Влијание на брзината нахемиската реакција врз цикличните волтаметриски одговор на дифузиски “ECrev” механизам

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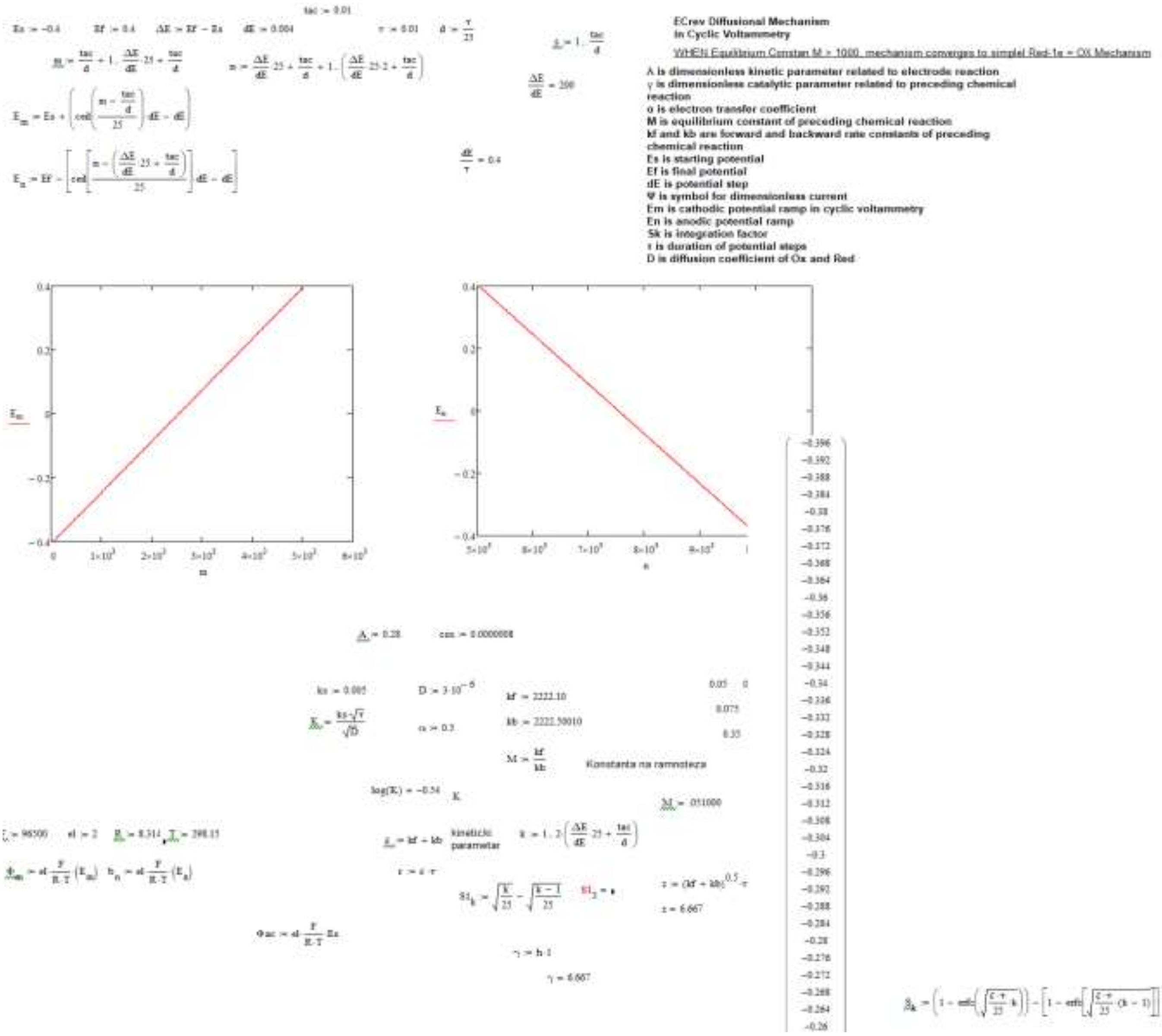
Abstract: Влијанието на брзината на хемиската рекација врз струјните компоненти од еднostепен дифусизки контролиран електрохемиски механизам комплициран со реверзибилна хемиска реакција на електрохемиски генерираниот продукт (во литература познат како „ECrev“ механизам) е студиран при различни вредности 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.



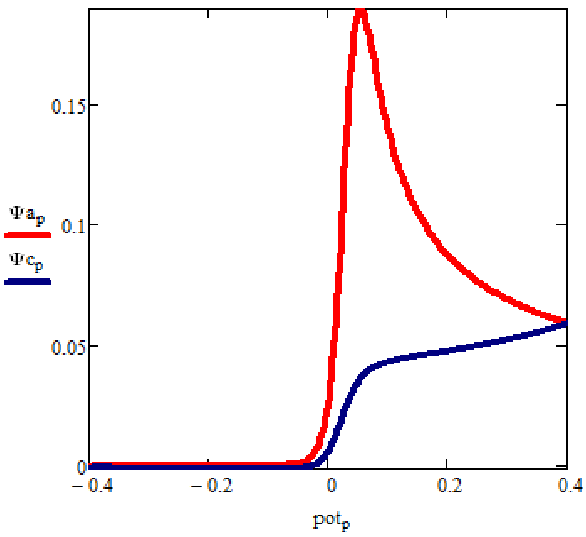
$$\Psi_1 := \frac{K\cdot e^{\alpha\cdot\Phi_1}}{\left[1+\frac{1\cdot K\cdot e^{-(1-\alpha)\cdot\Phi_1}}{\sqrt{\pi\cdot 1}}+\frac{1\cdot K\cdot e^{-(1-\alpha)\cdot\Phi_1}}{\sqrt{\pi\cdot 1}}\cdot\frac{M}{1+M}\right]+\frac{\gamma}{1+M}\cdot e^{-(1-\alpha)\cdot\Phi_1}\cdot S_1}$$

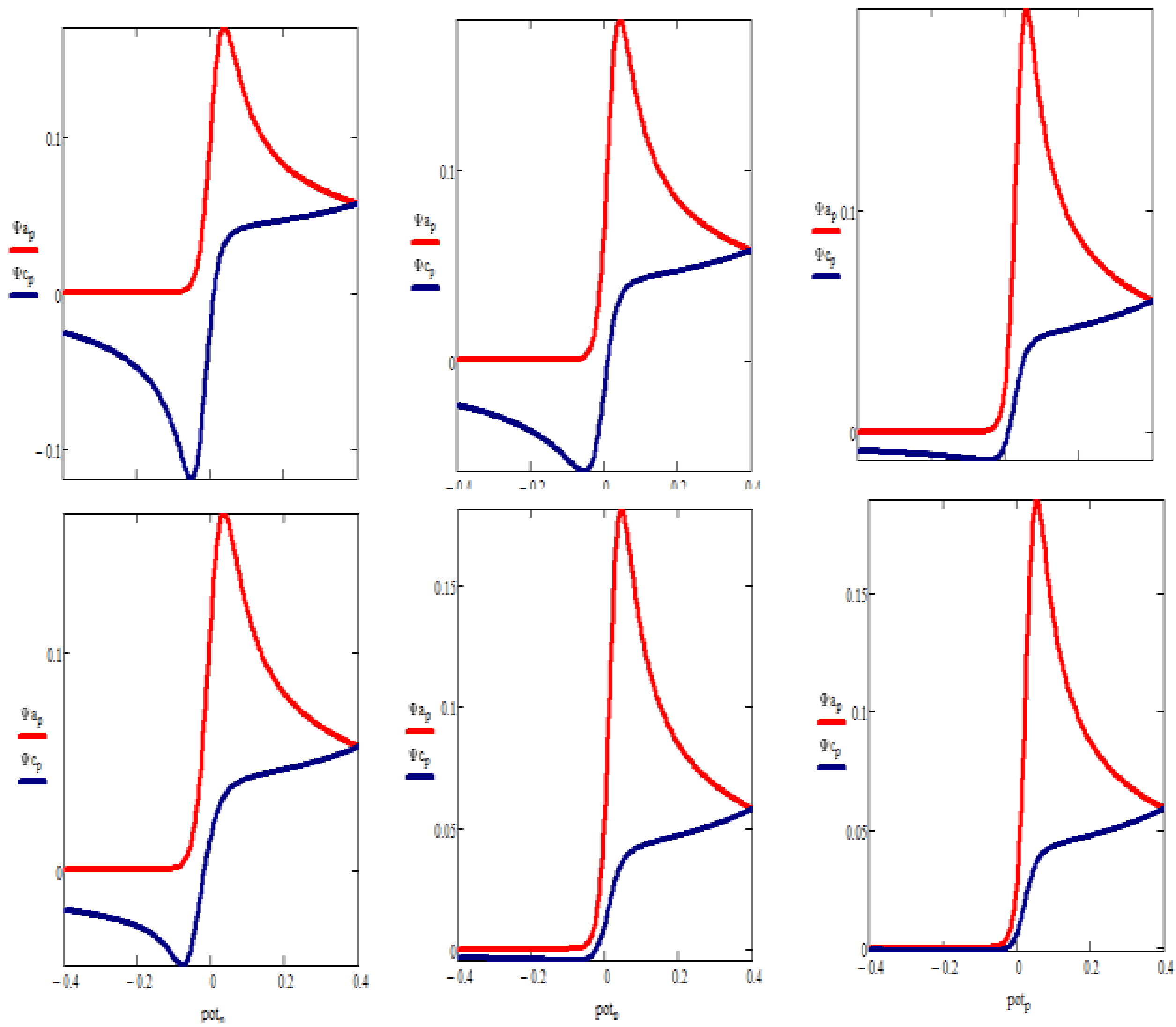
$$\Psi_s := \frac{K\cdot e^{\alpha\cdot\Phi ac}-\frac{2\cdot K\cdot e^{\alpha\cdot\Phi ac}}{\sqrt{\pi\cdot 1}}\cdot\sum_{j=1}^{s-1}\left(\Psi_j\cdot S1_{s-j+1}\right)-\frac{2\cdot K\cdot e^{-(1-\alpha)\cdot\Phi ac}}{\sqrt{\pi\cdot 1}}\cdot\frac{M}{1+M}\cdot\sum_{j=1}^{s-1}\left(\Psi_j\cdot S1_{s-j+1}\right)-\frac{\gamma}{1+M}\cdot e^{-(1-\alpha)\cdot\Phi ac}\cdot\sum_{j=1}^{s-1}\left(\Psi_j\cdot S_{s-j+1}\right)}{1+\frac{2\cdot K\cdot e^{\alpha\cdot\Phi ac}}{\sqrt{\pi\cdot 1}}+\frac{2\cdot K\cdot e^{-(1-\alpha)\cdot\Phi ac}}{\sqrt{\pi\cdot 1}}\cdot\frac{M}{1+M}+\frac{\gamma}{1+M}\cdot e^{-(1-\alpha)\cdot\Phi ac}\cdot S_1}$$

$$\Psi_m := \frac{K\cdot e^{\alpha\cdot\Phi_m}-\frac{2\cdot K\cdot e^{\alpha\cdot\Phi_m}}{\sqrt{\pi\cdot 1}}\cdot\sum_{j=1}^{m-1}\left(\Psi_j\cdot S1_{m-j+1}\right)-\frac{2\cdot K\cdot e^{-(1-\alpha)\cdot\Phi_m}}{\sqrt{\pi\cdot 1}}\cdot\frac{M}{1+M}\cdot\sum_{j=1}^{m-1}\left(\Psi_j\cdot S1_{m-j+1}\right)-\frac{\gamma}{1+M}\cdot e^{-(1-\alpha)\cdot\Phi_m}\cdot\sum_{j=1}^{m-1}\left(\Psi_j\cdot S_{m-j+1}\right)}{1+\frac{2\cdot K\cdot e^{\alpha\cdot\Phi_m}}{\sqrt{\pi\cdot 1}}+\frac{2\cdot K\cdot e^{-(1-\alpha)\cdot\Phi_m}}{\sqrt{\pi\cdot 1}}\cdot\frac{M}{1+M}+\frac{\gamma}{1+M}\cdot e^{-(1-\alpha)\cdot\Phi_m}\cdot S_1}$$

$$\Psi_n := \frac{K\cdot e^{\alpha\cdot b_n}-\frac{2\cdot K\cdot e^{\alpha\cdot b_n}}{\sqrt{\pi\cdot 1}}\cdot\sum_{j=1}^{n-1}\left(\Psi_j\cdot S1_{n-j+1}\right)-\frac{2\cdot K\cdot e^{-(1-\alpha)\cdot b_n}}{\sqrt{\pi\cdot 1}}\cdot\frac{M}{1+M}\cdot\sum_{j=1}^{n-1}\left(\Psi_j\cdot S1_{n-j+1}\right)-\frac{\gamma}{1+M}\cdot e^{-(1-\alpha)\cdot b_n}\cdot\sum_{j=1}^{n-1}\left(\Psi_j\cdot S_{n-j+1}\right)}{1+\frac{2\cdot K\cdot e^{\alpha\cdot b_n}}{\sqrt{\pi\cdot 1}}+\frac{2\cdot K\cdot e^{-(1-\alpha)\cdot b_n}}{\sqrt{\pi\cdot 1}}\cdot\frac{M}{1+M}+\frac{\gamma}{1+M}\cdot e^{-(1-\alpha)\cdot b_n}\cdot S_1}$$

$p := 1 .. \frac{\Delta E}{dE}$ $\quad \Psi a_p := (\Psi)_{\left(\frac{\tau}{d\cdot 25}+p\right)\cdot 25}$ $\quad \Psi c_p := (\Psi)_{\left[\left[\frac{\Delta E}{dE}\cdot 2+\left(\frac{\tau}{25\cdot d}\right)\right]-p\right]\cdot 25}$ $\quad pot_p := Es + p\cdot dE$





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

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