

# Влијание на брзината на хемиската реакција врз цикличните волтаметриски одговор на дифузионски "ECrev" механизам

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**Abstract:** Влијанието на брзината на хемиската реакција врз струјните компоненти од едностепен дифузионски контролиран електрохемиски механизам комплициран со реверзибилна хемиска реакција на електрохемиски генерираниот продукт (во литература познат како „ECrev“ механизам) е студираан при различни вредности на константата на рамнотежа на хемиската реакција. Во трудот е даден MATHCAD симулациски протокол во слободна форма, кој овозможува симулирање на циклични волтамограми за овој исклучително важен механизам во електрохемијата.

$$E_a = -0.4 \quad E_f = 0.4 \quad \Delta E = E_f - E_a \quad dE = 0.004 \quad \tau = 0.01 \quad d = \frac{\gamma}{25}$$

$$m = \frac{\Delta E}{dE} \cdot 25 + \frac{\tau \alpha c}{d} + 1 \quad \left( \frac{\Delta E}{dE} \cdot 25 + \frac{\tau \alpha c}{d} \right)$$

$$E_m = E_a + \left[ \text{erfc} \left( \frac{m - \frac{\tau \alpha c}{d}}{25} \right) dE - dE \right]$$

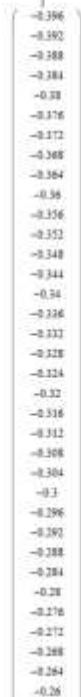
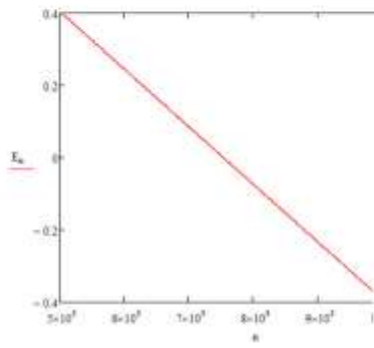
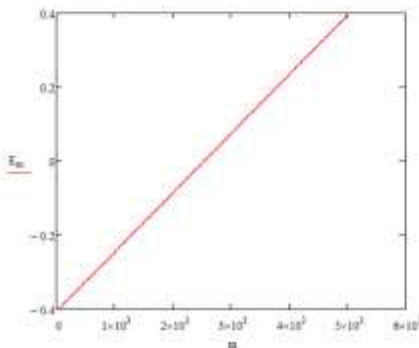
$$E_m = E_f - \left[ \text{erfc} \left( \frac{m - \left( \frac{\Delta E}{dE} \cdot 25 + \frac{\tau \alpha c}{d} \right)}{25} \right) dE - dE \right]$$

$$\beta_k = 1 - \frac{\tau \alpha c}{d}$$

$$\frac{\Delta E}{dE} = 100$$

ECrev Diffusional Mechanism  
in Cyclic Voltammetry  
WHEN Equilibrium Constant  $M > 1000$ , mechanism converges to simple Red-Ox Mechanism

$\alpha$  is electron transfer coefficient related to electrode reaction  
 $\gamma$  is dimensionless catalytic parameter related to preceding chemical reaction  
 $M$  is equilibrium constant of preceding chemical reaction  
 $k_f$  and  $k_b$  are forward and backward rate constants of preceding chemical reaction  
 $E_s$  is starting potential  
 $E_f$  is final potential  
 $dE$  is potential step  
 $\Psi$  is symbol for dimensionless current  
 $E_m$  is cathodic potential ramp in cyclic voltammetry  
 $E_n$  is anodic potential ramp  
 $S_k$  is integration factor  
 $\tau$  is duration of potential steps  
 $D$  is diffusion coefficient of Ox and Red.



$$\beta_k = 0.28 \quad \text{con} = 0.0000008$$

$$k_f = 0.005 \quad D = 3 \cdot 10^{-6} \quad M = 2222.10 \quad 0.05 \quad 0$$

$$\beta_{k_0} = \frac{k_f \sqrt{\tau}}{\sqrt{D}} \quad \alpha = 0.3 \quad k_b = 2222.50010 \quad 0.075 \quad 0$$

$$M = \frac{k_f}{k_b} \quad \text{Konstanta na ramnотежа}$$

$$\log(K) = -0.54 \quad K$$

$$\frac{\Delta E}{dE} = 0.1000$$

$$E_m = k_f - k_b \quad \text{kinetic parameter} \quad k = 1.2 \left( \frac{\Delta E}{dE} \cdot 25 + \frac{\tau \alpha c}{d} \right)$$

$$\tau = d \cdot t$$

$$S_{1,k} = \sqrt{\frac{k}{25}} - \sqrt{\frac{k-1}{25}} \quad S_{1,2} = k \quad \tau = (k^2 + 2k)^{0.5} \cdot d$$

$$\tau = 6.667$$

$$\gamma = h \cdot d$$

$$\gamma = 6.667$$

$$\beta_k = \left( 1 - \text{erfc} \left( \sqrt{\frac{c}{25}} \cdot k \right) \right) - \left[ 1 - \text{erfc} \left( \sqrt{\frac{c}{25}} \cdot (k-1) \right) \right]$$

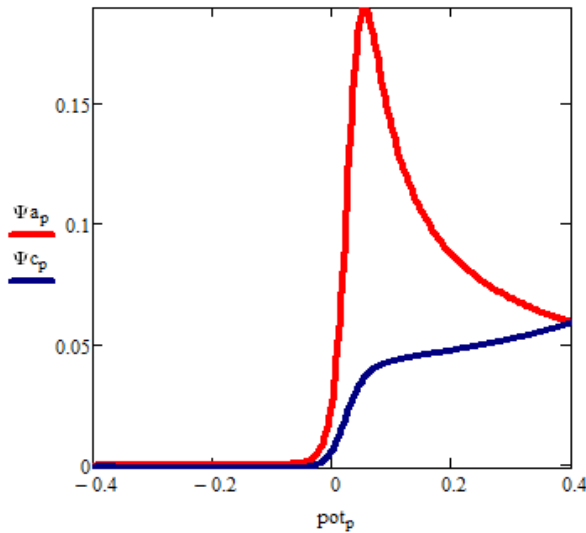
$$\Psi_1 := \frac{K \cdot e^{\alpha \cdot \Phi_1}}{\left[ 1 + \frac{1 \cdot K \cdot e^{-(1-\alpha) \cdot \Phi_1}}{\sqrt{\pi \cdot 1}} + \frac{1 \cdot K \cdot e^{-(1-\alpha) \cdot \Phi_1}}{\sqrt{\pi \cdot 1}} \cdot \frac{M}{1+M} \right] + \frac{\gamma}{1+M} \cdot e^{-(1-\alpha) \cdot \Phi_1} \cdot S_1}$$

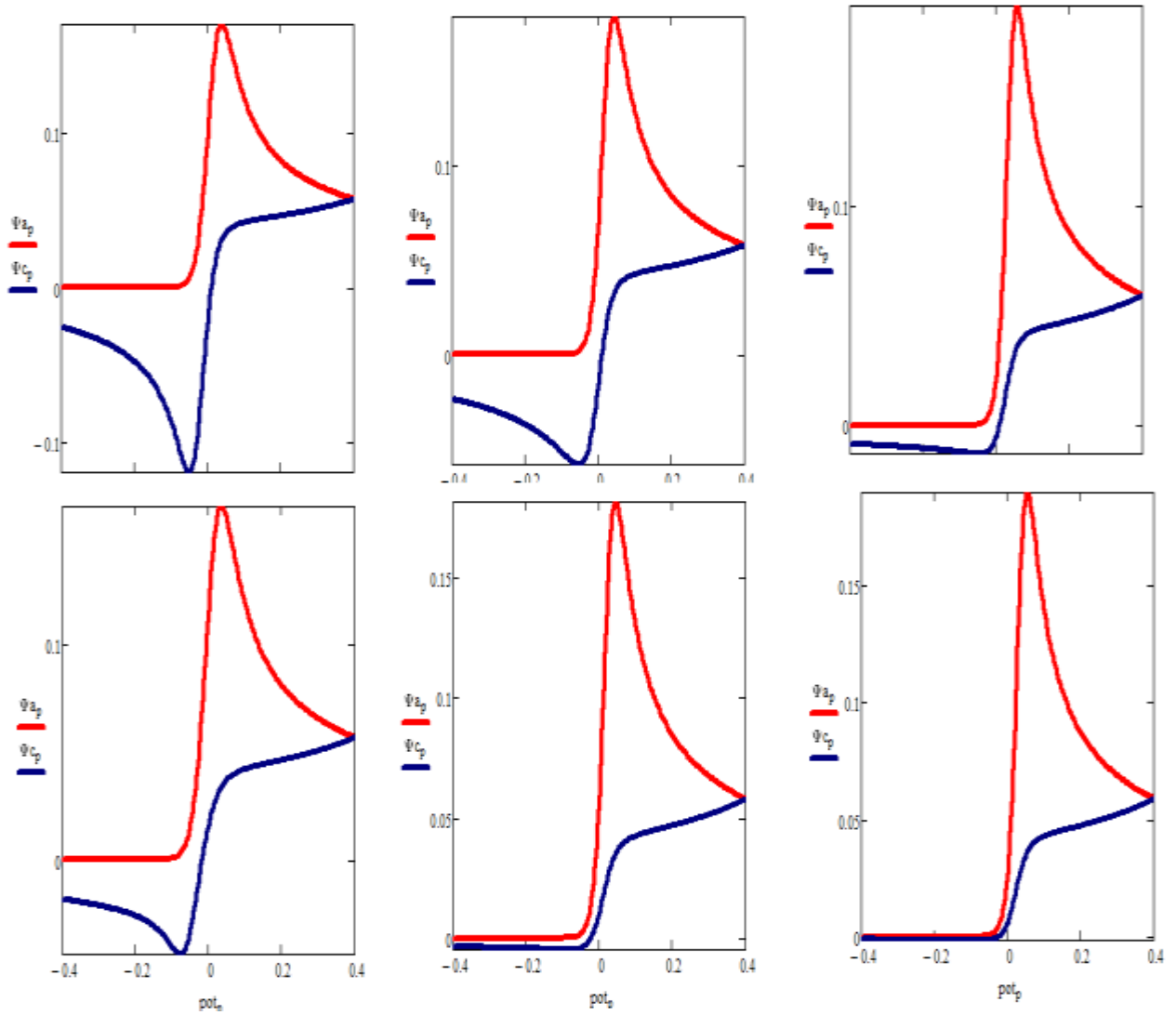
$$\Psi_s := \frac{K \cdot e^{\alpha \cdot \Phi_{ac}} - \frac{2 \cdot K \cdot e^{\alpha \cdot \Phi_{ac}}}{\sqrt{\pi \cdot 1}} \cdot \sum_{j=1}^{s-1} (\Psi_j \cdot S_{1-s-j+1}) - \frac{2 \cdot K \cdot e^{-(1-\alpha) \cdot \Phi_{ac}}}{\sqrt{\pi \cdot 1}} \cdot \frac{M}{1+M} \cdot \sum_{j=1}^{s-1} (\Psi_j \cdot S_{1-s-j+1}) - \frac{\gamma}{1+M} \cdot e^{-(1-\alpha) \cdot \Phi_{ac}} \cdot \sum_{j=1}^{s-1} (\Psi_j \cdot S_{s-j+1})}{1 + \frac{2 \cdot K \cdot e^{\alpha \cdot \Phi_{ac}}}{\sqrt{\pi \cdot 1}} + \frac{2 \cdot K \cdot e^{-(1-\alpha) \cdot \Phi_{ac}}}{\sqrt{\pi \cdot 1}} \cdot \frac{M}{1+M} + \frac{\gamma}{1+M} \cdot e^{-(1-\alpha) \cdot \Phi_{ac}} \cdot S_1}$$

$$\Psi_m := \frac{K \cdot e^{\alpha \cdot \Phi_m} - \frac{2 \cdot K \cdot e^{\alpha \cdot \Phi_m}}{\sqrt{\pi \cdot 1}} \cdot \sum_{j=1}^{m-1} (\Psi_j \cdot S_{1-m-j+1}) - \frac{2 \cdot K \cdot e^{-(1-\alpha) \cdot \Phi_m}}{\sqrt{\pi \cdot 1}} \cdot \frac{M}{1+M} \cdot \sum_{j=1}^{m-1} (\Psi_j \cdot S_{1-m-j+1}) - \frac{\gamma}{1+M} \cdot e^{-(1-\alpha) \cdot \Phi_m} \cdot \sum_{j=1}^{m-1} (\Psi_j \cdot S_{m-j+1})}{1 + \frac{2 \cdot K \cdot e^{\alpha \cdot \Phi_m}}{\sqrt{\pi \cdot 1}} + \frac{2 \cdot K \cdot e^{-(1-\alpha) \cdot \Phi_m}}{\sqrt{\pi \cdot 1}} \cdot \frac{M}{1+M} + \frac{\gamma}{1+M} \cdot e^{-(1-\alpha) \cdot \Phi_m} \cdot S_1}$$

$$\Psi_n := \frac{K \cdot e^{\alpha \cdot b_n} - \frac{2 \cdot K \cdot e^{\alpha \cdot b_n}}{\sqrt{\pi \cdot 1}} \cdot \sum_{j=1}^{n-1} (\Psi_j \cdot S_{1-n-j+1}) - \frac{2 \cdot K \cdot e^{-(1-\alpha) \cdot b_n}}{\sqrt{\pi \cdot 1}} \cdot \frac{M}{1+M} \cdot \sum_{j=1}^{n-1} (\Psi_j \cdot S_{1-n-j+1}) - \frac{\gamma}{1+M} \cdot e^{-(1-\alpha) \cdot b_n} \cdot \sum_{j=1}^{n-1} (\Psi_j \cdot S_{n-j+1})}{1 + \frac{2 \cdot K \cdot e^{\alpha \cdot b_n}}{\sqrt{\pi \cdot 1}} + \frac{2 \cdot K \cdot e^{-(1-\alpha) \cdot b_n}}{\sqrt{\pi \cdot 1}} \cdot \frac{M}{1+M} + \frac{\gamma}{1+M} \cdot e^{-(1-\alpha) \cdot b_n} \cdot S_1}$$

$$p := 1 \cdot \frac{\Delta E}{dE} \quad \Psi_{a_p} := (\Psi) \left( \frac{\tau}{d \cdot 25} + p \right) \cdot 25 \quad \Psi_{c_p} := (\Psi) \left[ \left[ \frac{\Delta E}{dE} \cdot 2 + \left( \frac{\tau}{25 \cdot d} \right) \right] - p \right] \cdot 25 \quad \text{pot}_p := E_s + p \cdot dE$$





Влијание на кинетиката на хемиска реакција врз својства на оксидациски и редукциски струјни компненти од циклични волтамограми кај ECrev дифузиски механизам при големи (горен ред) и мали (волтамограми во долен ред) вредности на константата на рамнотежа на хемиската реакција вклучена во овој механизам.

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