Regenerative Mechanism in Two-Step Diffusional EEC' Mechanism in Square-Wave Voltammetry

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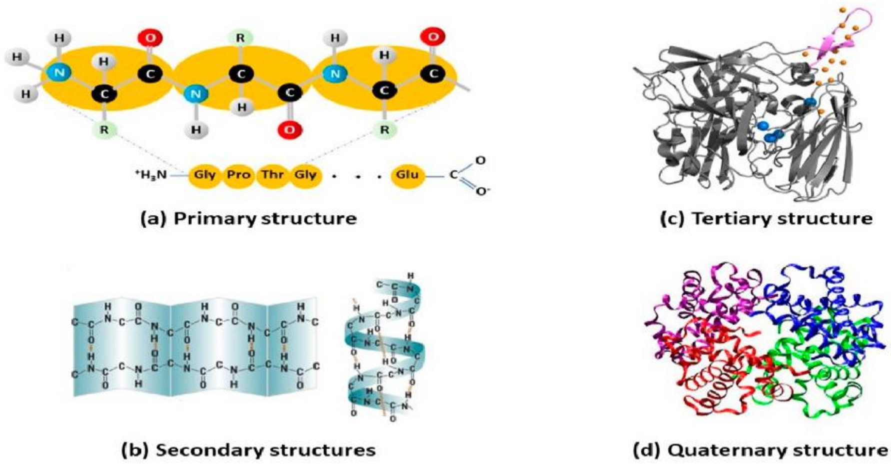
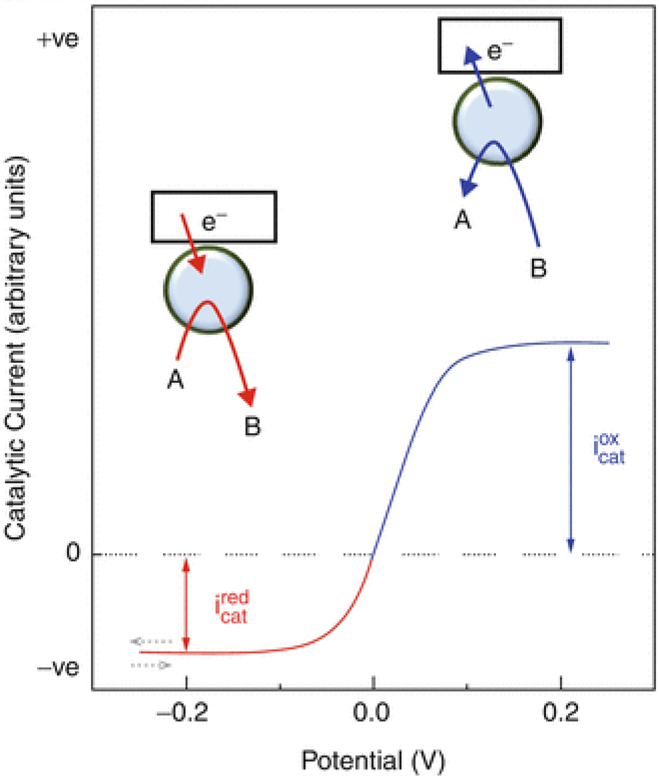
Abstract

The regenerative mechanism in two-step diffusional ***EEC' mechanism*** associated to the product of second electrochemical step is studied theoretically under conditions of square-wave voltammetry. As many water-soluble redox enzymes commonly undergo electrochemical transformation in two consecutive electron transfer steps, the regeneration of the intermediate product via homogeneous chemical reaction of the last electrochemically generated product of the second electron transfer is a fundamental process to understand enzyme-substrate kinetics of such complex systems. This work gives entire MATHCAD simulation protocol of this complex mechanism in square-wave voltammetry,





TWO STEP DIFFUSIONAL EEC'cat Mechanism in SWV---Dec 2023

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

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15 \quad KI_r := 10^{.75 \cdot r}$

$KII := 10^{.75}$

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

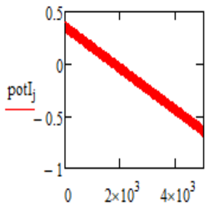
$\alpha 2 := 0.5$

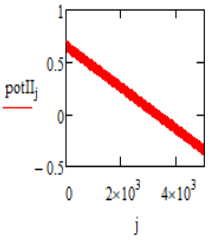
$\alpha 1 := 0.5 \qquad \log(KI_r) = 0.75$

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

$KI_1 = 5.623$

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





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

$z := 1.000000500$

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

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

z e kataliticki parametar vo ovoj model povrzan so hemiska regeneracija na reaktant od vtor elektrohemiski cekor

$x := 0.001$

$$\Psi I_{1,r} := \frac{KI_r \cdot e^{-\alpha 1 \cdot \Phi I_1}}{1 + KI_r \cdot \frac{2}{\sqrt{\pi \cdot 50}} \cdot M1_1 \cdot e^{-\alpha 1 \cdot \Phi I_1} + KI_r \cdot \frac{2}{\sqrt{\pi \cdot 50}} \cdot e^{\Phi I_1 \cdot (1-\alpha 1)} \cdot M1_1}$$

$$\Psi II_{1,r} := \frac{KII \frac{2}{\sqrt{\pi \cdot 50}} \cdot e^{-\alpha 2 \cdot \Phi II_1} \cdot \Psi I_{1,r} \cdot M1_1}{1 + \frac{1 \cdot B_1}{(\sqrt{z})} KII \cdot e^{1 \cdot \Phi II_1 \cdot (-\alpha 2)} + \frac{1 \cdot B_1}{(\sqrt{z})} KII \cdot e^{1 \cdot \Phi II_1 \cdot (1-\alpha 2)}}$$

$\Psi I_{1,1} = 1.081 \times 10^{-6}$

$\Psi II_{1,1} = 0$

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

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

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

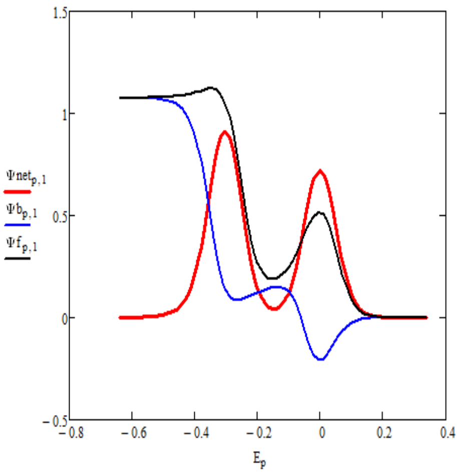
$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$

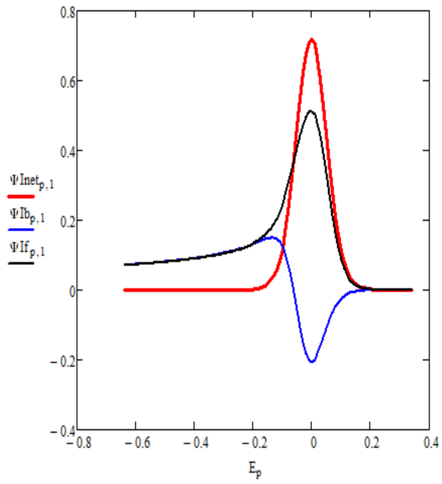
$\Psi If_{p,r} := \Psi I_{(p+1) \cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50 \cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

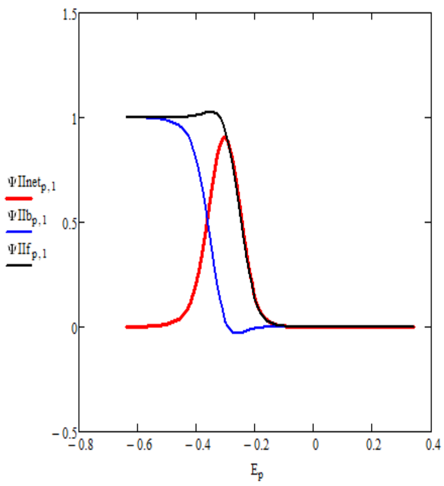
$\Psi IIb_{p,r} := \Psi II_{50 \cdot p+25,r}$ $\Psi IIf_{p,r} := \Psi II_{(p+1)}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

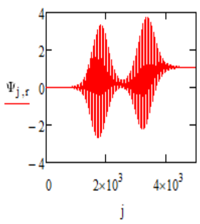
$E_p := EsI - p \cdot dE$

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









$\Psi f_{p,1} =$

$9.208 \cdot 10^{-6}$
$1.322 \cdot 10^{-5}$
$1.931 \cdot 10^{-5}$
$2.836 \cdot 10^{-5}$
$4.175 \cdot 10^{-5}$
$6.155 \cdot 10^{-5}$
$9.078 \cdot 10^{-5}$
$1.339 \cdot 10^{-4}$

$\Psi b_{p,1} =$

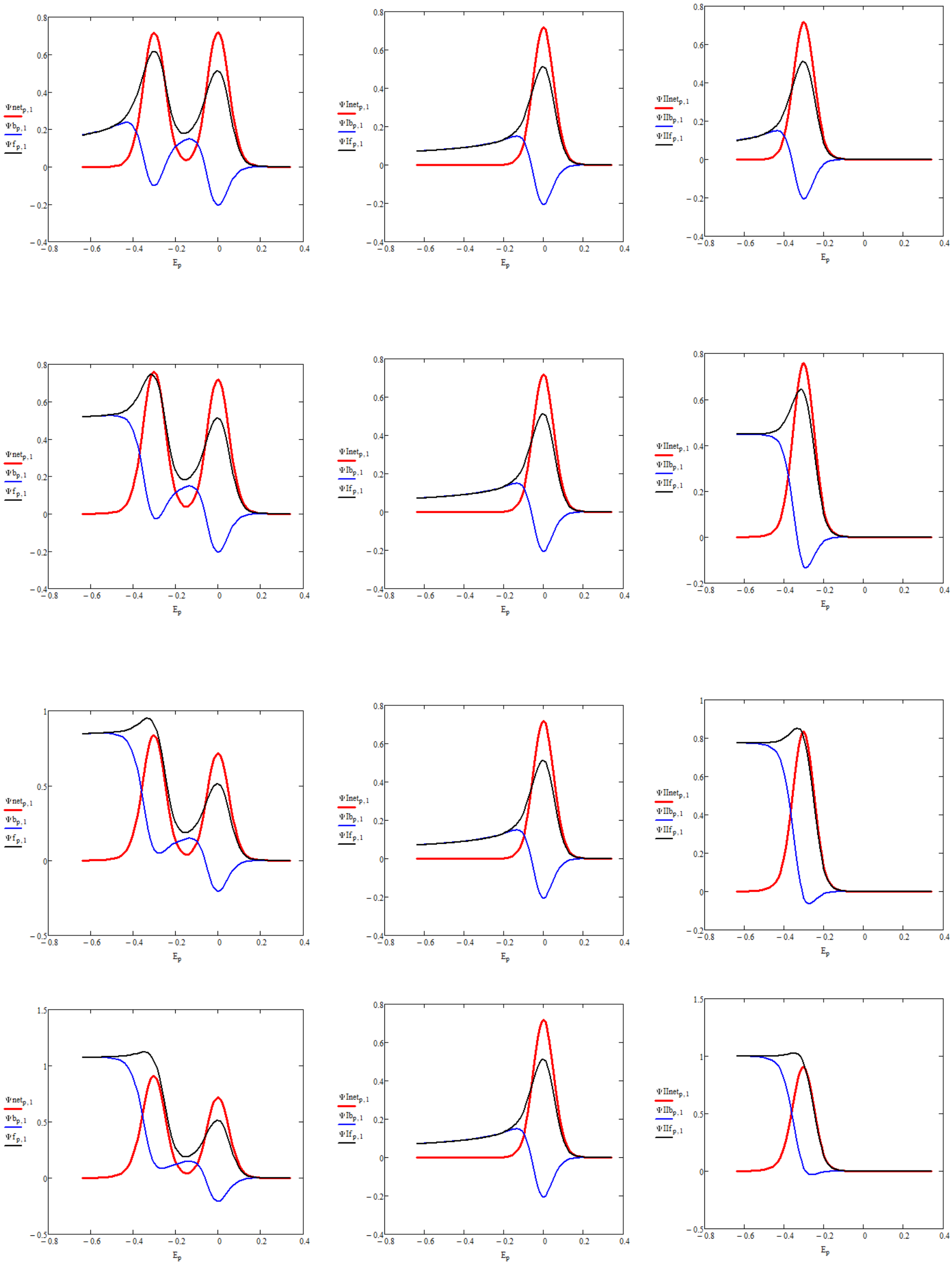
$-1.879 \cdot 10^{-6}$
$-3.312 \cdot 10^{-6}$
$-5.159 \cdot 10^{-6}$
$-7.781 \cdot 10^{-6}$
$-1.16 \cdot 10^{-5}$
$-1.721 \cdot 10^{-5}$
$-2.546 \cdot 10^{-5}$
$-3.762 \cdot 10^{-5}$
[illegible]

$\Psi net_{p,1} =$

$1.109 \cdot 10^{-5}$
$1.654 \cdot 10^{-5}$
$2.447 \cdot 10^{-5}$
$3.614 \cdot 10^{-5}$
$5.335 \cdot 10^{-5}$
$7.875 \cdot 10^{-5}$
$1.162 \cdot 10^{-4}$
[illegible]

$E_p =$

0.34
0.33
0.32
0.31
0.3
0.29
0.28



Ψnet p,1
Ψb p,1
Ψf p,1
E p
ΨInet p,1
ΨIb p,1
ΨIf p,1
E p
ΨIInet p,1
ΨIIb p,1
ΨIIf p,1
E p
Ψnet p,1
Ψb p,1
Ψf p,1
E p
ΨInet p,1
ΨIb p,1
ΨIf p,1
E p
ΨIInet p,1
ΨIIb p,1
ΨIIf p,1
E p
Ψnet p,1
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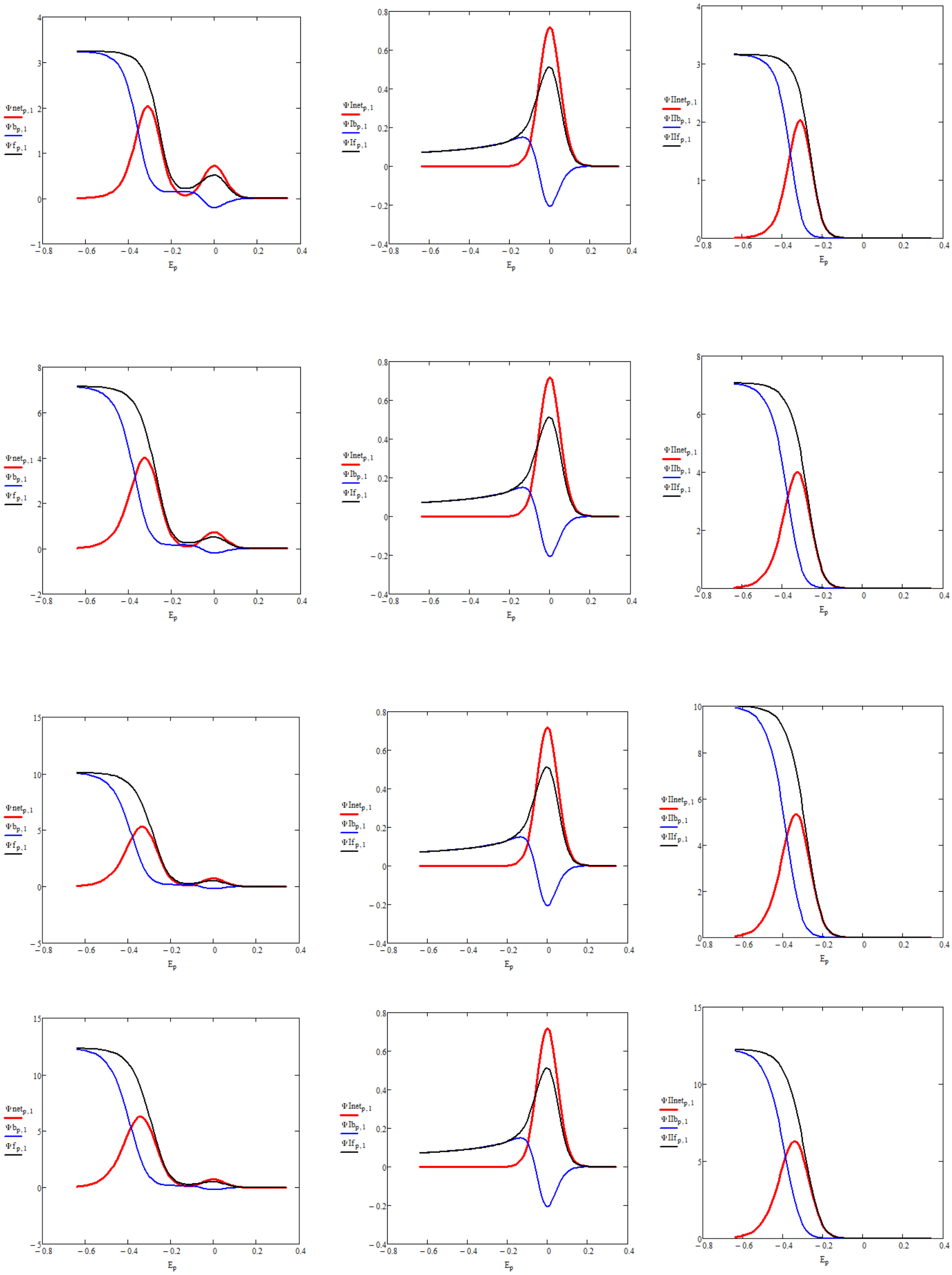
Ψnet p,1
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Ψf p,1
ΨInet p,1
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ΨIf p,1
ΨIInet p,1
ΨIIb p,1
ΨIIf p,1
E p

REFERENCES

1. R. Gulaboski, E. S. Ferreira, C. M. Pereira, M. N. D. S. Cordeiro, A. Garau, V. Lippolis, A. F. Silva, ***J. Phys. Chem. C*** 112 (2008) 153-161
2. R. Gulaboski, V. Mirceski, M. Lovric, I. Bogeski, ***Electrochemistry Communications*** 7 (2005) 515-522.
3. R Gulaboski, V Mirceski, ***Macedonian Journal of Chemistry and Chemical Engineering*** 39 (2020) 153-166
4. V. Mirceski, R. Gulaboski, ***Macedonian Journal of Chemistry and Chemical Engineering*** 33 (2014), 1-12
5. V. Mirceski, R. Gulaboski, ***Journal of Solid State Electrochemistry*** 7 (2003) 157-165
6. M. Janeva, P. Kokoskarova, V. Maksimova, R. Gulaboski, ***Electroanalysis*** 31 (2019) 2488-2506
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.