Dissolution and Deposition of Dental Metallic Biomaterials-A Theoretical Model in Cyclic Voltammetry

Pavle Apostoloski, Rubin Gulaboski

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

Abstract: An on-line MATHCAD protocol is presented, suitable to calculate cyclic voltammograms related to dissolution and deposition of dental metallic biomaterials. The provided protocol provides insights on how the temperature, applied scan rate and the kinetics of electron transfer related to dissolution/deposition process affect the cyclic voltammograms of the system considered. This part of the Model displays plethora of cyclic voltammograms calculated at various kinetics of electron transfer steps of dissolution/deposition process of metallic dental biomaterials.

$tac := 0.01$

$Es := -0.4 \quad Ef := 0.4 \quad \Delta E := Ef - Es \quad dE := 0.004 \qquad \tau := 0.01 \quad d := \frac{\tau}{25}$

$m := \frac{tac}{d} + 1 .. \frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d} \qquad n := \frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d} + 1 .. \left(\frac{\Delta E}{dE} \cdot 25 \cdot 2 + \frac{tac}{d}\right)$

$i := 1 .. \frac{tac}{d}$

$\frac{\Delta E}{dE} = 200$

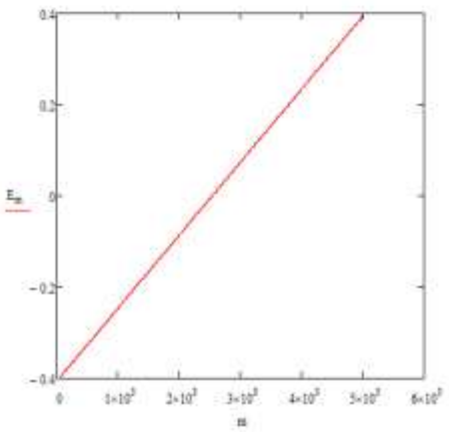
$E_m := Es + \left(\text{ceil}\left(\frac{m - \frac{tac}{d}}{25}\right) \cdot dE - dE\right)$

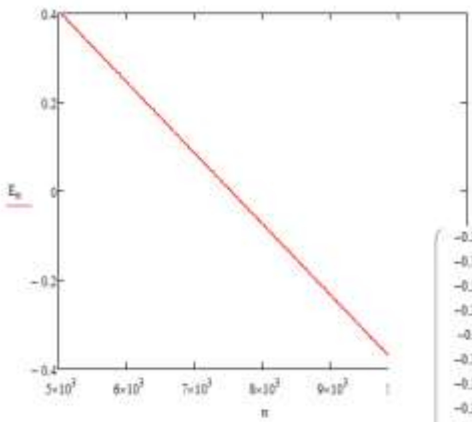
$E_n := Ef - \left[\text{ceil}\left[\frac{n - \left(\frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d}\right)}{25}\right] \cdot dE - dE\right]$

$\frac{dE}{\tau} = 0.4$

ECrev **Mechsnism of Metallic Dissolution/Deposition**
Red(ads) -1e- = Ox(dissolved)
in Cyclic Voltammetry
IF Equilibrium Constan M > 100, mechanism converges to simple(Red(ads) -1e = OX(dissolved)
Mechanism

K is dimensionless kinetic parameter related to electrde reaction
γ is dimensionless catalytic parameter related to follow up chemical reaction
α is electron transfer coefficient
M is equilibrium constant of follow up chemical reaction
kf and kb are forward and backward rate constants of folow up chemical reaction
Es is starting potential
Ef is final potential
dE is potential step
Ψ is symbol for dimensionless current
Em is cathodic potential ramp in cyclic voltammetry
En is anodic potential ramp
Sk is integration factor
τ is duration of potential steps
D is diffusion coefficient of Ox





−0.396
−0.392
−0.388
−0.384
−0.38
−0.376
−0.372
−0.368
−0.364
−0.36
−0.356
−0.352
−0.348
−0.344
−0.34
−0.336
−0.332
−0.328
−0.324
−0.32
−0.316
−0.312
−0.308
−0.304
−0.3
−0.296
−0.292
−0.288
−0.284
−0.28
−0.276
−0.272

$A := 0.28 \qquad cox := 0.0000008 \qquad w := 1.000001000062$

$ks := 0.2 \qquad D := 3 \cdot 10^{-6} \qquad kf := .000222210 \qquad 0.05$

$K := \frac{ks \cdot \sqrt{\tau}}{\sqrt{D}} \qquad \alpha := 0.5 \qquad kb := .000222250010 \qquad 0.075$

0.35

$M := \frac{kf}{kb}$ Konstanta na ramnoteza

$\log(K) = 1.062$ K

$M := 22222.1000$

$F := 96500 \quad el := 2 \quad R := 8.314 \quad T := 298.15$

$\varepsilon := kf + kb$ kineticki parametar $\qquad k := 1 .. 2 \cdot \left(\frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d}\right)$

$\Phi_m := el \cdot \frac{F}{R \cdot T} \cdot (E_m) \quad \Phi_n := el \cdot \frac{F}{R \cdot T} \cdot (E_n)$

$r := \varepsilon \cdot \tau$

$z := (kf + kb)^{0.5} \cdot \tau$

$S1_k := \sqrt{\frac{k}{25}} - \sqrt{\frac{k-1}{25}}$

$z = 2.108 \times 10^{-3}$

$\Phi ac := el \cdot \frac{F}{R \cdot T} \cdot Es$

$\gamma := h \cdot 1$

$\gamma = 2.108 \times 10^{-3}$

$S_k := \left(1 - \text{erfc}\left(\sqrt{\frac{\varepsilon \cdot \tau}{25} \cdot k}\right)\right) - \left[1 - \text{erfc}\left[\sqrt{\frac{\varepsilon}{2}}\right.\right.$

$$\Phi ac := el \cdot \frac{F}{R \cdot T} \cdot Es$$

$$\gamma := h \cdot 1$$

$$\gamma = 2.108 \times 10^{-3}$$

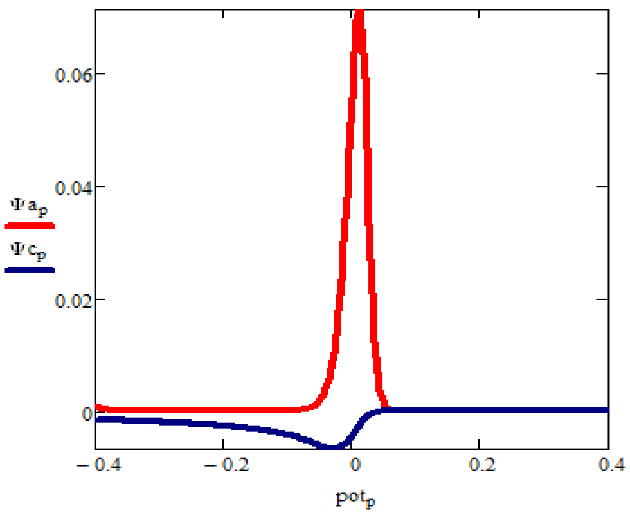
$$\Psi_1 := \frac{K \cdot e^{\alpha \cdot \Phi_1}}{\left[1 + \frac{0.04 \cdot K \cdot e^{(1-\alpha)\cdot \Phi_1} \cdot 1}{\sqrt{1 \cdot 1}} + \frac{1 \cdot K \cdot e^{-(1-\alpha)\cdot \Phi_1}}{\sqrt{\pi \cdot 1}} \cdot \frac{M}{1+M}\right] + \frac{\gamma}{1+M} \cdot e^{-(1-\alpha)\cdot \Phi_1} \cdot S_1}$$

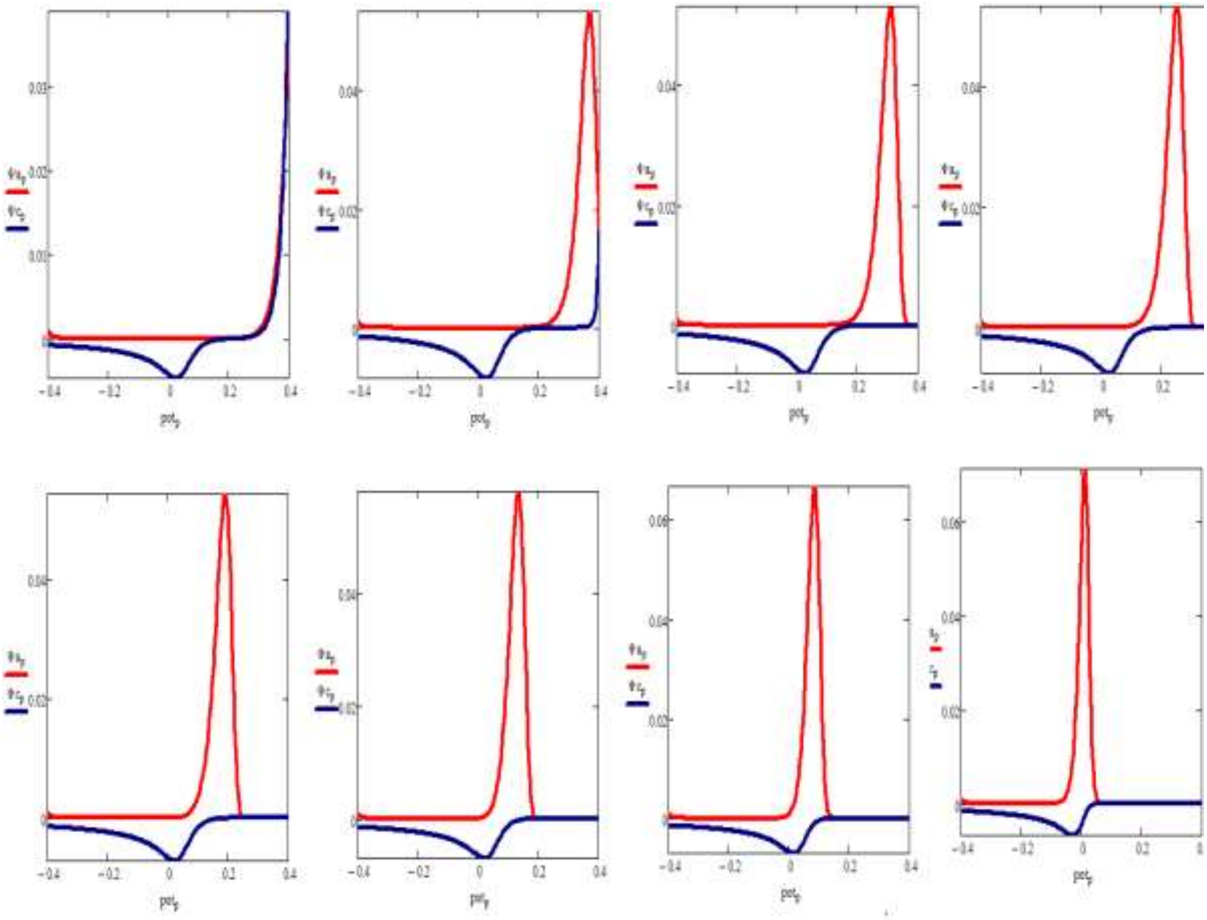
$$\Psi_s := \frac{K \cdot e^{\alpha \cdot \Phi ac} - \frac{0.04 \cdot K \cdot e^{\alpha \cdot \Phi ac}}{\sqrt{1 \cdot 1}} \cdot \sum_{j=1}^{s-1} \left(\Psi_j \cdot 1\right) - \frac{2 \cdot K \cdot e^{-(1-\alpha)\cdot \Phi ac}}{\sqrt{\pi \cdot 25}} \cdot \frac{M}{1+M} \cdot \sum_{j=1}^{s-1} \left(\Psi_j \cdot S1_{s-j+1}\right) - \frac{\gamma}{1+M} \cdot e^{-(1-\alpha)\cdot \Phi ac} \cdot \sum_{j=1}^{s-1} \left(\Psi_j \cdot S_{s-j+1}\right.}{1 + \frac{0.04 \cdot K \cdot e^{\alpha \cdot \Phi ac} \cdot 1}{\sqrt{1 \cdot 1}} + \frac{2 \cdot K \cdot e^{-(1-\alpha)\cdot \Phi ac}}{\sqrt{\pi \cdot 25}} \cdot \frac{M}{1+M} + \frac{\gamma}{1+M} \cdot e^{-(1-\alpha)\cdot \Phi ac} \cdot S_1}$$

$$\Psi_m := \frac{w \cdot e^{\alpha \cdot \Phi_m} - \frac{0.04 \cdot w \cdot e^{\alpha \cdot \Phi_m}}{\sqrt{1 \cdot 1}} \cdot \sum_{j=1}^{m-1} \left(\Psi_j \cdot 1\right) - \frac{2 \cdot K \cdot e^{-(1-\alpha)\cdot \Phi_m}}{\sqrt{\pi \cdot 25}} \cdot \frac{M}{1+M} \cdot \sum_{j=1}^{m-1} \left(\Psi_j \cdot S1_{m-j+1}\right) - \frac{\gamma}{1+M} \cdot e^{-(1-\alpha)\cdot \Phi_m} \cdot \sum_{j=1}^{m-1} \left(\Psi_j \cdot S_{m-j+1}\right)}{1 + \frac{0.04 \cdot w \cdot e^{\alpha \cdot \Phi_m} \cdot 1}{\sqrt{1 \cdot 1}} + \frac{2 \cdot K \cdot e^{-(1-\alpha)\cdot \Phi_m}}{\sqrt{\pi \cdot 25}} \cdot \frac{M}{1+M} + \frac{\gamma}{1+M} \cdot e^{-(1-\alpha)\cdot \Phi_m} \cdot S_1}$$

$$\Psi_n := \frac{w \cdot e^{\alpha \cdot b_n} - \frac{0.04 \cdot w \cdot e^{\alpha \cdot b_n}}{\sqrt{1 \cdot 1}} \cdot \sum_{j=1}^{n-1} \left(\Psi_j \cdot 1\right) - \frac{2 \cdot K \cdot e^{-(1-\alpha)\cdot b_n}}{\sqrt{\pi \cdot 25}} \cdot \frac{M}{1+M} \cdot \sum_{j=1}^{n-1} \left(\Psi_j \cdot S1_{n-j+1}\right) - \frac{\gamma}{1+M} \cdot e^{-(1-\alpha)\cdot b_n} \cdot \sum_{j=1}^{n-1} \left(\Psi_j \cdot S_{n-j+1}\right)}{1 + \frac{0.04 \cdot w \cdot e^{\alpha \cdot b_n} \cdot 1}{\sqrt{1 \cdot 1}} + \frac{2 \cdot K \cdot e^{-(1-\alpha)\cdot b_n}}{\sqrt{\pi \cdot 25}} \cdot \frac{M}{1+M} + \frac{\gamma}{1+M} \cdot e^{-(1-\alpha)\cdot b_n} \cdot S_1}$$

$p := 1 .. \frac{\Delta E}{dE}$ $\quad \Psi a_p := (\Psi)_{\left(\frac{\tau}{d \cdot 25} + p\right) \cdot 25}$ $\quad \Psi c_p := (\Psi)_{\left[\left[\frac{\Delta E}{dE} \cdot 2 + \left(\frac{\tau}{25 \cdot d}\right)\right] - p\right] \cdot 25}$ $\quad pot_p := Es + p \cdot dE$





Effect of kinetics of the electron transfer step of dissolution/deposition process of dental metallic biomaterial to the features of calculated cyclic voltammograms at room temperature

LITERATURE

1. R. Gulaboski, ***Journal of Solid State Electrochemistry*** 24 (**2020**) 2081-2081
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. R. Gulaboski, V. Mirceski, M. Lovric, I. Bogeski, ***Electrochemistry Communications*** 7 (2005) 515-522.
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. V. Mirceski, R. Gulaboski, ***Bulletin of the Chemists and Technologists of Macedonia*** 18 (1999) 57-64.
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 (10) **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