A Unified Theory of All Mechanisms in Protein-Film Voltammetry

Pavle Apostoloski, Rubin Gulaboski

Faculty of Medical Sciences, Goce Delcev University Stip, Macedonia

$EfI := 0.8 \qquad EfII := .5 \qquad \tau := 0.05$

$EsI := -0.4 \quad \Delta E := 1.2 \qquad dE := 0.01 \qquad EsII := -0.7$

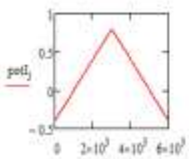
$n := 1 \qquad F := 96500 \qquad R := 8.314 \qquad T := 298.15 \qquad \Delta EI := EfI - EsI \quad KI := 10^{-1}$

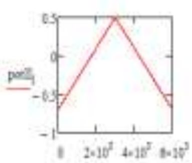
$M := 25 \qquad \Delta EII := EfII - EsII \quad KII := 10^{-1}$

$j := 1 .. 2\frac{\Delta E}{dE}\cdot 25 \qquad d := \frac{\tau}{M} \qquad \alpha 1 := 0.5 \quad \alpha 2 := 0.5$

$$potI_j := \text{if}\left[j \le \frac{\Delta E}{dE}\cdot 25, EsI + \left(\text{ceil}\left(\frac{j}{25}\right)\cdot dE - dE\right), EfI - \left[\text{ceil}\left[\frac{j - \left(\frac{\Delta E}{dE}\cdot 25\right)}{25}\right]\cdot dE - dE\right]\right]$$

$$potII_j := \text{if}\left[j \le \frac{\Delta E}{dE}\cdot 25, EsII + \left(\text{ceil}\left(\frac{j}{25}\right)\cdot dE - dE\right), EfII - \left[\text{ceil}\left[\frac{j - \left(\frac{\Delta E}{dE}\cdot 25\right)}{25}\right]\cdot dE - dE\right]\right]$$





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

ΦI and ΦII are dimensionless potentials of first and second electrode reaction, correspondingly

$$\Phi I_1 := \frac{KI\cdot e^{\alpha 1\cdot \Phi I_1}}{1 - KI\cdot e^{\alpha 1\cdot \Phi I_1}\left[\frac{-L_1}{u} + \frac{-1}{25}\left(\left(1 + \frac{e^{-\Phi I_1}}{1 + Keq}\right)\right) - \frac{1\cdot e^{-\Phi I_1}\cdot A_1}{\lambda\cdot(Keq + 1)}\right]}$$

$$\Phi II_1 := \frac{KII\cdot\frac{1}{25}\cdot e^{\alpha 2\cdot \Phi II_1}}{1 + \frac{1\cdot B_1}{(z)}KII\cdot e^{\Phi II_1\cdot \alpha 2} + \frac{1\cdot B_1}{(z)}KII\cdot e^{-\Phi II_1\cdot(1-\alpha 2)}}$$

$kc1 := 100$

$kc := 2.5$

u, λ and z are defined as
u = kc1x τ
λ = kchem x τ and
z = kc x τ

$KII = 0.1$

$u := 01.50$

u is Kchem,1

$\lambda := 1.02000000000000500$

λ is Kchem,2

$Keq := 2.51000$

$z := 0.125$

z is Kcat

α1 and α2 are electron transfer coefficients

τ is duration of potential step
dE is potential step

Cirr. A--->Red (kc1)

$$E_1:\ Red \rightleftarrows Int1 + e^- \quad (k_{s,1}, \alpha_1) \qquad (a)$$

$$C_{rev}:\ Int1 \rightleftarrows Int2 \quad \left(k_f, k_b;\ K_{eq} = \frac{k_f}{k_b};\ k_{chem} = k_f + k_b\right) \qquad (b)$$

$$E_2:\ Int2 \rightleftarrows Ox + e^- \quad (k_{s,2}, \alpha_2) \qquad (c)$$

$$C'(regenerative):\ Ox + Y \rightarrow Int2 \quad (k_c) \qquad (d)$$

Surface CirrE1CrevE2C' in Cyclic Voltammetry-meaning of symbols

Kchem1 is chemical rate parameter of precedning irreversible chemical step

Keq is equilibrium constant of reversible chemical step

Kchem2 is chemical rate parameter of reversible chemical step

Kcat is chemical rate parameter of renegenerative reaction C'

KI is parameter related to the rate of first electron transfer

KII is parameter reletaed to the rate of second electron transfer

MODEL ASSUMES ALL ADSORBED redox species

PROTEIN-FILM CYCLIC VOLTAMMETRY

$$L_j := e^{-u\cdot\frac{j}{25}} - e^{-u\cdot\frac{j+1}{25}} \qquad A_j := e^{-\lambda\cdot\frac{j}{25}} - e^{-\lambda\cdot\frac{j+1}{25}} \qquad B_j := e^{-z\cdot\frac{j}{25}} - e^{-z\cdot\frac{j+1}{25}}$$

$$p := 1..2\cdot\frac{\Delta EI}{dE} - 1$$

p is serial number of potential steps

$$\Psi I_p := \Psi I_{\left(\frac{\tau}{d\cdot 25}+p\right)\cdot 25}$$

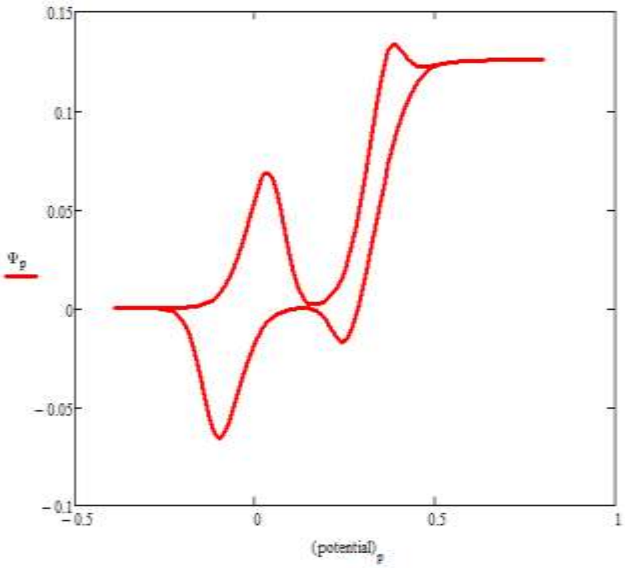
$$\Psi II_p := \Psi II_{\left(\frac{\tau}{d\cdot 25}+p\right)\cdot 25}$$

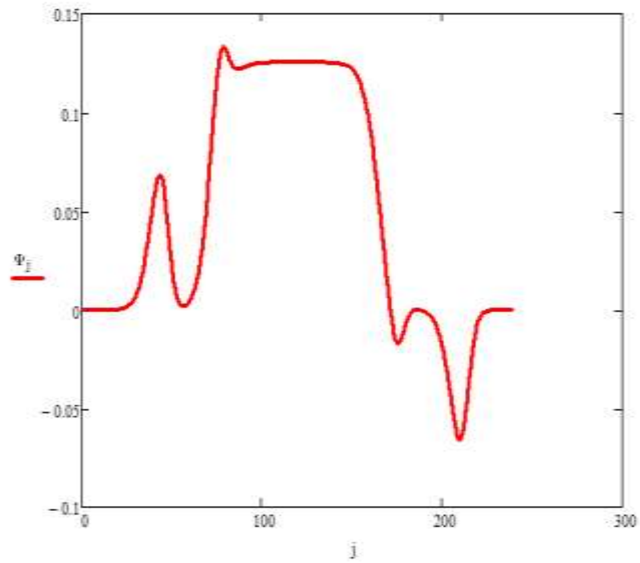
$$\Psi_p := \Psi I_p + \Psi II_p$$

dimesnioless current at the end of each potential step of first electrode reaction ΨI and of second selectrode reaction ΨII Ψp is symbol the cumulative current measured as final output

$$\text{potential}_p := \text{if}\left[p \le \frac{\Delta EI}{dE}, EsI + p\cdot dE, EfI - \left(p - \frac{\Delta EI}{dE}\right)\cdot dE\right]$$

potential value of each potential step in V





$$\Psi I_j := \frac{}{1 - KI\cdot e^{\alpha 1\cdot \Phi I_j}\cdot\left[\frac{-L_1}{u} - \frac{1}{25}\cdot\left(\left(1 + \frac{e^{-\Phi I_j}}{1 + Keq}\right)\right) - \frac{1\cdot e^{-\Phi I_j}\cdot A_1}{\lambda\cdot(Keq + 1)}\right]}$$

$$\Psi II_j := \frac{\frac{KII\cdot e^{-\Phi II_j\cdot(1-\alpha 2)}}{(1 + Keq)\cdot\lambda}\cdot\left[\sum_{i=1}^{j}\left(\Psi I_i\cdot A_{j-i+1}\right)\right] - KII\cdot e^{\alpha 2\cdot\Phi II_j}\cdot\left[-1 + \frac{1 + e^{-\Phi II_j}}{z}\cdot\sum_{i=1}^{j-1}\left(\Psi II_i\cdot B_{j-i+1}\right)\right]}{1 + \frac{KII\cdot e^{-\Phi II_j\cdot(1-\alpha 2)}\cdot A_1}{(1 + Keq)\cdot\lambda} + \frac{KII\cdot e^{\alpha 2\cdot\Phi II_j}\cdot B_1}{z}\left(1 + e^{-\Phi II_j}\right) + KII\cdot e^{\alpha 2\cdot\Phi II_j}\cdot B_1} = ...$$

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. R. Gulaboski, P. Kokoskarova, S. Petkovska, Croatica Chemica Acta **91** (2018) 377-382

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

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