Nernstian Behavior of Simple Diffusional Electrode Transformation in Square-Wave Voltammetry

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Abstract

Reversible Electrode Transformation, with mass transfer occurring via diffusion

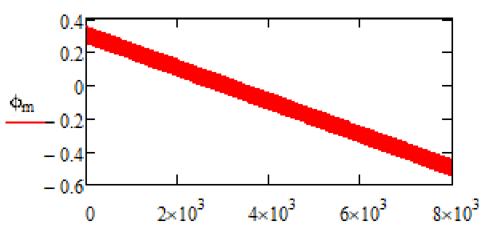
Ox(dissolved) + ne = Red(dissolved)

In this work, parameters affecting the features of dimensionless square-wave voltammograms of simple diffusional electrode reaction following Nernst reversible behavior are evaluated.

$dE := \frac{0.005}{1}$ $\quad Esw := \frac{0.05}{1}$ $\quad \Delta E := 0.8$ $\quad m := 1 .. \frac{\Delta E}{dE} \cdot 50$ $\quad Es := 0.3$ $\quad i := 1 .. 1$

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

$$\phi_m := Es + Esw - relativenpot_m$$



$D := 5 \cdot 10^{-6}$ $\quad f := 36$

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

$$k := 1 .. \frac{\Delta E}{dE} \cdot 50$$

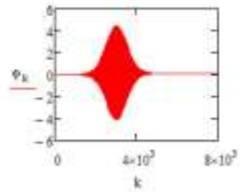
$S_k := \sqrt{k} - \sqrt{k-1}$ $\quad S_3 = 0.318$

$$\Psi_1 := \frac{\left(\frac{2}{\sqrt{\pi \cdot 50}}\right)^{-1}}{1 + e^{\Phi_1}}$$

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

$S_1 = 1$

$\Psi_1 = 0$



za Esw/dE = 1.5 constanta e 0/375
Za Esw/dE = 2.0, constanta e 0.375
za Esw/dE = 3.0, constanta e 0.375
za Esw.dE e 4.0, constanta e 0.352
Za Esw/dE = 5.0, constanta e 0.329
Za Esw/dE -= 6.0, constanta e 0.328
ovie pri dE = 1 mV
Za Esw/dE = 60, const e 0.097
za Esw/dE = 50, comnst e 0.107
za Esw/dE = 40, const e 112
za Esw/dE od 30, const e 0.123
za Esw/dE od 20, const e 0.130
Za Esw/dE 0d 15, const e 0.132
Za Esw.dE od 10, const e 0/133
Za Esw.dE =5, const e 0.132

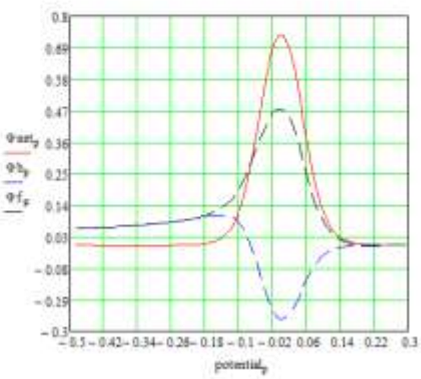
$p := 1..\frac{\Delta E}{dE} - 2 \quad \Psi f_p := \Psi_{(p+1)\cdot 50} \quad \Psi b_p := \Psi_{50\cdot p+25} \quad \Psi net_p := \Psi f_p - \Psi b_p$

$potential_p := Es - (p)\cdot dE$

$$\frac{2\cdot 7.0}{(50\cdot\pi)^{0.5}}\left(\frac{F}{R\cdot T}\cdot dE\right)^{0.5}\cdot\left(\frac{Esw\cdot F}{R\cdot T}\right)^{0.5} = 0.688$$

Da se najde konstantata za
razlicni odnosi na Esw/dE pri T od 298 i toa e toa

za Esw/dE 60; 50; 40; 25; 15; 10



$\Psi b_p =$ $\quad potential_p =$

$$\frac{2\cdot 0.585}{(25\cdot\pi)^{0.5}} = 0.132$$

$\frac{Esw}{dE} = 10$

$$i_p = 0.4463\, nFAC\left(\frac{nFvI}{RT}\right.$$

Or if the solution is at 25 °C:[2]

$$i_p = 2.69\times10^5\, n^{3/2} AC\sqrt{I}$$

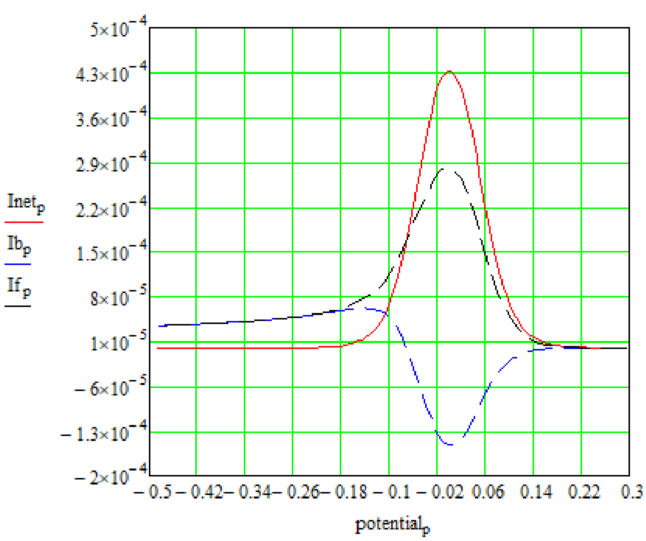
$\underline{L} := 20..40$

$A := 0.28$

Ψnetp e definirana so $\frac{2\cdot 1.45}{(50\cdot\pi)^{0.5}}\left(\frac{F}{R\cdot T}\cdot dE\right)^{0.5}\cdot\left(\frac{Esw}{dE}\right) = 1.021$

$$Inet_p := F\cdot A\cdot D^{0.5}\cdot f^{0.5}\cdot \Psi net_p\cdot c\cdot 0.325\cdot\left(\frac{Esw}{dE}\right)$$

$$If_p := F\cdot A\cdot D^{0.5}\cdot f^{0.5}\cdot \Psi f_p\cdot c\cdot 0.325\cdot\left(\frac{Esw}{dE}\right) \qquad Ib_p := F\cdot A\cdot D^{0.5}\cdot f^{0.5}\cdot \Psi b_p\cdot c\cdot 0.325\cdot\left(\frac{Esw}{dE}\right)$$



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