

Assessing Activity of Dental Metallic Biomaterials from Cyclic Voltammetry- Effect of the Kinetics of Electron Transfer and the Kinetics of Coupled Chemical Reaction

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Abstract: In this work, we present set of results obtained from MATHCAD simulation protocol performed in conditions of cyclic voltammetry. Model is related to assess the activity of dental metallic biomaterials in presence of chemical systems that get into interactions with the dental metallic material. The results show how the temperature, the kinetics of electron transfer step, and the kinetics of coupled chemical reaction affect the activity of the metallic dental biomaterial. Results are relevant to study dissolution of metallic biomaterials.

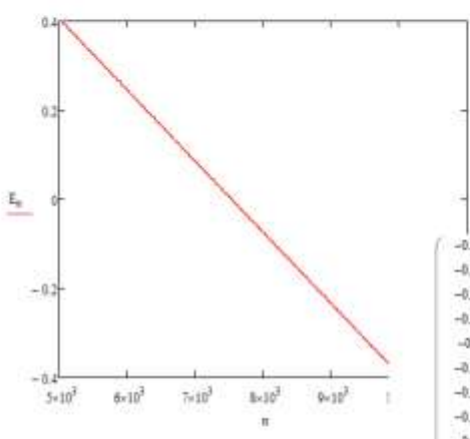
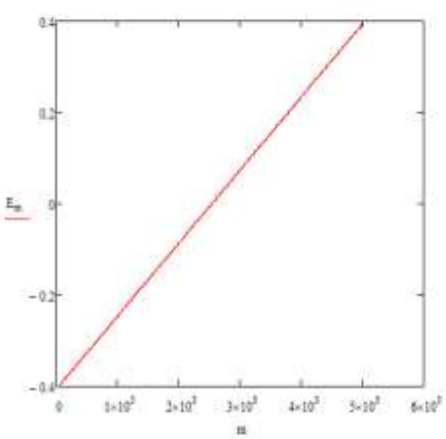
$$E_s = -0.4 \quad E_f = 0.4 \quad \Delta E = E_f - E_s \quad dE = 0.004 \quad \tau = 0.01 \quad d = \frac{\tau}{25}$$

$$m = \frac{tac}{d} + 1 + \frac{\Delta E}{dE} 25 = \frac{tac}{d} + 1 + \left(\frac{\Delta E}{dE} 25 + \frac{tac}{d} \right)$$

$$E_{ca} = E_s + \left[\cos \left(\frac{m - \frac{tac}{d}}{25} \right) dE - dE \right]$$

$$E_{ca} = E_f - \left[\cos \left(\frac{m - \left(\frac{\Delta E}{dE} 25 + \frac{tac}{d} \right)}{25} \right) dE - dE \right]$$

ECrev Mechanism of Metallic Dissolution/Deposition
Red(ads) -1e- = Ox(dissolved)
in Cyclic Voltammetry
F Equilibrium Constant M > 100, mechanism converges to simple Red(ads) -1e- = Ox(dissolved)
Mechanism
K is dimensionless kinetic parameter related to electrode 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 follow 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



$$\frac{\Delta E}{dE} = 0.28 \quad \cos = 0.00000008 \quad w = 1.000001000002$$

$$k = 0.1 \quad D = 3 \cdot 10^{-6} \quad k_f = 0.00222210 \quad 0.05 \quad k$$

$$\frac{k_b}{k_f} = \frac{k_s \sqrt{\tau}}{\sqrt{D}} \quad \alpha = 0.5 \quad k_b = 0.000222150010 \quad 0.075$$

$$M = \frac{k_f}{k_b} \quad \text{Konstanta na ravnoteza} \quad 0.35$$

$$\log(K) = 1.042 \quad K = 11.0 \quad M = 2222.1000$$

$$z = kf + kb \quad \text{kinetski parametar} \quad k = 1.2 \left(\frac{\Delta E}{dE} 25 + \frac{tac}{d} \right)$$

$$r = \epsilon \tau \quad z = (kf + kb)^{0.5} \tau \quad z = 2.108 \times 10^{-3}$$

$$S_{1,k} = \sqrt{\frac{k}{25}} - \sqrt{\frac{k-1}{25}} \quad \gamma = h \cdot l \quad \gamma = 2.108 \times 10^{-3}$$

$$E_s = 96500 \quad \epsilon = 2 \quad R_s = 8.314 \quad T_s = 298.15$$

$$\Phi_{ca} = \epsilon \frac{F}{R T} (E_{ca}) \quad \Phi_{ca} = \epsilon \frac{F}{R T} (E_{ca})$$

$$\Phi_{ca} = \epsilon \frac{F}{R T} E_s$$

$$S_k = \left(1 - \operatorname{erfc} \left(\frac{\epsilon \tau}{25} k \right) \right) - \left[1 - \operatorname{erfc} \left(\frac{\epsilon}{25} \right) \right]$$

$$\Phi_{ac} := eI \cdot \frac{F}{R \cdot T} \cdot Es$$

$$\gamma := h \cdot l$$

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

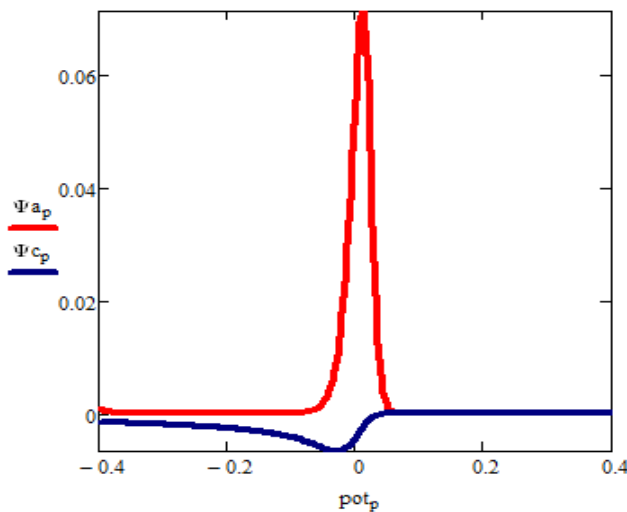
$$\Psi_1 := \frac{K \cdot e^{\alpha \cdot \Phi_1}}{1 + \frac{0.04 \cdot K \cdot e^{(1-\alpha) \cdot \Phi_1} \cdot 1}{\sqrt{1 \cdot 1}} + \frac{1 \cdot K \cdot e^{-(1-\alpha) \cdot \Phi_1}}{\sqrt{\pi \cdot 1}} \cdot \frac{M}{1+M}} + \frac{\gamma}{1+M} \cdot e^{-(1-\alpha) \cdot \Phi_1} \cdot S_1$$

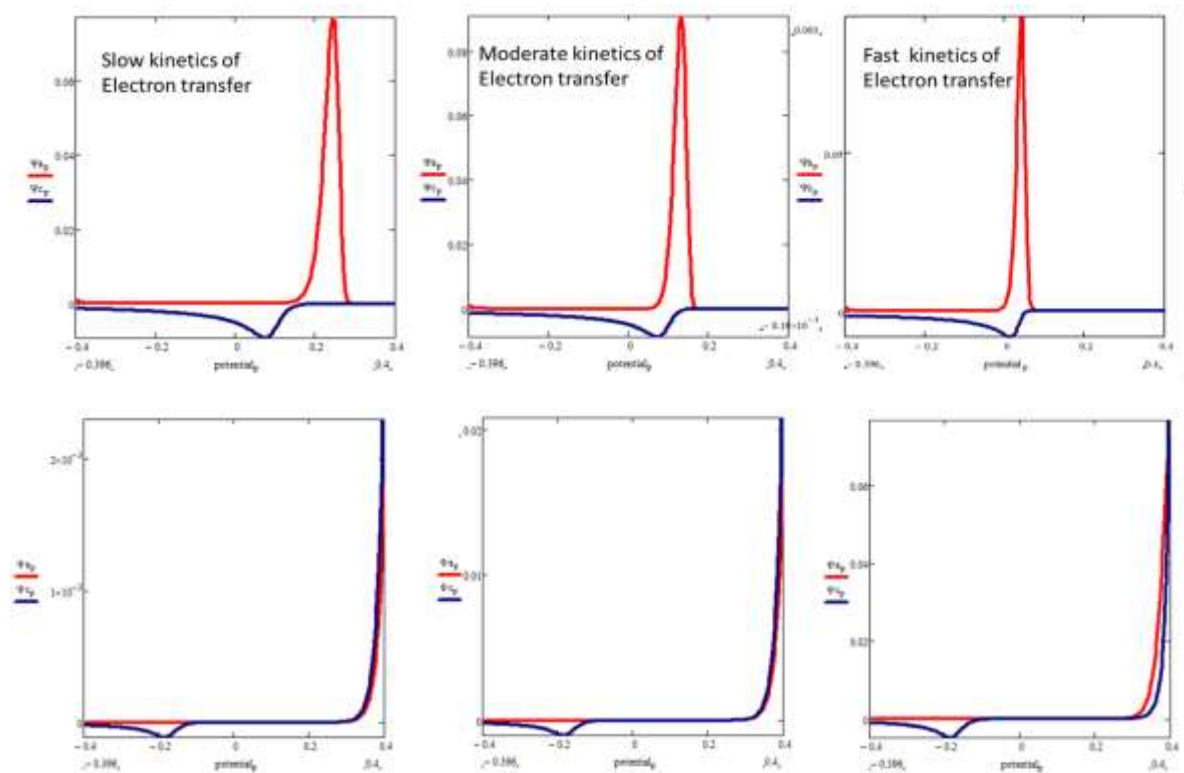
$$\Psi_s := \frac{K \cdot e^{\alpha \cdot \Phi_{ac}} - \frac{0.04 \cdot K \cdot e^{\alpha \cdot \Phi_{ac}}}{\sqrt{1 \cdot 1}} \cdot \sum_{j=1}^{s-1} (\Psi_j \cdot 1) - \frac{2 \cdot K \cdot e^{-(1-\alpha) \cdot \Phi_{ac}}}{\sqrt{\pi \cdot 25}} \cdot \frac{M}{1+M} \cdot \sum_{j=1}^{s-1} (\Psi_j \cdot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

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

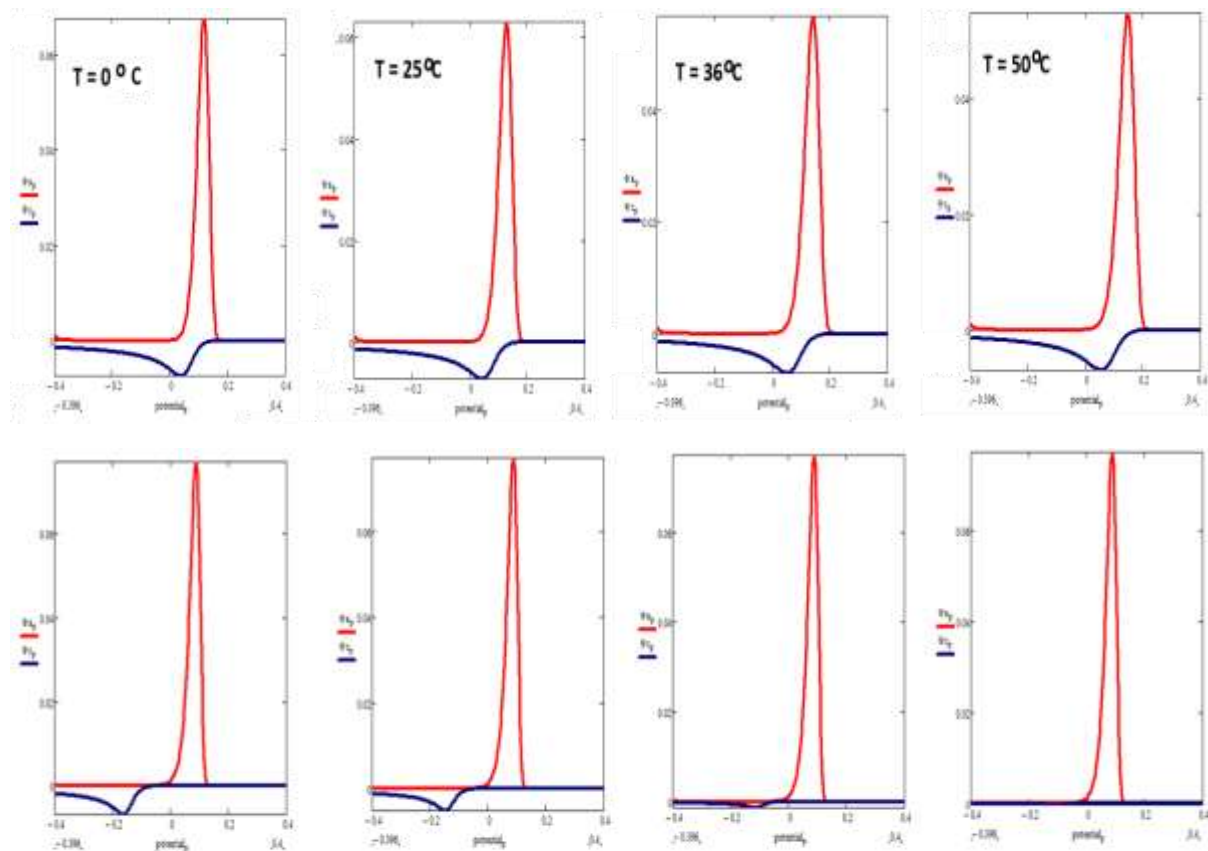
$$\Psi_n := \frac{w \cdot e^{\alpha \cdot b_n} - \frac{0.04 \cdot w \cdot e^{\alpha \cdot b_n}}{\sqrt{1 \cdot 1}} \cdot \sum_{j=1}^{n-1} (\Psi_j \cdot 1) - \frac{2 \cdot K \cdot e^{-(1-\alpha) \cdot b_n}}{\sqrt{\pi \cdot 25}} \cdot \frac{M}{1+M} \cdot \sum_{j=1}^{n-1} (\Psi_j \cdot S_{1_{n-j+1}}) - \frac{\gamma}{1+M}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

$$p := 1 \cdot \frac{\Delta E}{dE} \quad \Psi_{a_p} := (\Psi) \left(\frac{\tau}{d \cdot 25} + p \right) \cdot 25 \quad \Psi_{c_p} := (\Psi) \left[\left[\frac{\Delta E}{dE} \cdot 2 + \left(\frac{\tau}{25 \cdot d} \right) \right] \cdot p \right] \cdot 25 \quad \text{pot}_p := Es + p \cdot dE$$





Effect of concentration of the system that interacts with the metallic dental biomaterial (cyclic voltammograms at the end of the potential window show increase in the current)



Effect of the rate of coupled chemical reaction to the features of voltammograms representing Dissolution of dental material in physiological conditions

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