Modeling of Two Step Diffusional ECirrECrev Mechanism in Square-Wave Voltammetry

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Abstract

The two-step successive electrochemical diffusional mechanism, coupled with an irreversible chemical step related to the product of first electron transfer, and reversible chemical step associated to the product of second electron transfer step (***ECirrECrev mechanism***), is considered for the first time under conditions of square-wave voltammetry. The voltammetric patterns depend on the elctron tramsfer coefficient of both electron transfer steps, on kinetics of electron transfer of both electron transfer steps. In addition, the kinetics of chemical affects the features of both SWV peaks, while the chemical kinetics and thermodynamics of second step affects the features of the second peak only. While the entire simulation protocol to calculate voltammograms of this complex mechanism is given in MATHCAD, hints are given on how to estimate the kinetic and thermodynamic parameters related to both chemical steps involved in this complex electrochemical mechanism.

TWO STEP DIFFUSIONAL ECirrECrev Mechanism in SWV---Tocen 17 Oct 2023

$EsI := 0.35 \quad \Delta E := 1 \quad dE := 0.01 \quad Esw := 0.05 \quad EsII := 0.65 \quad r := 1..1$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15$

$KI_r := 10^{.75 \cdot r} \qquad KII := 10^{.75}$

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

$\alpha 2 := 0.5 \qquad \alpha 1 := 0.5 \qquad \log(KI_r) = 0.75$

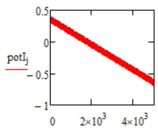
$\lambda := 5.0000$

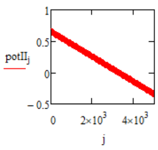
λ e hemiski parametar na ireverzibilna hemiska reakcija povrzana so prv elektroden cekor

$KI_1 = 5.623$

$$potI_j := EsI + Esw - \left[\left(ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right) \cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw\right) - dE\right]$$

$$potII_j := EsII + Esw - \left[\left(ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right) \cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw\right) - dE\right]$$





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$$M1_j := \sqrt{\frac{j}{1}} - \sqrt{\frac{j-1}{1}}$$

$$A_j := \left(1 - erfc\left(\sqrt{\frac{\lambda}{50 \times 1} \cdot j}\right)\right) - \left[1 - erfc\left[\sqrt{\frac{\lambda}{50 \times 1} \cdot (j-1)}\right]\right]$$

$z := 00.001$

z e hem parametar na follow up

$$B_j := \left(1 - erfc\left(\sqrt{\frac{z}{50 \times 1} \cdot j}\right)\right) - \left[1 - erfc\left[\sqrt{\frac{z}{50 \times 1} \cdot (j-1)}\right]\right]$$

$$\Phi I_j := n \cdot \frac{F}{R \cdot T} \cdot potI_j \qquad \Phi II_j := n \cdot \frac{F}{R \cdot T} \cdot potII_j$$

L e konst na ramnoteza na hem follow up

$x := 0.001$

$L := 100.000001000$

$$\Psi I_{1,r} := \frac{\frac{KI_r}{1} \cdot e^{-\alpha 1 \cdot \Phi I_1} - 0}{1 + KI_r \cdot \lambda^{-.5} \cdot A_1 \cdot e^{-\alpha 1 \cdot \Phi I_1} + 1\lambda^{-.5} \cdot e^{\Phi I_1 \cdot (1-\alpha 1)} \cdot A_1}$$

$$\Psi II_{1,r} := \frac{\frac{2}{\sqrt{\pi \cdot 50}} KII \cdot e^{-\alpha 2 \cdot \Phi II_1}}{1 + \frac{KII \cdot M1_1 \cdot 2}{\sqrt{\pi \cdot 50}} \cdot e^{-\alpha 2 \cdot \Phi II_1} \cdot \left(1 + e^{\Phi II_1}\right)} \cdot \Psi I_{1,r} \cdot A_1 + \frac{KII \cdot e^{-\alpha 2 \cdot \Phi II_1}}{1 + \frac{2 \cdot KII \cdot M1_1 \cdot e^{-\alpha 2 \cdot \Phi II_1}}{\sqrt{\pi \cdot 50}} + \frac{2 \cdot KII \cdot e^{(1-\alpha 2) \cdot \Phi II_1}}{\sqrt{\pi \cdot 50}} \cdot 1} \cdot 1$$

$\Psi I_{1,1} = 6.271 \times 10^{-6}$

$\Psi II_{1,1} = 9.165 \times 10^{-12}$

$$\Psi I_{j,r} := \frac{KI_r \cdot e^{-\alpha 1 \cdot \Phi I_j} - KI_r \cdot \frac{2}{\sqrt{\pi \cdot 50}} \cdot e^{-\alpha 1 \cdot \Phi I_j} \cdot \sum_{i=1}^{j-1} \left(\Psi I_{i,r} \cdot M1_{j-i+1}\right) - KI_r \lambda^{-0.5} \cdot e^{\Phi I_j \cdot (1-\alpha 1)} \cdot \sum_{i=1}^{j-1} \left(\Psi I_{i,r} \cdot A_{j-i+1}\right)}{1 + KI_r \cdot \frac{2}{\sqrt{\pi \cdot 50}} \cdot M1_1 \cdot e^{-\alpha 1 \cdot \Phi I_j} + \lambda^{-0.5} \cdot e^{\Phi I_j \cdot (1-\alpha 1)} \cdot A_1 \cdot KI_r}$$

$$\Psi II_{j,r} := \frac{KII \frac{2}{\sqrt{\pi \cdot 50}} \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot \sum_{i=1}^{j} \left(\Psi I_{i,r} \cdot M1_{j-i+1}\right) - KII \frac{1}{\sqrt{\lambda}} \cdot e^{(-\alpha 2) \cdot \Phi II_j} \cdot \sum_{i=1}^{j} \left(\Psi I_{i,r} \cdot A_{j-i+1}\right) - \frac{2}{\sqrt{\pi \cdot 50}} \frac{KII}{1+0} \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} \cdot (1) \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot M1_{j-i+1}\right) - \frac{L}{(\sqrt{z}) \cdot (1+L)} KII \cdot e^{1 \cdot \Phi II_j \cdot (1-\alpha 2)} \cdot (1) \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot B_{j-i+1}\right) - \frac{2}{(\sqrt{50 \cdot \pi}) \cdot (1+L)} KII \cdot e^{1 \cdot \Phi II_j \cdot (1-\alpha 2)} \cdot (1) \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot B_{j-i+1}\right)}{1 + KII \frac{A_1 \cdot 1}{\sqrt{\lambda}} \cdot e^{(-\alpha 2) \cdot \Phi II_j} + \frac{2M1_1}{\sqrt{\pi \cdot 50}} \frac{KII}{1+0} \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} + \frac{2 \cdot B_1}{(\sqrt{50 \cdot \pi}) \cdot (1+L)} KII \cdot e^{1 \cdot \Phi II_j \cdot (1-\alpha 2)} + \frac{L \cdot B_1}{(\sqrt{z}) \cdot (1+L)} KII \cdot e^{1 \cdot \Phi II_j \cdot (1-\alpha 2)}}$$

$\Psi_{j,r} := \Psi I_{j,r} + \Psi II_{j,r}$

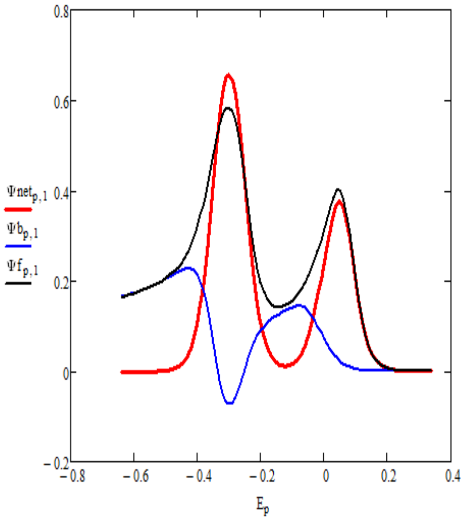
$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$

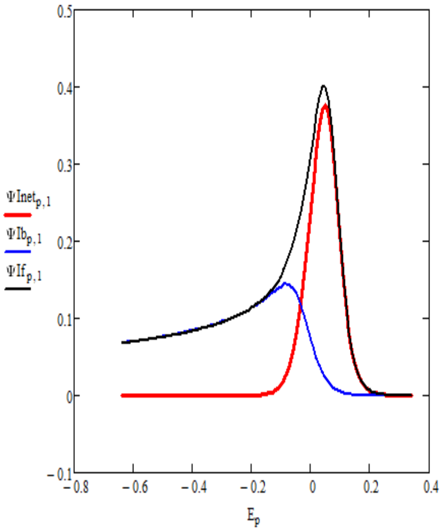
$\Psi If_{p,r} := \Psi I_{(p+1)\cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50\cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

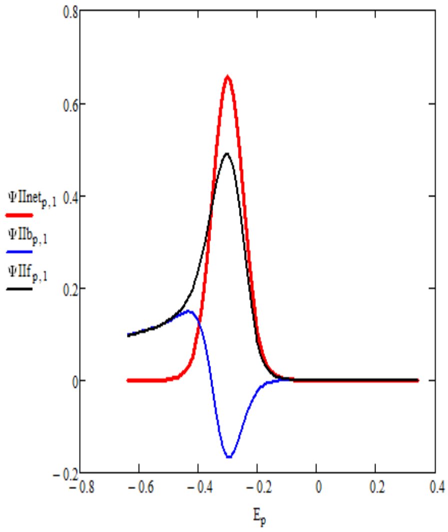
$\Psi IIb_{p,r} := \Psi II_{50\cdot p+25,r}$ $\Psi IIf_{p,r} := \Psi II_{(p+1)}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

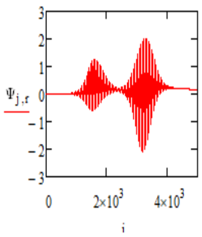
$E_p := EsI - p\cdot dE$

$\Psi b_{p,r} := \Psi_{50\cdot p+25,r}$ $\Psi f_{p,r} := \Psi_{(p+1)\cdot 5(}$ $\Psi net_{p,r} := \Psi f_{p,r} - \Psi b_{p,r}$



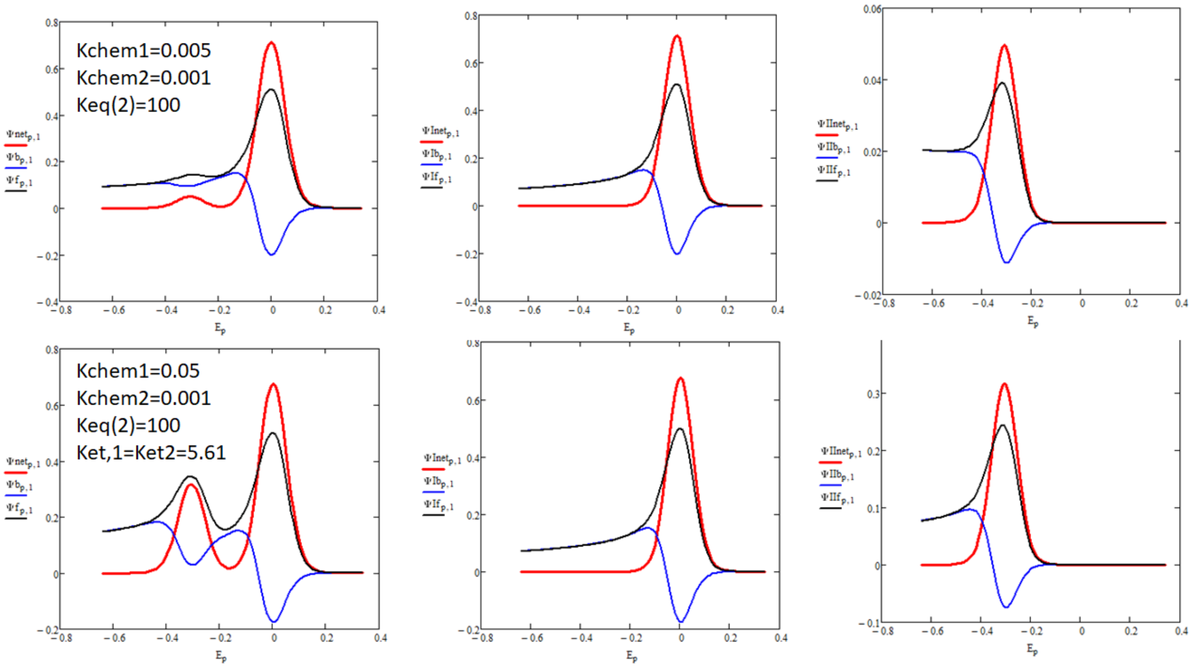






$\Psi f_{p,1} =$	$\Psi b_{p,1} =$	$\Psi net_{p,1} =$	$E_p =$
$2.804\cdot10^{-5}$	$4.887\cdot10^{-7}$	$2.755\cdot10^{-5}$	0.34
$4.137\cdot10^{-5}$	$7.212\cdot10^{-7}$	$4.065\cdot10^{-5}$	0.33
$6.103\cdot10^{-5}$	$1.064\cdot10^{-6}$	$5.997\cdot10^{-5}$	0.32
$9.004\cdot10^{-5}$	$1.571\cdot10^{-6}$	$8.847\cdot10^{-5}$	0.31
$1.328\cdot10^{-4}$	$2.319\cdot10^{-6}$	$1.305\cdot10^{-4}$	0.3
$1.959\cdot10^{-4}$	$3.422\cdot10^{-6}$	$1.925\cdot10^{-4}$	0.29
[illegible]	$5.05\cdot10^{-6}$		

Scheme of the Electrochemical Mechanism Cosnidered (ECirrECrev Mechanism)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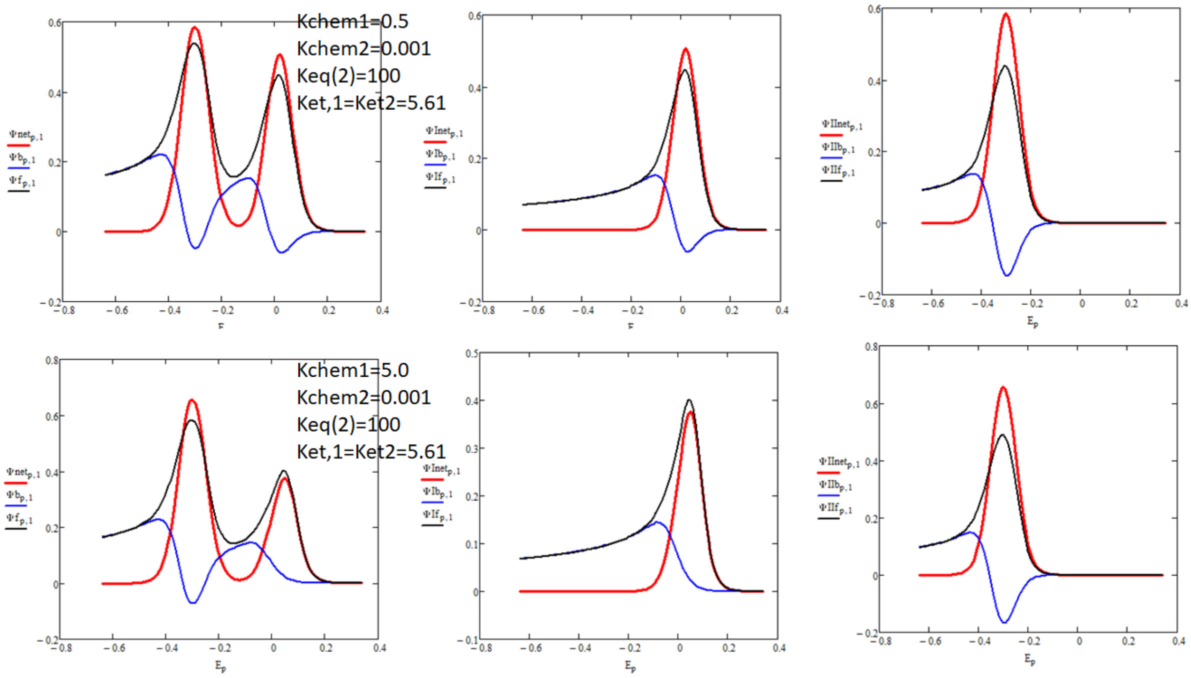
Kchem2=0.001
Keq(2)=100
Kchem1=0.05
Kchem2=0.001
Keq(2)=100
Ket,1=Ket2=5.61
Ψnet p,1
Ψb p,1
Ψf p,1
ΨInet p,1
ΨIb p,1
ΨIf p,1
ΨIInet p,1
ΨIIb p,1
ΨIIf p,1
E p


Kchem1=0.5
Kchem2=0.001
Keq(2)=100
Ket,1=Ket2=5.61
Kchem1=5.0
Kchem2=0.001
Keq(2)=100
Ket,1=Ket2=5.61
Ψnet p,1
Ψb p,1
Ψf p,1
ΨInet p,1
ΨIb p,1
ΨIf p,1
ΨIInet p,1
ΨIIb p,1
ΨIIf p,1
E p

REFERENCES

1. R. Gulaboski, V. Mirceski, M. Lovric, I. Bogeski, ***Electrochemistry Communications*** 7 (2005) 515-522.
2. R Gulaboski, V Mirceski, ***Macedonian Journal of Chemistry and Chemical Engineering*** 39 (2020) 153-166
3. V. Mirceski, R. Gulaboski, ***Macedonian Journal of Chemistry and Chemical Engineering*** 33 (2014), 1-12
4. V. Mirceski, R. Gulaboski, ***Journal of Solid State Electrochemistry*** 7 (2003) 157-165
5. M. Janeva, P. Kokoskarova, V. Maksimova, R. Gulaboski, ***Electroanalysis*** 31 (2019) 2488-2506
6. R. Gulaboski, M. Chirea, C. M. Pereira, M. N. D. S. Cordeiro, R. B. Costa, A. F. Silva, ***J. Phys. Chem. C*** 112 (2008) 2428-2435
7. R. Gulaboski, V. Mirceski, S. Komorsky-Lovric, M. Lovric, ***Electroanalysis*** 16 (2004) 832-842
8. R. Gulaboski, C. M. Pereira, M. N. D. S. Cordeiro, A. F. Silva, M. Hoth, I. Bogeski, ***Cell Calcium*** 43 (2008) 615-621
9. B. Sefer, R. Gulaboski, V. Mirceski, ***Journal of Solid State Electrochemistry*** 16 (2012) 2373-2381.
10. V. Mirceski, R. Gulaboski, ***Bulletin of the Chemists and Technologists of Macedonia*** 18 (1999) 57-64.
11. R. Gulaboski, C. M. Pereira, ***Electroanalytical Techniques and Instrumentation in Food Analysis***; in Handbook of Food Analysis Instruments (2008) 379-402.
12. M. Jorge, R. Gulaboski, C. M. Pereira, M. N. D. S. Cordeiro, ***Journal of Physical Chemistry B*** 110 (2006) 12530-12538.
13. V. Mirceski, D. Guziejewski, L. Stojanov, R. Gulaboski, ***Analytical Chemistry*** 91 (2019) 14904-14910.
14. V. Mirceski, R. Gulaboski, F. Scholz, ***Journal of Electroanalytical Chemistry*** 566 (2004) 351-360.

15. R. Gulaboski, M. Chirea, C. M. Pereira, M. N. D. S. Cordeiro, R. B. Costa, A. F. Silva, ***J. Phys. Chem. C*** 112 (2008) 2428-2435

16. R. Gulaboski, V. Mirceski, S. Komorsky-Lovric, M. Lovric, ***Electroanalysis*** 16 (2004) 832-842

17. R. Gulaboski, C. M. Pereira, M. N. D. S. Cordeiro, A. F. Silva, M. Hoth, I. Bogeski, ***Cell Calcium*** 43 (2008) 615-621

18. R. Gulaboski, V. Mirceski, F. Scholz, ***Amino Acids*** 24 (2003) 149-154

19. V. Mirceski, R. Gulaboski, ***Croatica Chemica Acta*** 76 (2003) 37-48.

20. F. Scholz, R. Gulaboski, ***Faraday Discussions*** 129 (2005) 169-177.

21. V. Mirceski, R. Gulaboski, F. Scholz, ***Electrochemistry Communications*** 4 (2002) 814-819.

22. R. Gulaboski, K. Caban. Z. Stojek, F. Scholz, ***Electrochemistry Communications*** 6 (2004) 215-218.