Electrochemical fingerprints of sequential double-regenerative enzymatic mechanisms in protein-film voltammetry

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A. Mathcad Simulation Protocol in Square-Wave Voltammetry

TWO STEP SURFACE EC'EC" Mechanism in SWV

$EsI := -0.4 \quad \Delta E := 1 \quad dE := 0.01 \quad Esw := 0.05$

$EsII := -0.7$

$r := 1..1$

$KI_r := 10^{-0.2r}$

$KII := 10^{0.15}$

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

$f := 10$

$kc1 := 100$

$kc2 := 200$

λ i z se definirani kako odnos na Kc1/f i kc2/f

A - 1e = B
B+Y-->A
B - 1e = C
C+Z -->B

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

$\alpha 2 := 0.5$

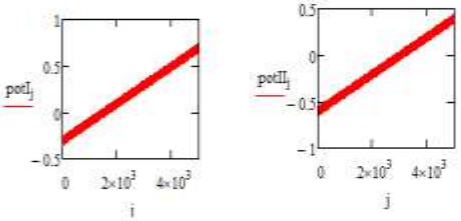
$\alpha 1 := 0.5 \qquad \log(KI_r) =$

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

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

$KI_1 = 0.631$ Dimensionless rate parameter related to first electron transfer

$KII = 1.413$ Dimensionless rate parameter related to second electron transfer



$\lambda := .001$

$\lambda = Kc.1$

Kchemical rate parameter of first regenerative reaction

$z := .5$

$z = Kc.2$

Kchemical rate parameter of second eregenerative reaction

$$A_j := e^{-\lambda\cdot\frac{j}{50}} - e^{-\lambda\cdot\frac{j+1}{50}}$$

$$B_j := e^{-z\cdot\frac{j}{50}} - e^{-z\cdot\frac{j+1}{50}}$$

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

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

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

$\Psi I_{1,1} = 5.562\times 10^{-5}$

$\Psi II_{1,1} = 2.696\times 10^{-13}$

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

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

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

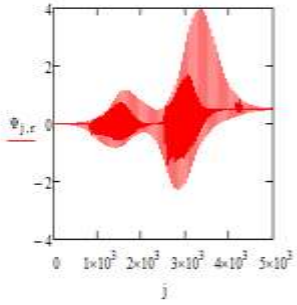
$$p := 1 .. \left(\frac{\Delta E}{dE} \right) - 1$$

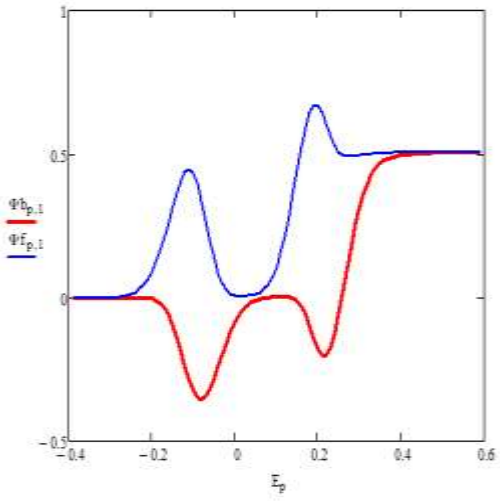
$$\Psi If_{p,r} := \Psi I_{(p+1) \cdot 50,r} \quad \Psi Ib_{p,r} := \Psi I_{50 \cdot p+2} \quad \Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$$

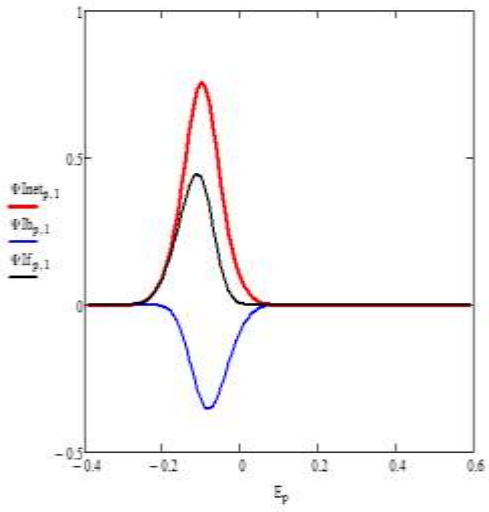
$$\Psi IIb_{p,r} := \Psi II_{50 \cdot p+25,r} \quad \Psi IIf_{p,r} := \Psi II_{(p+1) \cdot 50,r} \quad \Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$$

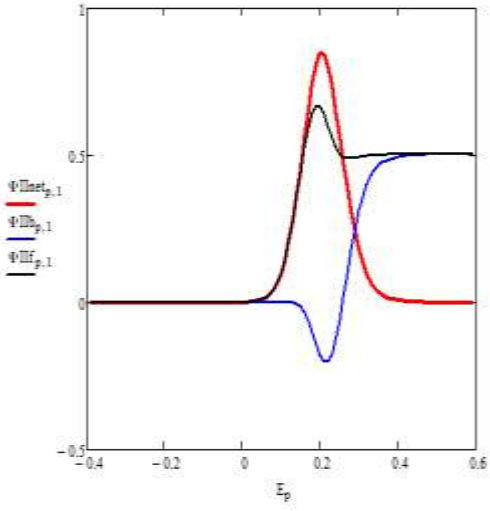
$$E_p := Esl + p \cdot dE$$

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









B. Supplementary Figures in 2D format

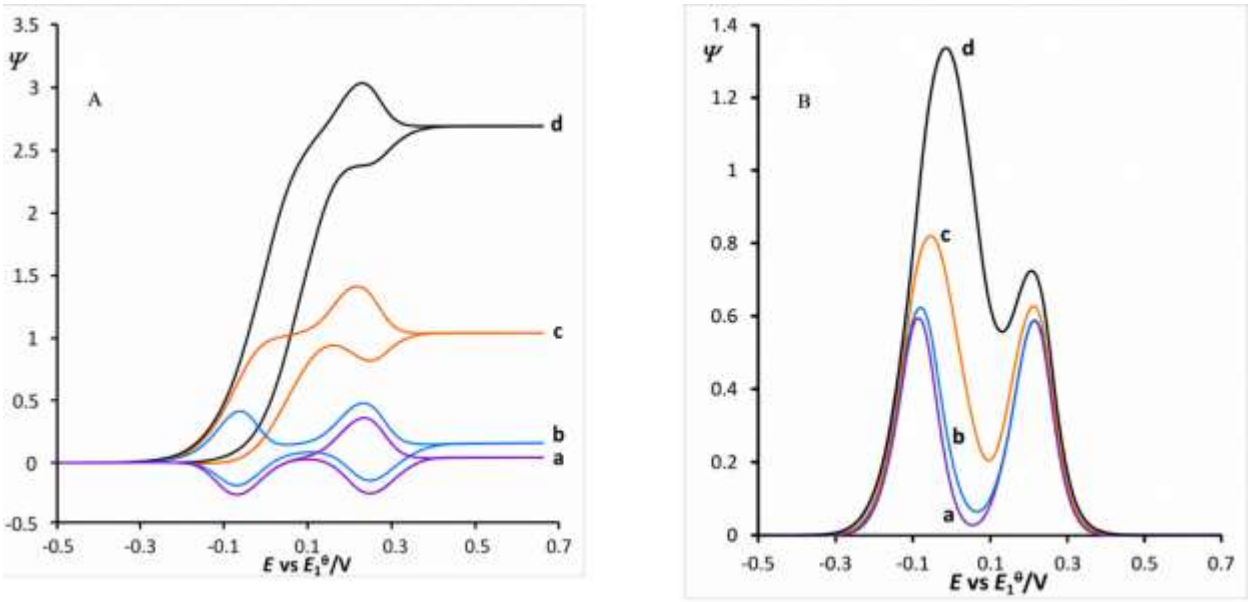


Figure S1. Two-dimensional representations of the corresponding three-dimensional plots presented in Figure 1 of the main text. All conditions are identical to those specified in Figure 1.

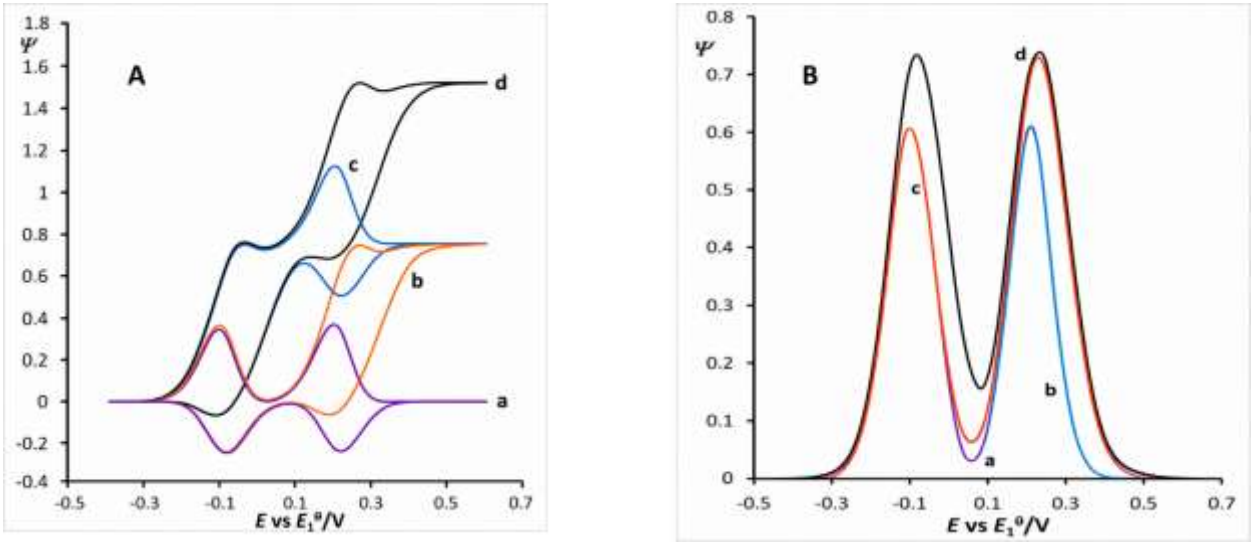


Figure S2. Two-dimensional representations of the corresponding three-dimensional plots presented in Figure 2 of the main text. All conditions are identical to those specified in Figure 2.

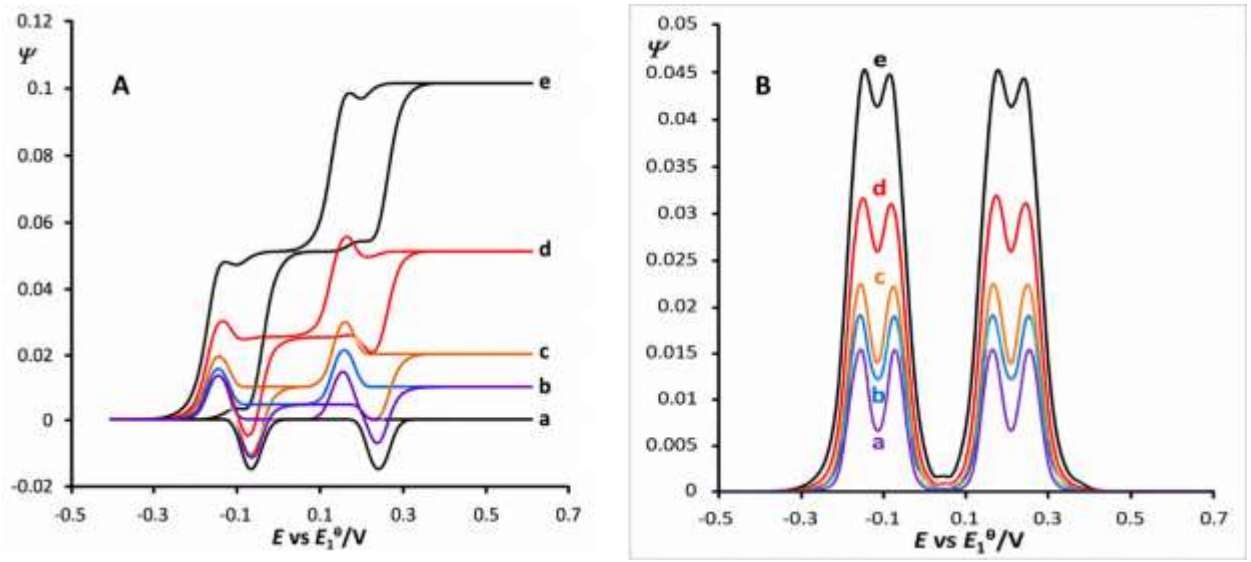


Figure S3. Two-dimensional representations of the corresponding three-dimensional plots presented in Figure 3 of the main text. All conditions are identical to those specified in Figure 3.

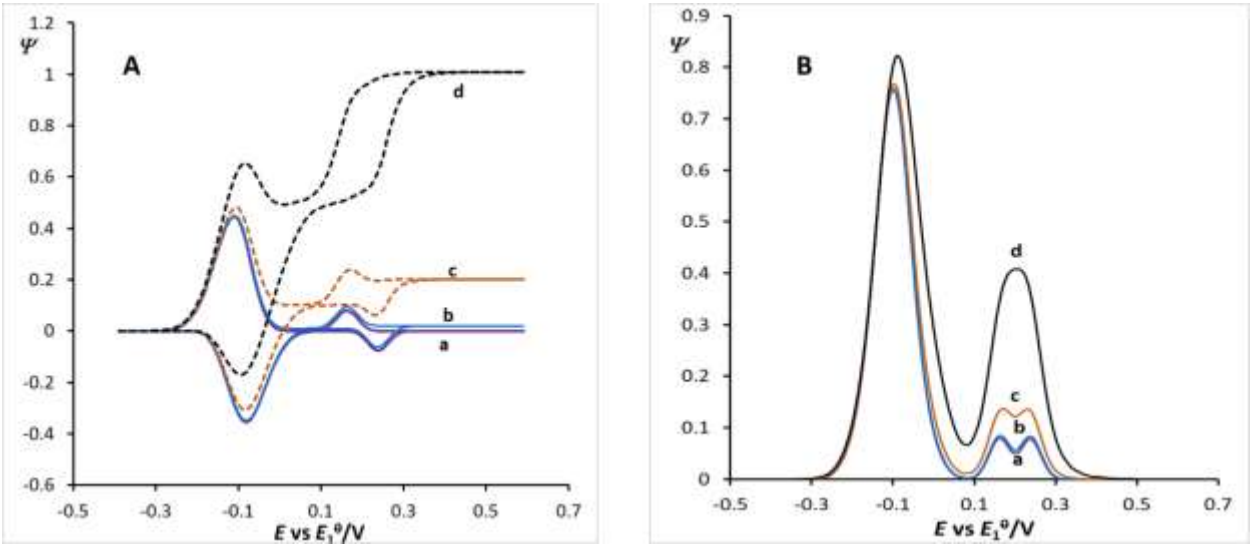


Figure S4. Two-dimensional representations of the corresponding three-dimensional plots presented in Figure 4 of the main text. All conditions are identical to those specified in Figure 4.

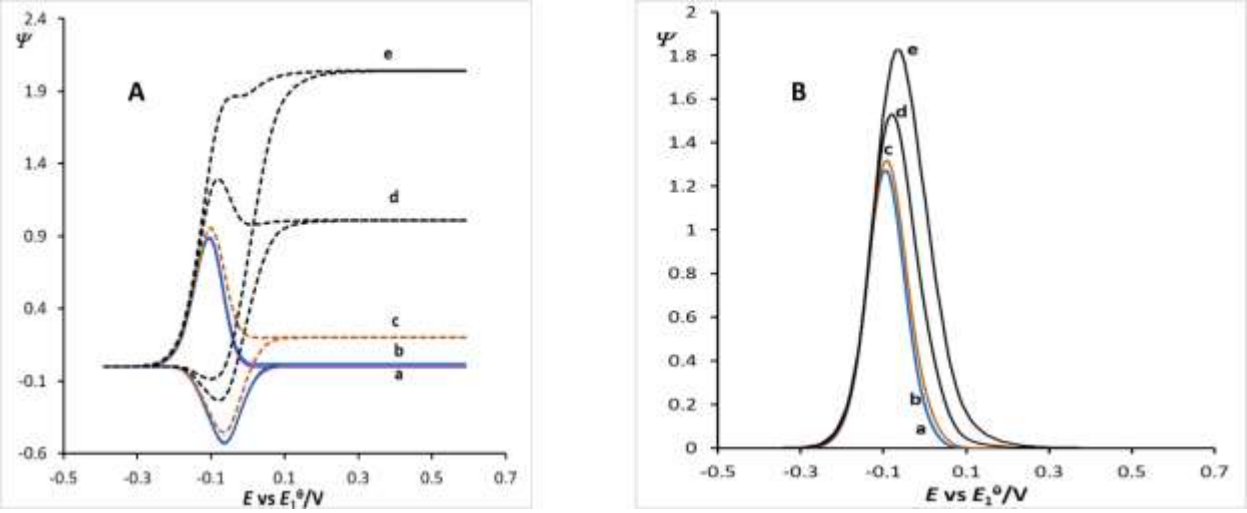


Figure S5. Two-dimensional representations of the corresponding three-dimensional plots presented in Figure 5 of the main text. All conditions are identical to those specified in Figure 5.

REFERENCES

1. V. Mirceski, S. B. Hocevar, B. Ogorevc, R. Gulaboski, I. Drangov, Diagnostics of Anodic Stripping Mechanisms under Square-Wave Voltammetry Conditions Using Bismuth Film Substrates, *Analytical Chemistry* **84** (2012) 4429-4436. https://doi.org/10.1021/ac300135x
2. R. Gulaboski, E. S. Ferreira, C. M. Pereira, M. N. D. S. Cordeiro, A. Garau, V. Lippolis, A. F. Silva, Journal of Physical Chemistry C 112 (2008) 153-161
3. V. Mirceski, M. Lovric, R. Gulaboski, Journal of Electroanalytical Chemistry 515 (2001) 91-100.
4. R Gulaboski, V Mirceski, Macedonian Journal of Chemistry and Chemical Engineering 39 (2020) 153-166
5. V. Mirceski, R. Gulaboski, Macedonian Journal of Chemistry and Chemical Engineering 33 (2014), 1-12
6. V. Mirceski, R. Gulaboski, Journal of Solid State Electrochemistry 7 (2003) 157-165
7. M. Janeva, P. Kokoskarova, V. Maksimova, R. Gulaboski, Electroanalysis 31 (2019) 2488-2506

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

9. R. Gulaboski, C.M. Pereira, M.N.D.S Cordeiro, I. Bogeski, F. Silva, Journal of Solid State Electrochemistry 9 (2005) 469-474

10. B. Sefer, R. Gulaboski, V. Mirceski, Journal of Solid State Electrochemistry 16 (2012) 2373-2381.

11. P. Kokoskarova, Rubin Gulaboski, Electroanalysis 32 (2020) 333-344.

https://doi.org/10.1002/elan.201900491

12. R. Gulaboski, C. M. Pereira, Electroanalytical Techniques and Instrumentation in Food Analysis; in Handbook of Food Analysis Instruments (2008) 379-402.

13. M. Jorge, R. Gulaboski, C. M. Pereira, M. N. D. S. Cordeiro, Journal of Physical Chemistry B 110 (2006) 12530-12538.

14. V. Mirceski, D. Guziejewski, L. Stojanov, R. Gulaboski, Analytical Chemistry 91 (2019) 14904-14910.

15. V. Mirceski, R. Gulaboski, F. Scholz, Journal of Electroanalytical Chemistry 566 (2004) 351-360.

16. 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

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

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

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

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

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

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

23. V. Mirceski, R. Gulaboski, Journal of Physical Chemistry B, 110 (2006) 2812-2820.

24. V. Mirceski, R. Gulaboski, B. Jordanoski, S. Komorsky-Lovric, Journal of Electroanalytical Chemistry, 490 (2000) 37-47.

25. R. Gulaboski, Macedonian Journal of Chemistry and Chemical Engineering 41 (2022) 151-162

26. R. Gulaboski, P. Kokoskarova, S. Petkovska, Analytical&Bioanalytical Electrochemistry, 12 (2020) 345-364.

27. V. Mirčeski, R. Gulaboski, F. Scholz, Electrochemistry Communications 4 (2002) 814-819

28. M. Jorge, R. Gulaboski, C. M. Pereira, M. N. D. S Cordeiro, Molecular Physics 104 (2006) 3627-3634.

29. R. Gulaboski, V. Mirceski, M. Lovric, Macedonian Journal of Chemistry and Chemical Engineering 40 (2021) 1-9.

30. R. Gulaboski, P. Kokoskarova, S. Risafova, J. Electroanal. Chem. 868 (2020) 114189.

31. R. Gulaboski, V. Mirceski, Journal of Solid State Electrochemistry **28** (2024) 1121-1130.

32. V. Mirceski, B. Mitrova, V. Ivanovski, N. Mitreska, A. Aleksovska, R. Gulaboski, Journal of Solid State Electrochemistry **19** (2015) 2331-2342.

33. I. Spirevska, L. Soptrajanova, R. Gulaboski, Analytical Letters **33** (2000) 919-928.

34. R. Gulaboski, B. Jordanoski, Bulletin of Chemists and Technologist of Macedonia **19** (2000) 177-181

35. R. Gulaboski, M. Lovrić, V. Mirčeski, I. Bogeski, M. Hoth, Biophysical Chemistry **137** (2008) 49-55.

36. R. Gulaboski, V. Mirčeski, S. Mitrev, Food Chemistry, **138** (2013) 116-121.

37. R. Gulaboski, V. Mirčeski, M. Lovrić, Journal of Solid State Electrochemistry **23** (2019) 2493-2506

38. V. Mirceski, R. Gulaboski, F. Scholz, Electrochemistry Communications **4** (2019) 814-819.

39. R. Gulaboski, V. Mirceski, Journal of Solid State Electrochemistry **28** (2024) 1121-1130.

40. R. Gulaboski, F Borges, C.M. Pereira, M. Cordeiro, J. Garrido, A.F. Silva, Combinatorial chemistry & high throughput screening **10** (2007), 514-526

41. Gulaboski, R.; Bogeski, I.; Kokoskarova, P.; Haeri, H. H.; Mitrev, S.; Stefova, M.; Stanoeva, J. P.; Markovski, V.; Mirčeski, V.; Hoth, M.; Kappl, R. New Insights into the Chemistry of Coenzyme Q-0: A Voltammetric and Spectroscopic Study. *Bioelectrochemistry* **2016**, *111*, 100– 108.

DOI: 10.1016/j.bioelechem.2016.05.008

42. V. Mirceski, R/ Gulaboski, I. Bogeski, M. Hoth, The Journal of Physical Chemistry C **111** (2007), 6068-6076

43. R. Gulaboski, M. Lovrić, V. Mirceski, I. Bogeski, M. Hoth, Biophysical chemistry **138** (2008), 130-137