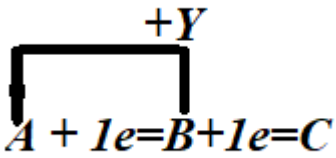
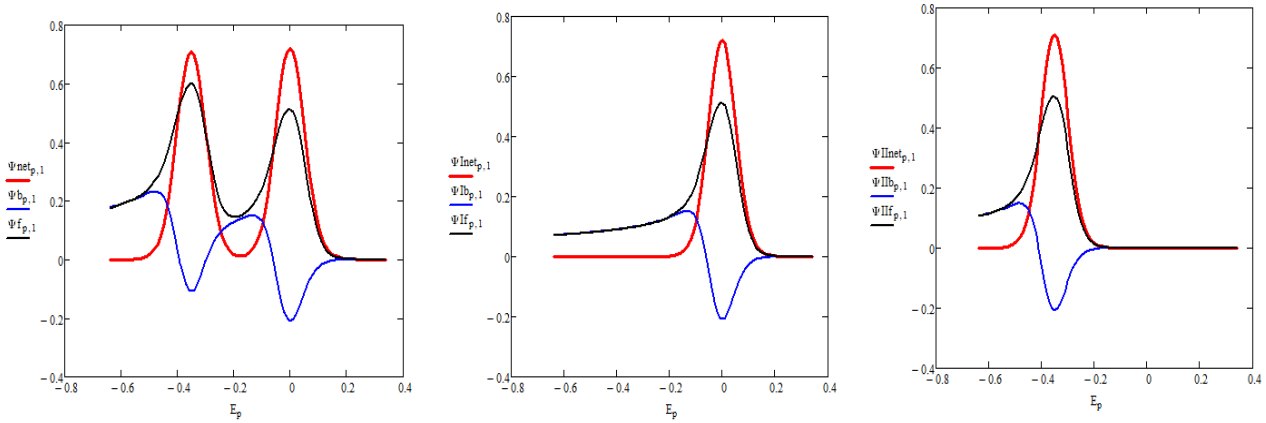
Modeling of EC'E Mechanism in Square-Wave Voltammetry



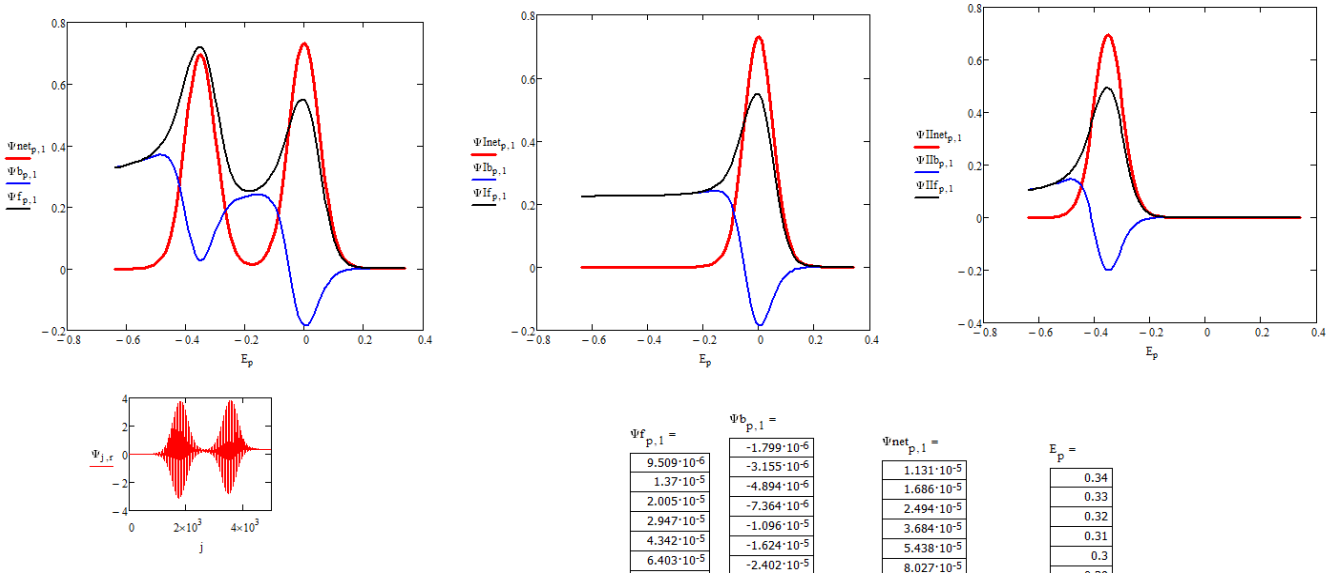
Rubin Gulaboski

Faculty of Medical Sciences, Goce Delcev University, Stip, Macedonia



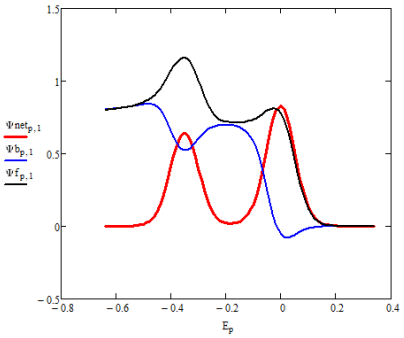
$\Psi f_{p,1}$ =	$\Psi b_{p,1}$ =	$\Psi net_{p,1}$ =	E_p =
$9.211 \cdot 10^{-6}$	$-1.874 \cdot 10^{-6}$	$1.109 \cdot 10^{-5}$	0.34
$1.322 \cdot 10^{-5}$	$-3.311 \cdot 10^{-6}$	$1.654 \cdot 10^{-5}$	0.33
$1.931 \cdot 10^{-5}$	$-5.159 \cdot 10^{-6}$	$2.447 \cdot 10^{-5}$	0.32
$2.836 \cdot 10^{-5}$	$-7.784 \cdot 10^{-6}$	$3.614 \cdot 10^{-5}$	0.31
$4.175 \cdot 10^{-5}$	$-1.161 \cdot 10^{-5}$	$5.336 \cdot 10^{-5}$	0.3
	$-1.722 \cdot 10^{-5}$		

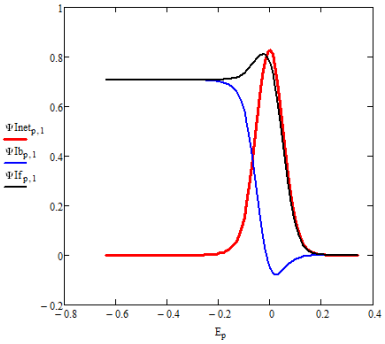
Ket1-=Ket2=5.62; **Kcat = 0.000005**

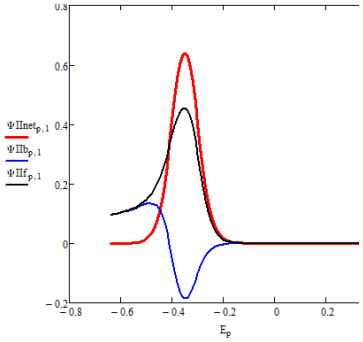


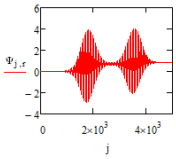
$\Psi f_{p,1}$ =	$\Psi b_{p,1}$ =	$\Psi net_{p,1}$ =	E_p =
$9.509 \cdot 10^{-6}$	$-1.799 \cdot 10^{-6}$	$1.131 \cdot 10^{-5}$	0.34
$1.37 \cdot 10^{-5}$	$-3.155 \cdot 10^{-6}$	$1.686 \cdot 10^{-5}$	0.33
$2.005 \cdot 10^{-5}$	$-4.894 \cdot 10^{-6}$	$2.494 \cdot 10^{-5}$	0.32
$2.947 \cdot 10^{-5}$	$-7.364 \cdot 10^{-6}$	$3.684 \cdot 10^{-5}$	0.31
$4.342 \cdot 10^{-5}$	$-1.096 \cdot 10^{-5}$	$5.438 \cdot 10^{-5}$	0.3
$6.403 \cdot 10^{-5}$	$-1.624 \cdot 10^{-5}$	$8.027 \cdot 10^{-5}$	
	$-2.402 \cdot 10^{-5}$		

Kcat = 0.05









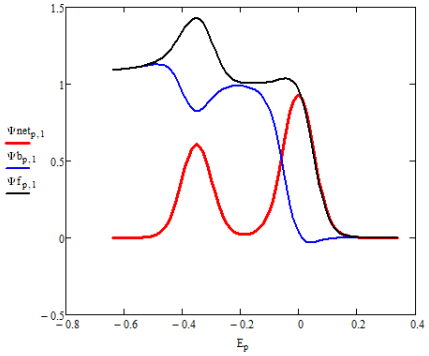
$\Psi f_{p,1}$ =
$1.199 \cdot 10^{-5}$
$1.757 \cdot 10^{-5}$
$2.589 \cdot 10^{-5}$
$3.819 \cdot 10^{-5}$
$5.635 \cdot 10^{-5}$
$8.315 \cdot 10^{-5}$
$1.227 \cdot 10^{-4}$

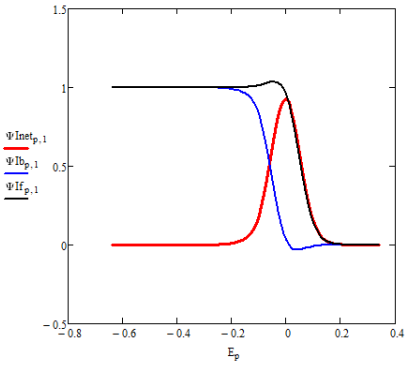
$\Psi b_{p,1}$ =
$-1.224 \cdot 10^{-6}$
$-2.038 \cdot 10^{-6}$
$-3.078 \cdot 10^{-6}$
$-4.569 \cdot 10^{-6}$
$-6.754 \cdot 10^{-6}$
$-9.972 \cdot 10^{-6}$
$-1.472 \cdot 10^{-5}$

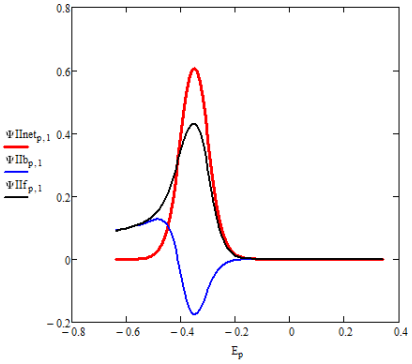
$\Psi net_{p,1}$ =
$1.321 \cdot 10^{-5}$
$1.961 \cdot 10^{-5}$
$2.896 \cdot 10^{-5}$
$4.275 \cdot 10^{-5}$
$6.31 \cdot 10^{-5}$
$9.313 \cdot 10^{-5}$

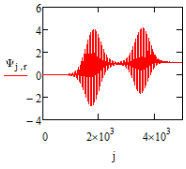
E_p =
0.34
0.33
0.32
0.31
0.3
0.29

Kcat=0.5









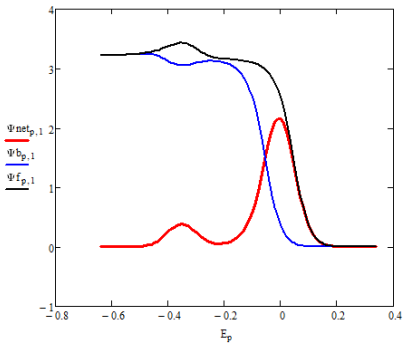
$\Psi f_{p,1}$ =
$1.44 \cdot 10^{-5}$
$2.121 \cdot 10^{-5}$
$3.13 \cdot 10^{-5}$
$4.618 \cdot 10^{-5}$
$6.815 \cdot 10^{-5}$

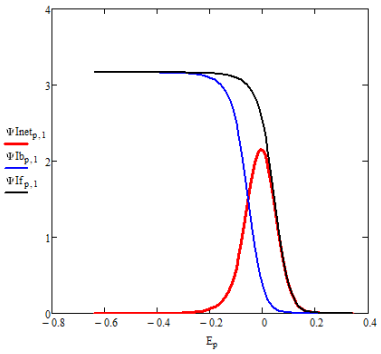
$\Psi b_{p,1}$ =
$-7.566 \cdot 10^{-7}$
$-1.216 \cdot 10^{-6}$
$-1.813 \cdot 10^{-6}$
$-2.679 \cdot 10^{-6}$
$-3.955 \cdot 10^{-6}$
$-5.836 \cdot 10^{-6}$

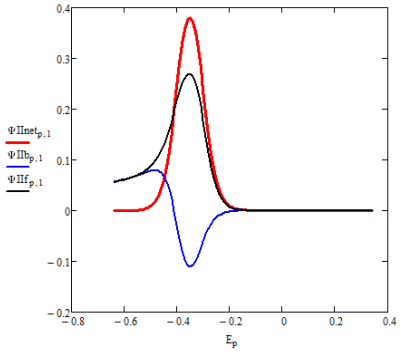
$\Psi net_{p,1}$ =
$1.516 \cdot 10^{-5}$
$2.243 \cdot 10^{-5}$
$3.311 \cdot 10^{-5}$
$4.886 \cdot 10^{-5}$
$7.211 \cdot 10^{-5}$

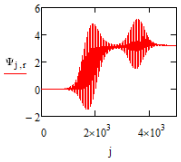
E_p =
0.34
0.33
0.32
0.31
0.3

Kcat=1.0









Ψf p,1 =

3.95·10-5
5.828·10-5
8.599·10-5
1.269·10-4
1.872·10-4

Ψb p,1 =

8.013·10-7
1.183·10-6
1.745·10-6
2.576·10-6
3.802·10-6
5.611·10-6

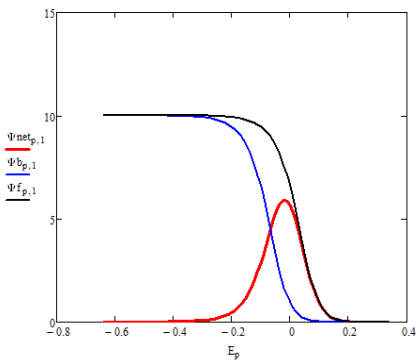
Ψnet p,1 =

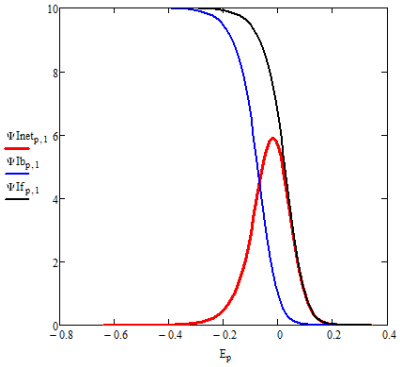
3.869·10-5
5.71·10-5
8.425·10-5
1.243·10-4
1.834·10-4

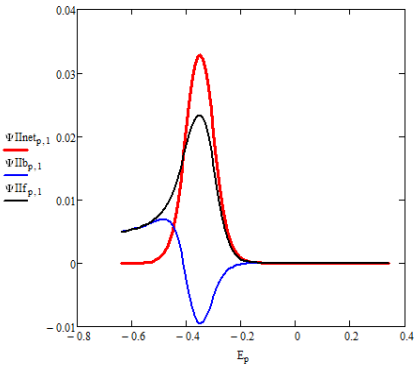
Ep =

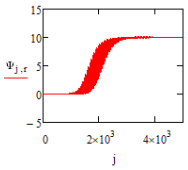
0.34
0.33
0.32
0.31
0.3

Kcat=10









Ψf p,1 =

1.246·10-4
1.837·10-4
2.709·10-4
3.994·10-4
5.887·10-4

Ψb p,1 =

2.547·10-6
3.759·10-6
5.547·10-6
8.186·10-6
1.208·10-5
1.783·10-5

Ψnet p,1 =

1.22·10-4
1.8·10-4
2.654·10-4
3.912·10-4
5.766·10-4

Ep =

0.34
0.33
0.32
0.31
0.3

Kcat=100

TWO STEP DIFFUSIONAL EC'E Mechanism in SWV--
this is EE diffusional mechanism with regenerative irreversible reaction associated with the product of first electrode transformation in which λ regenerative chemical parameter is very low

$EsI := 0.35 \quad \Delta E := 1 \quad dE := 0.01 \quad Esw := 0.05 \quad EsII := 0.7 \quad r := 1..1$

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

$KII := 10^{1}$

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

$\alpha 2 := 0.5$

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

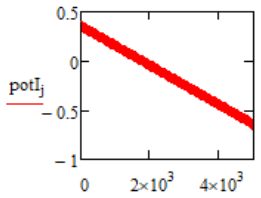
1

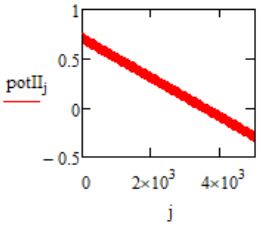
$$potI_j := EsI + Esw - \left[\left(ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right)\cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - dE\right]$$

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

$KI_1 = 10$

λ
n





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

$A_j := \left(1 - erf$

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

$x := 0.001$

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

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

$\Psi I_{1,1} = 1.085\times 10^{-5}$

$\Psi II_{1,1} = 1.308\times 10^{-12}$

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

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

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

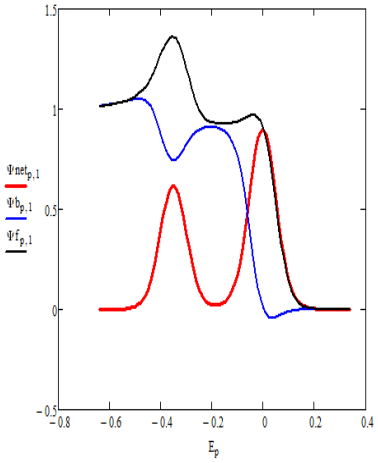
$p := 1..\left(\frac{\Delta E}{dE}\right) - 1$

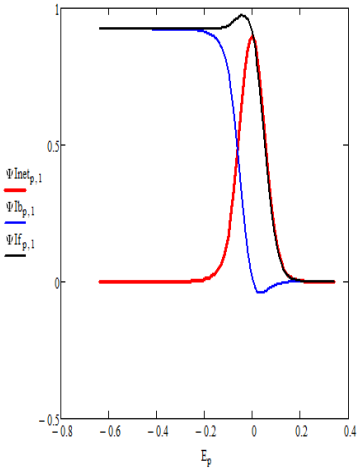
$\Psi If_{p,r} := \Psi I_{(p+1)\cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50\cdot p+2,r}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

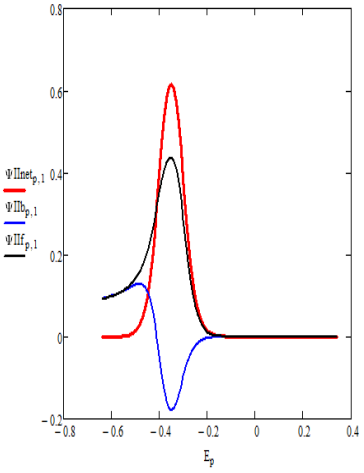
$\Psi IIb_{p,r} := \Psi II_{50\cdot p+25,r}$ $\Psi IIf_{p,r} := \Psi II_{(p+1),r}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

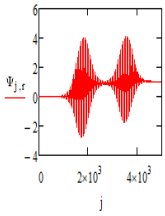
$E_p := EsI - p\cdot dE$

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









$\Psi f_{p,1} =$

$1.371\cdot10^{-5}$
$2.017\cdot10^{-5}$
$2.976\cdot10^{-5}$
$4.391\cdot10^{-5}$
$6.48\cdot10^{-5}$
$9.563\cdot10^{-5}$
$1.411\cdot10^{-4}$
$2.082\cdot10^{-4}$
$3.072\cdot10^{-4}$
$4.533\cdot10^{-4}$
$6.686\cdot10^{-4}$
$9.862\cdot10^{-4}$
$1.454\cdot10^{-3}$
$2.144\cdot10^{-3}$
$3.159\cdot10^{-3}$
...

$\Psi b_{p,1} =$

$-8.812\cdot10^{-7}$
$-1.429\cdot10^{-6}$
$-2.136\cdot10^{-6}$
$-3.159\cdot10^{-6}$
$-4.664\cdot10^{-6}$
$-6.882\cdot10^{-6}$
$-1.016\cdot10^{-5}$
$-1.498\cdot10^{-5}$
$-2.211\cdot10^{-5}$
$-3.261\cdot10^{-5}$
$-4.809\cdot10^{-5}$
$-7.092\cdot10^{-5}$
$-1.046\cdot10^{-4}$
$-1.541\cdot10^{-4}$
$-2.27\cdot10^{-4}$
$-3.341\cdot10^{-4}$
$-4.915\cdot10^{-4}$
$-7.221\cdot10^{-4}$
$-1.059\cdot10^{-3}$
$-1.55\cdot10^{-3}$
$-2.262\cdot10^{-3}$
$-3.285\cdot10^{-3}$

$\Psi net_{p,1} =$

$1.459\cdot10^{-5}$
$2.16\cdot10^{-5}$
$3.189\cdot10^{-5}$
$4.707\cdot10^{-5}$
$6.946\cdot10^{-5}$
$1.025\cdot10^{-4}$
$1.513\cdot10^{-4}$
$2.232\cdot10^{-4}$
$3.293\cdot10^{-4}$
$4.859\cdot10^{-4}$
$7.167\cdot10^{-4}$
$1.057\cdot10^{-3}$
$1.559\cdot10^{-3}$
$2.298\cdot10^{-3}$
$3.386\cdot10^{-3}$
...

$E_p =$

0.34
0.33
0.32
0.31
0.3
0.29
0.28
0.27
0.26
0.25
0.24
0.23
0.22
0.21
0.2
...

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.

23. Stanoeva-Petreska, V. Markovski, V. Mirceski, M. Hoth, and R. Kappl, Rubin Gulaboski, I Bogeski, P Kokoskarova, HH Haeri, S Mitrev, M Stefova, J Marina, New insights into the chemistry of Coenzyme Q-0: A voltammetric and spectroscopic study. ***Bioelectrochem***. 111 (2016) 100-108