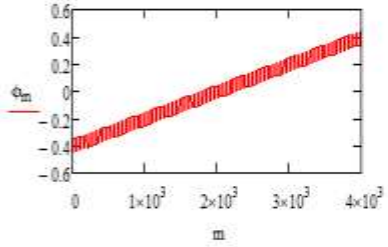
Abstract: The electrochemical diffusional mechanism coupled with reversible homogeneous chemical reaction (CrevErev mechanism) is considered theoretically under condition of square-wave voltammetry. In this experimental data set, we present a MATHCAD simulation protocol of this important electrochemical mechanism. It is of outmost importance to understand how the chemical rate affects the features of simulated voltammetric patterns for different magnitudes of equilibrium constant of chemical step (Keq). MATHCAD file provides is free and ready to use.

$dE := 0.01$ $Esw := 0.05$ $\Delta E := 0.8$ $m := 1..\frac{\Delta E}{dE} \cdot 50$ $Es := -0.5$ $i := 1..1$ $f := 20$

CE difusional mechansim:
A <---> Red - 1e- <---> Ox

$$relativenpot_m := \left(ceil\left(\frac{m}{25}\cdot\frac{1}{2}\right)\cdot dE + if\left(\frac{ceil\left(\frac{m}{25}\right)}{2} = ceil\left(\frac{m}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - dE \qquad \phi_m := (Es + Esw) + relativenpot_m$$

$ks := 0.0200$ $D := 5\cdot 10^{-6}$ $kf := .5051001000001$ $dE \cdot f = 0.2$



$$\lambda := \frac{ks}{\sqrt{D\cdot f}} \quad .1 \qquad \alpha := 0.5$$

$kb := .510010001$

$\lambda = 2$ $U := \frac{kf}{kb}$ $U = 0.99$

$\log(\lambda) = 0.301$

$K := 00.05$

$F := 96500$ $n := 1$ $R := 8.314$ $T := 298.15$ $\Phi_m := n\cdot\frac{F}{R\cdot T}\cdot\phi_m$

$\varepsilon := kf + kb$ kineticki parametar $k := 1..\frac{\Delta E}{dE}\cdot 50$

K is equilibrium constant

$z := \frac{\varepsilon}{f}$ $S1_k := \sqrt{k} - \sqrt{k-1}$ $S1_3 = 0.318$

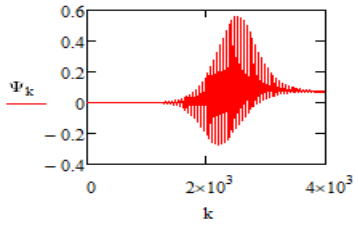
$z = 0.051$

$$S_k := erfc\left[\left(z\cdot\frac{k}{50}\right)^{0.5}\right] - erfc\left[\left(z\cdot\frac{(k-1)}{50}\right)^{0.5}\right]$$

$$\Psi_1 := \lambda\cdot e^{\alpha\cdot\Phi_1}\cdot\frac{K}{1+K}\cdot\left[1+\lambda\cdot e^{\alpha\cdot\Phi_1}\cdot\frac{K}{(1+K)\cdot 50} - \frac{\lambda\cdot e^{\alpha\cdot\Phi_1}\cdot S_1}{(K+1)\cdot z}\cdot(1) + \frac{\lambda\cdot e^{-(1-\alpha)\cdot\Phi_1}}{50}\right]^{-1}$$

$$\Psi_k := \frac{\frac{\lambda \cdot e^{\alpha \cdot \Phi_k} \cdot K}{1+K} \cdot \left[1 - \frac{2}{\sqrt{50 \cdot \pi}} \cdot \sum_{j=1}^{k-1} \left(\Psi_j \cdot S1_{k-j+1}\right)\right] - \gamma \cdot \left(\frac{1}{1+K}\right) \cdot (-1) \cdot e^{\alpha \cdot \Phi_k} \cdot \sum_{j=1}^{k-1} \left(\Psi_j \cdot S_{k-j+1}\right) - \lambda \cdot \frac{2}{\sqrt{50 \cdot \pi}} \cdot e^{-\Phi_k \cdot (1-\alpha)} \cdot \sum_{j=1}^{k-1} \left(\Psi_j \cdot S1_{k-j+1}\right)}{\left(\frac{\lambda \cdot e^{\alpha \cdot \Phi_k} \cdot K}{1+K} \cdot \frac{2 \cdot S1_1}{\sqrt{50 \cdot \pi}}\right) + 1 + \gamma \cdot (-1) \cdot \left(\frac{1}{1+K}\right) \cdot S_1 \cdot e^{\alpha \cdot \Phi_k} + \lambda \cdot \frac{2 \cdot S1_1}{\sqrt{50 \cdot \pi}} \cdot e^{-\Phi_k \cdot (1-\alpha)}}$$

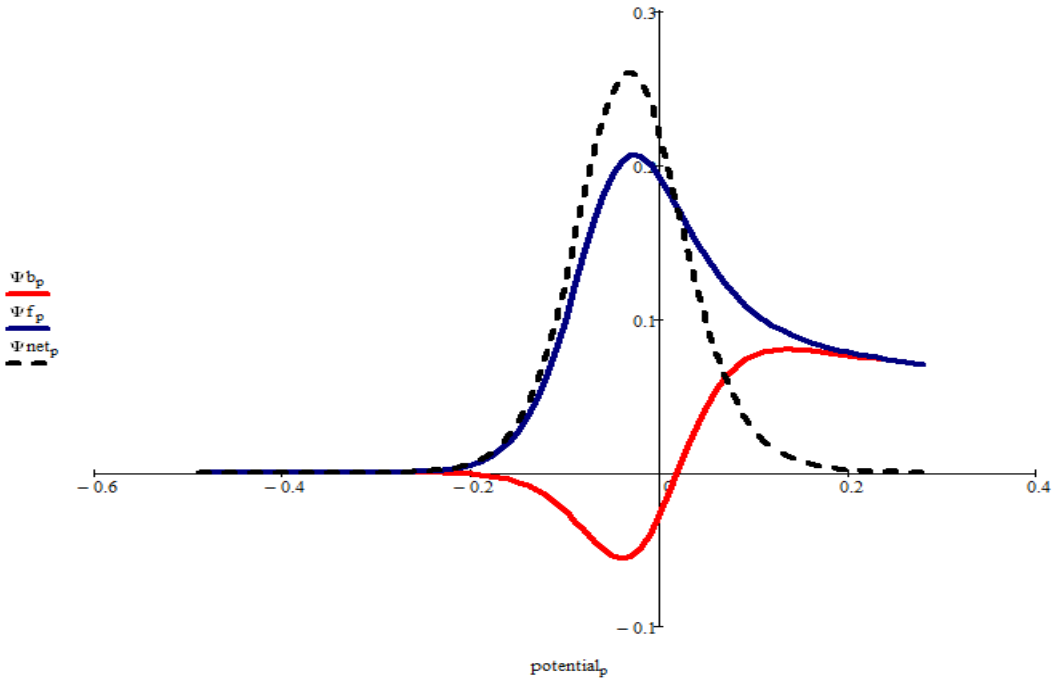
$\Psi_1 =$ -



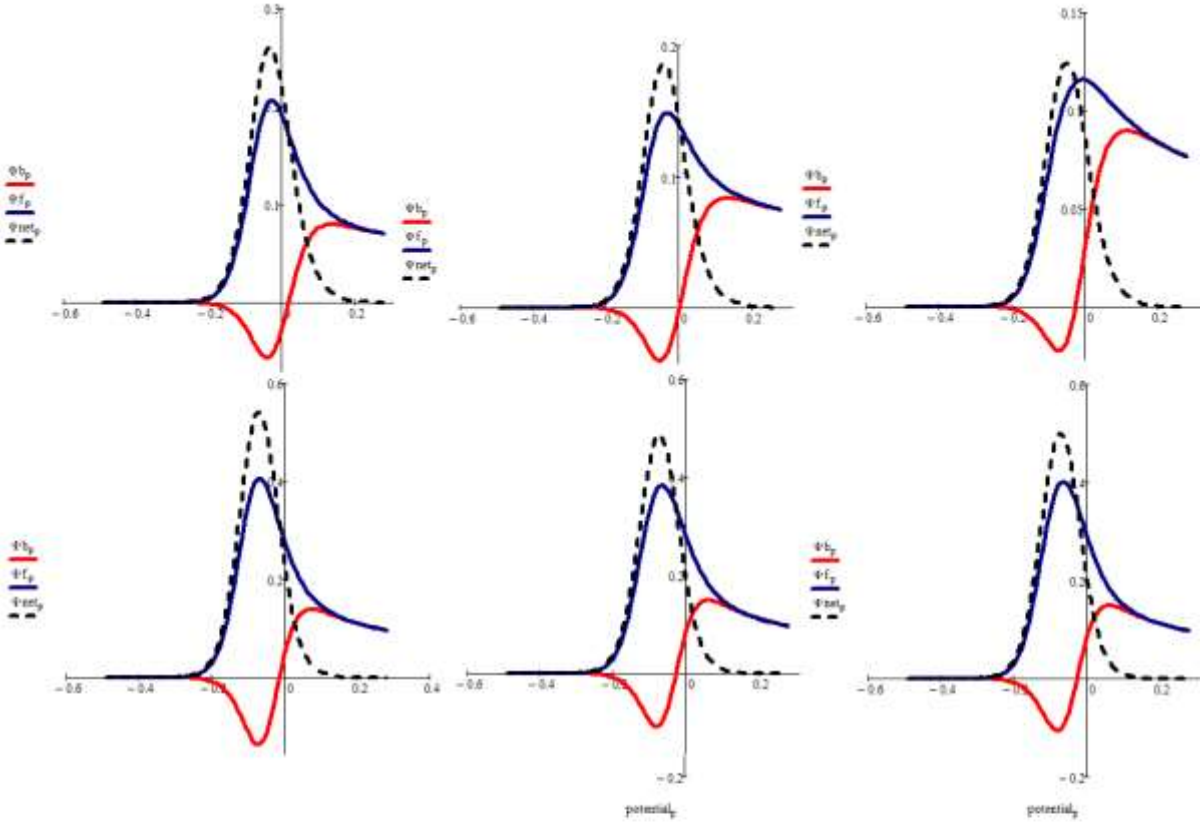
$\Psi_{k,i} =$

$p := 1 .. \frac{\Delta E}{dE} - 2$ $\quad \Psi f_p := (\Psi)_{(p+1)\cdot 50}$ $\quad \Psi b_p := (\Psi)_{50 \cdot p + 25}$

$\Psi net_p := \Psi f_p - \Psi b_p$ $\quad potential_p := Es + (p) \cdot dE$



6.747 × 10⁻
9.253 × 10⁻
1.33 × 10⁻
1.94 × 10⁻
2.848 × 10⁻
4.192 × 10⁻
6.179 × 10⁻
9.113 × 10⁻
1.344 × 10⁻
1.984 × 10⁻
2.928 × 10⁻
4.322 × 10⁻
6.38 × 10⁻
9.418 × 10⁻
1.39 × 10⁻
2.052 × 10⁻
3.03 × 10⁻
4.474 × 10⁻
6.605 × 10⁻
9.751 × 10⁻
1.44 × 10⁻
2.125 × 10⁻
3.137 × 10⁻
4.628 × 10⁻
6.825 × 10⁻
1.006 × 10⁻
1.48 × 10⁻



Effect of chemical reaction rate to the features of simulated square-wave voltammograms of a CErev mechanism, calculated for Keq = 0.05 (three voltammograms at the top) and Keq = 0.05 (three voltammograms at the bottom)

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