Theory of Square-wave Voltammetry of Diffusional Two-Step Mechanisms in which The Second Electrode Reaction is Coupled with Reversible Chemical Step-Diffusional EECrev Mechanism

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TWO STEP DIFFUSIONAL
EECrev Mechanism in
SWV

$EsI := 0.2$ $\Delta E := 0.8$ $dE := 0.01$ $Esw := 0.05$ $EsII := 0.5$ $r := 1..1$

$n := 2$ $F := 96500$ $R := 8.314$ $T := 298.15$ $KI_r := 10^{1.65 \cdot r}$

$KII := 10^{0.65}$

KI = ks1/(Df)0.5 ---e konst na brz na prenos na elektroni kaj prviot elektroden cekor od EECrev reakcija
KII = ks2/(Df)0.5 e konst na brzina na prenos na elektroni kaj vtoriot elektroden cekor od EECrev reakcija

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

$\alpha 2 := 0.5$

$\alpha 1 := 0.5$ $\log(KI_r) =$ 1.65

$\gamma := \frac{kc}{f}$

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

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

$KI_1 = 44.668$

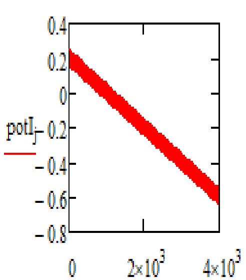
$\gamma := 00.1000001000001$

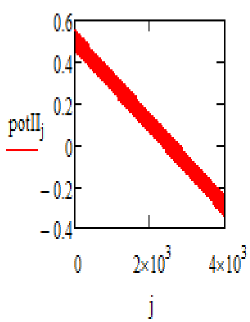
Ova γ e bezdimenzionalen kineticki parametar na hemiska reakcija definiran kako
γ = ε/f = (kf+kb)/f

U e konstanta na ramnoteza definirana kako U = kf/kb

$U := 10.105100100000010001$

kf-konst na brzina na direktna hemiska reakcija
kb-konst na brzina na povratna hemiska reakcija





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

Mechanism

Ox(aq) + 1e- = Red1(aq) +1- =Red2(aq) + Y ⇄ Z

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

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

$x := 0.001$

$$\Psi I_{1,r} := \mathrm{root}\left[\left[1+\frac{KI_r\cdot e^{-\alpha 1\cdot \Phi I_1}}{\sqrt{\pi\cdot 50}\cdot 0.5}\cdot\left(1+e^{\Phi I_1}\right)\right]\cdot x-\frac{KI_r}{\sqrt{\pi\cdot 50}\cdot 0.5}\cdot e^{(1-\alpha 1)\cdot \Phi I_1}\cdot\left[\frac{x\cdot\frac{KII\cdot e^{-\alpha 2\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}\cdot 0.5}}{1+\frac{KII\cdot e^{-\alpha 2\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}\cdot 0.5}\cdot\left(1+e^{\Phi II_1}\right)}\right]-KI_r\cdot e^{-\alpha 2\cdot \Phi I_1},x\right]$$

$$UII_{1,r} := \frac{\Psi I_{1,r}\cdot\frac{KII\cdot e^{-\alpha 2\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}\cdot 0.5}}{1+\frac{KII\cdot e^{-\alpha 2\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}\cdot 0.5}\cdot\left(1+e^{\Phi II_1}\right)}$$

$$\Psi II_{1,r} := \frac{1KII\cdot e^{-\alpha 2\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}\cdot 0.5+1KII\cdot e^{-\alpha 2\cdot \Phi II_1}\cdot\left(1+e^{\Phi II_1}\right)}\cdot \Psi I_{1,r}+\frac{\frac{UKII}{1+U}\cdot e^{(-\alpha 2)\cdot \Phi II_1}-\frac{KII\cdot e^{-\alpha 2\cdot \Phi II_1}}{1}\cdot 0}{\sqrt{\pi\cdot 50}\cdot 0.5+KII\cdot e^{-\alpha 2\cdot \Phi II_1}\cdot\left(1+e^{\Phi II_1}\right)+\frac{U\cdot KII}{(1+U)\cdot\sqrt{\pi\cdot 50}\cdot 0.5}\cdot e^{(1-\alpha 2)\cdot \Phi II_1}\cdot M1_1}+\frac{\frac{1\gamma}{1+U}\cdot e^{(1-\alpha 2)\cdot \Phi II_1}\cdot 0}{\sqrt{\pi\cdot 50}\cdot 0.5+KII\cdot e^{-\alpha 2\cdot \Phi II_1}\cdot\left(1+e^{\Phi II_1}\right)+\frac{\gamma}{1+U}\cdot e^{(1-\alpha 2)\cdot \Phi II_1}\cdot M_1}$$

$\Psi I_{1,1} = 2.206\times 10^{-8}$

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

$x := 0.001$

$$\Psi I_{j,r} := \mathrm{root}\left[x-\frac{KI_r\cdot e^{-\alpha 1\cdot \Phi I_j}}{M1_1}\cdot\left[1-\left[\frac{2}{\sqrt{\pi\cdot 50}}\cdot\left(1+e^{\Phi I_j}\right)\cdot\left[x+\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot M1_{j-i+1}\right)\right]+\frac{e^{\Phi I_j}}{\sqrt{\pi\cdot 50}\cdot 0.5}\cdot\left[\frac{1}{1+e^{\Phi II_j}}\cdot\left[x+\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot M1_{j-i+1}\right)\right]-\frac{\sqrt{\pi\cdot 50}\cdot 0.5}{KII\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot\left(1+e^{\Phi II_j}\right)}\cdot\left[KII\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot\left[\frac{2}{\sqrt{\pi\cdot 50}}\cdot\left[x+\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot M1_{j-i+1}\right)\right]-\frac{2}{\sqrt{\pi\cdot 50}}\cdot\left(1+e^{\Phi II_j}\right)\cdot\left[\frac{\sqrt{\pi\cdot 50}\cdot 0.5\cdot x}{KI_r\cdot e^{(1-\alpha 1)\cdot \Phi I_j}}-\sqrt{\pi\cdot 50}\cdot 0.5\cdot e^{-\Phi I_j}\cdot\left[1-\frac{1}{\sqrt{\pi\cdot 50}\cdot 0.5}\cdot\left(1+e^{\Phi I_j}\right)\cdot\left[x+\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot M1_{j-i+1}\right)\right]\right]\right]\right]\right]\right]\right]\right],x\right]$$

$$\Psi II_{j,r} := \frac{0.02KII\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot 1}{\sqrt{\pi\cdot 50}\cdot 0.5+2\frac{KII}{\sqrt{\pi\cdot 50}}\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot 1\cdot\left(1+e^{\Phi II_j}\right)}\cdot\sum_{i=1}^{j}\left(\Psi I_{i,r}\cdot M1_j\right)+\frac{1KII\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot 1-\frac{\frac{2KII}{\sqrt{\pi\cdot 50}}\cdot e^{(-\alpha 2)\cdot \Phi II_j}\cdot 1}{1}\cdot\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot M1_{j-i+1}\right)-\frac{\frac{1UKII}{\gamma\cdot(1+U)}\cdot e^{(1-\alpha 2)\cdot \Phi II_j}\cdot 1}{1}\cdot\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot M1_{j-i+1}\right)-\frac{1\gamma}{1+U}\cdot e^{(1-\alpha 2)\cdot \Phi II_j}\cdot 1\cdot\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot M_{j-1+1}\right)}{1+\frac{2KII}{\sqrt{\pi\cdot 50}}\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot M1_1+\frac{1UKII}{\gamma(1+U)}\cdot e^{(1-\alpha 2)\cdot \Phi II_j}\cdot M1_1+\frac{\gamma}{1+U}\cdot e^{(1-\alpha 2)\cdot \Phi II_j}\cdot M_1\cdot 1}\cdot 1$$

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

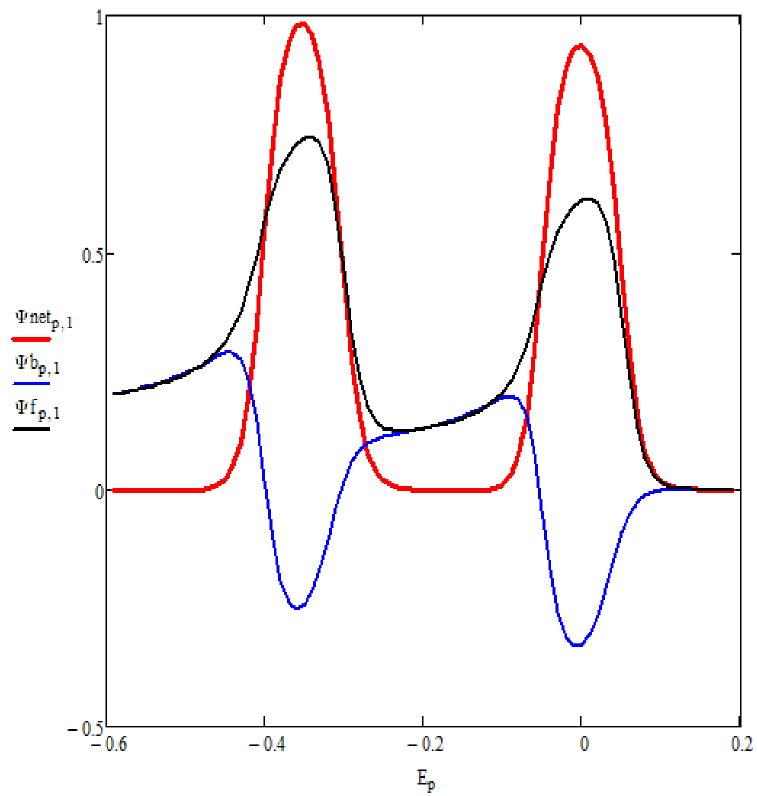
$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$

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

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

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

$E_p := EsI - p\cdot dE$



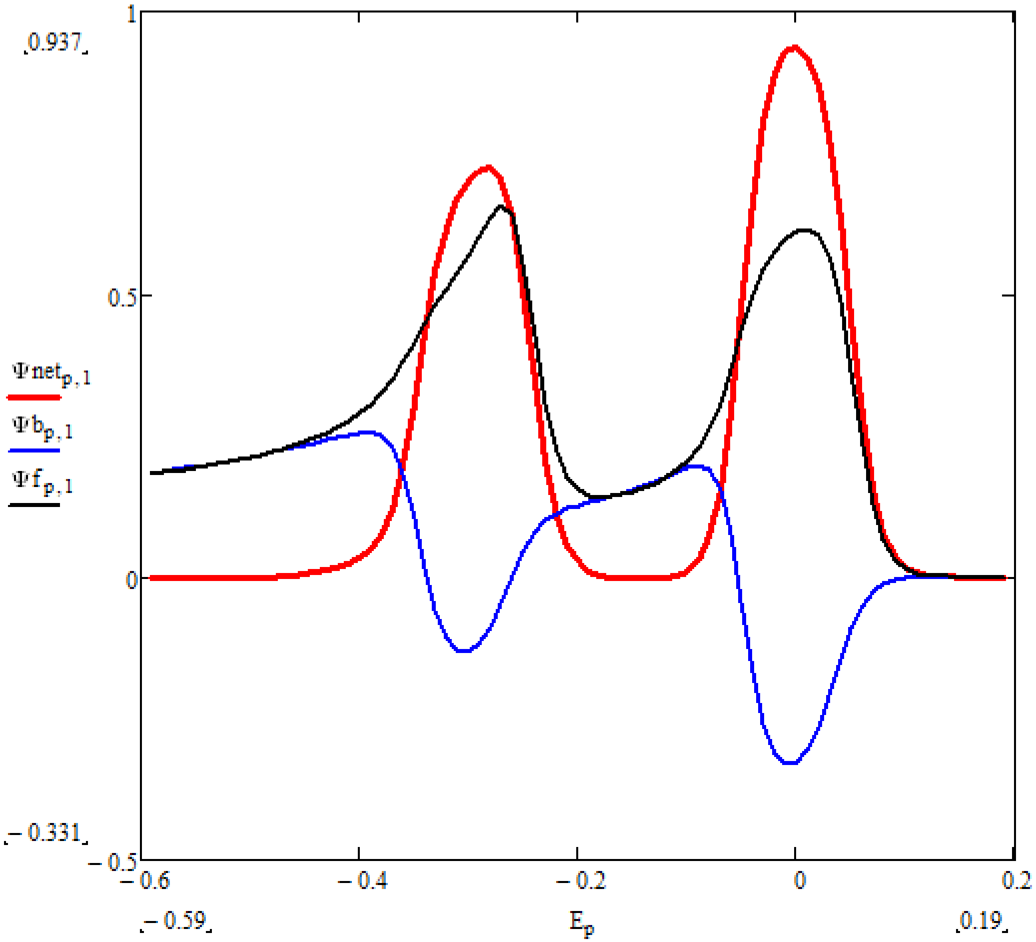
OVA E MODEL za DIFUZIONA EECreversible!!!
Koga U (U e konst na ramnoteza) e GOLEMA i γ (γ e konstana na hemiska reakcija) e MALA, togas pri isti KI i KII (ovie se bezdimenz parametri na elektronski transfer) ima ISTI voltamogrami

pr. γ = 0.00001; U = 100; KI = KII = 10, isti voltamogrami!!! isto kakosurface EE mehanizam

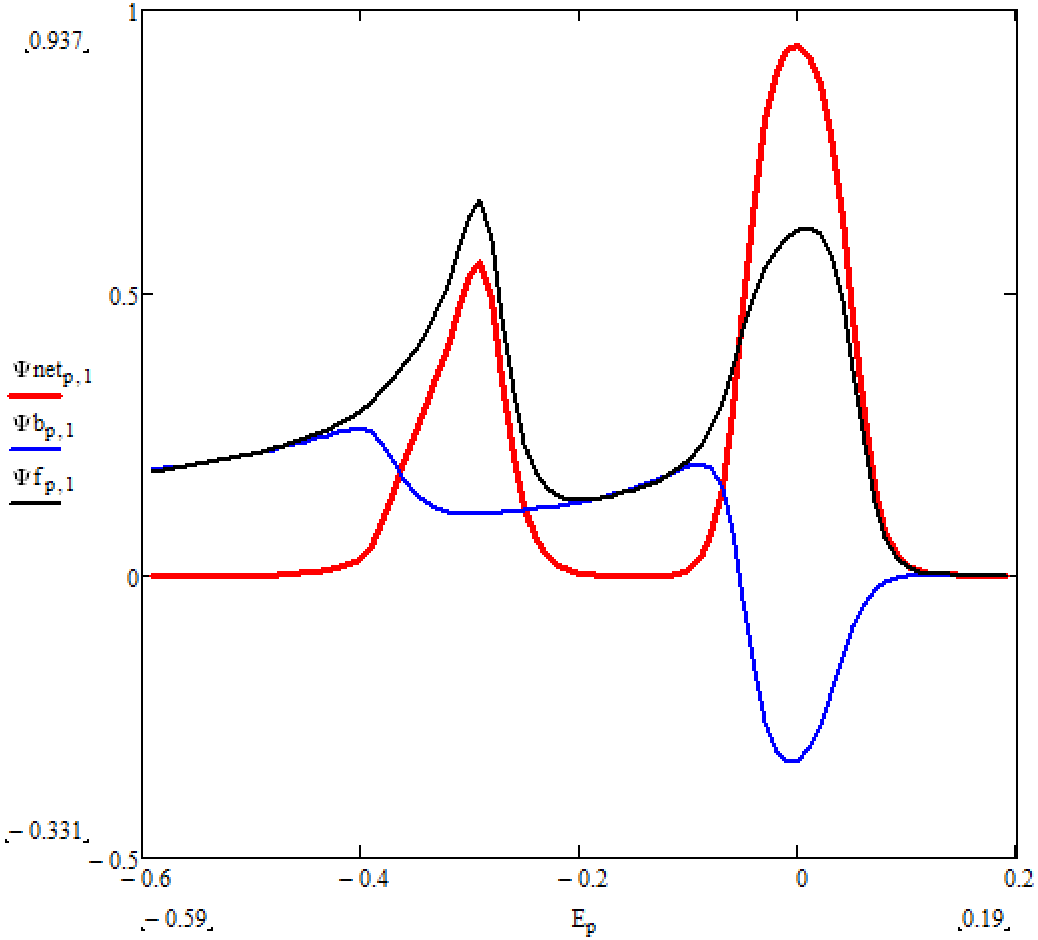
OVA E TOCHEN MEHANIZAM

$\Psi f_{p,1} =$

$1.412\cdot 10^{-5}$
$3.04\cdot 10^{-5}$
$6.602\cdot 10^{-5}$
$1.437\cdot 10^{-4}$
$3.128\cdot 10^{-4}$
$6.81\cdot 10^{-4}$
$1.482\cdot 10^{-3}$
[illegible]



Moderate
Rate of
Follow Up
Chemical
Reaction



High Rate of Reversible Follow Up Chemical Reaction

Keq is 1.0

REFERENCES

1. **Rubin Gulaboski**, Theoretical contribution towards understanding specific behaviour of "simple" protein-film reactions in square-wave voltammetry", ***Electroanalysis,*** 31 (**2019**) 545-553.

3. V. Mirceski, D. Guziejewski, L. Stojanov, **Rubin Gulaboski,** Differential Square-Wave Voltammetry, ***Analytical Chemistry*** 91 (**2019**) 14904-14910 https://pubs.acs.org/doi/abs/10.1021/acs.analchem.9b03035.

4. Rubin Gulaboski, P. Kokoskarova, S. Petkovska, Time independent methodology to assess Michaelis Menten constant by exploring electrochemical-catalytic mechanism in protein-film cyclic staircase voltammetry, ***Croat. Chem. Acta***, 91 (**2018**) 377-382.

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

6. Rubin Gulaboski, V. Markovski, and Z. Jihe, *Redox chemistry of coenzyme Q—a short overview of the voltammetric features*, ***Journal of Solid State Electrochemistry*** 20 (**2016**) 3229-3238.

7. Haeri, Haleh H. I. Bogeski, **Rubin Gulaboski,** V. Mirceski, M. Hoth, and R. Kappl, *An EPR and DFT study on the primary radical formed in hydroxylation reactions of 2,6-dimethoxy-1,4-benzoquinone.* ***Mol. Phys***. 114 (**2016**) 1856-1866.

8. V. Mirceski, D. Guzijewski and **Rubin Gulaboski**, Electrode kinetics from a single square-wave voltammograms, ***Maced. J. Chem. Chem. Eng.*** 34 (**2015**) 1-12.

9. Rubin Gulaboski and V. Mirceski, New aspects of the electrochemical-catalytic (EC') mechanism in square-wave voltammetry, ***Electrochimica Acta***, *167* (**2015**) *219-225.*

11.R Gulaboski, S Petkovska, A Time-Independent Approach to Evaluate the Kinetics of Enzyme-Substrate Reactions in Cyclic Staircase Voltammetry, ANALYTICAL & BIOANALYTICAL ELECTROCHEMISTRY 10 (5), 566-575

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

13. R. Gulaboski, V. Markovski, and Z. Jihe, Redox chemistry of coenzyme Q—a short overview of the voltammetric features, J. Solid State Electrochem.,20 (2016) 3229-3238.

14. V. Mirceski, D. Guzijewski and R. Gulaboski, Electrode kinetics from a single square-wave voltammograms, Maced. J. Chem. Chem. Eng. 34 (2015) 1-12.

15. V. Mirceski, D. Guzijewski and R. Gulaboski, Electrode kinetics from a single square-wave voltammograms, Maced. J. Chem. Chem. Eng. 34 (2015) 1-12. 7. Gulaboski and V. Mirceski, New aspects of the electrochemical-catalytic (EC’) mechanism in square-wave voltammetry, Electrochim. Acta, 167 (2015) 219-225.

16. V. Mirceski, Valentin and R. Gulaboski, Recent achievements in square-wave voltammetry (a review). Maced. J. Chem. Chem. Eng. 33 (2014). 1-12.

17. V. Mirceski, R. Gulaboski, M. Lovric, I. Bogeski, R. Kappl and M. Hoth, Square-Wave Voltammetry: A Review on the Recent Progress, Electroanal. 25 (2013) 2411–2422.

18. R. Gulaboski, I. Bogeski, V. Mirčeski, S. Saul, B. Pasieka, H. H. Haeri, M. Stefova, J. Petreska Stanoeva, S. Mitrev, M. Hoth and R. Kappl, "Hydroxylated derivatives of dimethoxy-1,4-benzoquinone as redox switchable earth-alkaline metal ligands and radical scavengers Sci. Reports, 3 (2013) 1-8.

19. V. Mirčeski and R. Gulaboski, "Surface Catalytic Mechanism in Square-Wave Voltammetry", Electroanal. 13 (2001) 1326-1334.

20. V. Mirčeski, R. Gulaboski and I. Kuzmanovski, "Mathcad-a Tool for Numerical Calculation of Square-Wave Voltammograms", Bull. Chem. Technol. Macedonia, 18 (1999) 57-64.

21. Scholz, F.; Schroeder U.; Gulaboski R. Electrochemistry of Immobilized Particles and Droplets Springer Verlag, New York, pp. 1-269, 2005.

22. Gulaboski R. in Electrochemical Dictionary, A J. Bard, G. Inzelt, F. Scholz (eds.) Springer, 2nd Edition in 2012.

23. I. Bogeski, R. Kappl, C. Kumerow, R. Gulaboski, M. Hoth and B. A. Niemeyer "Redox regulation of calcium ion channels: Chemical and physiological aspects, Cell Calcium 50 (2011) 407-423.

24. V. Mirceski, S. Komorsky Lovric, M. Lovric, Square-wave voltammetry, Theory and Application, Springer 2008 (F. Scholz, Ed.)

25. Rubin Gulaboski, **Theoretical Contribution Towards Understanding Specific Behaviour of "Simple" Protein-film Reactions in Square-wave Voltammetry**, **Electroanalysis** 2018, https://doi.org/10.1002/elan.201800739

26. R. Gulaboski, V. Mirčeski, M. Lovrić and I. Bogeski, "Theoretical study of a surface electrode reaction preceded by a homogeneous chemical reaction under conditions of square-wave voltammetry**." Electrochem. Commun. 7 (2005) 515-522.**

28. R. Gulaboski, C. M. Pereira. M. N. D. S. Cordeiro, I. Bogeski, E. Fereira, D. Ribeiro, M. Chirea and A. F. Silva, "Electrochemical study of ion transfer of acetylcholine across the interface of water and a lipid-modified 1,2-dichloroethane " J. Phys. Chem. B 109 (2005) 12549-12559.

29. F. Scholz and R. Gulaboski "Determining the Gibbs energy of ion transfer across water-organic liquid interfaces with three-phase electrodes ." Chem. Phys. Chem., 6 (2005) 1-13.

31. V. Mirčeski and R. Gulaboski, "A Theoretical and Experimental Study of Two-Step Quasireversible Surface Reaction by Square-Wave Voltammetry" Croat. Chem. Acta 76 (2003) 37-48.

33. **R. Gulaboski,** F Borges, CM Pereira, M Cordeiro, J Garrido, AF Silva, Voltammetric insights in the transfer of ionizable drugs across biomimetic membranes-Recent achievements Combinatorial chemistry & high throughput screening 10 (2007), 514-526.

34. **Rubin Gulaboski**, Fernanda Borges, CM Pereira, M. N. D. S Cordeiro, J Garrido, AF Silva, ***Combinatorial chemistry & high throughput screening*** 10 (2007), 514-526

35. V Mirceski, **R Gulaboski**, Simple Electrochemical Method for Deposition and Voltammetric Inspection of Silver Particles at the Liquid− Liquid Interface of a Thin-Film Electrode, The Journal of Physical Chemistry B 110 (2006), 2812-2820

36. **R Gulaboski**, V Markovski, Z Jihe, Redox chemistry of coenzyme Q—a short overview of the voltammetric features, Journal of Solid State Electrochemistry 20 (2016), 3229-3238

37. **Rubin Gulaboski**, Valentin Mirceski, Milivoj Lovric, Square-wave protein-film voltammetry: new insights in the enzymatic electrode processes coupled with chemical reactions, ***Journal of Solid State Electrochemistry***, 23 (**2019)** 2493-2506**.**

38. V Mirčeski, **Rubin Gulaboski**, F Scholz, ***Electrochemistry Communications*** 4 (2002), 814-819