Supplementary File: Surface Electrode Mechanism Associated with Preceding and Follow up Chemical Reactions-Theoretical Analysis in Square-Wave Voltammetry

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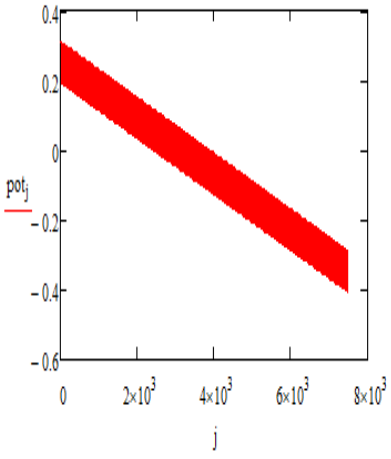
$Es := 0.25 \quad \Delta E := 0.6 \quad dE := 0.004 \quad Esw := 0.06$

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

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

$\alpha := 0.5$

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



$\Phi_j := n \cdot \frac{F}{R \cdot T} \cdot pot_j$

$r := 1..1$

$f := 10$

$ks_r := \frac{10^{2 \cdot r}}{1}$

$\lambda_r := \frac{ks_r}{f} \quad K := 10^{-1}$

$\varepsilon := 10^{-0} \quad U := 0.1$

$g := 0.1$

$z := \frac{\varepsilon}{f}$

$b := \frac{g}{f}$

$k := 1..\frac{\Delta E}{dE} \cdot 50 \quad b = 0.01$

$\varepsilon = 1$

$S_k := e^{\frac{z}{50} \cdot (-k)} - e^{\frac{z}{50} \cdot (-k+1)} \quad z = 0.1$

$L_k := e^{\frac{b}{50} \cdot (-k)} - e^{\frac{b}{50} \cdot (-k+1)}$

SURFACE "CrevECrev MEchanism in SWV
working MATHCAD File for simulations

$\lambda = K_{ET}$ is = dimensionless electrode rate parameter
K = Keq, preceding = equilibrium constant of preceding chemical reaction
z = ε/f = Kchem-preceding-dimensionless chemical rate parameter of preceding chemical reaction
U = Keq, follow up = equilibrium constant of follow up chemical step
b = g/f = Kchem-follow up-dimensionless chemical rate parameter of follow up chemical step
f-SW frequency
ks-standard rate constant of electron transfer
n-number of exhanged electrons
α -electron transfer coefficient
Esw -Square wave amplitude
dE-potential step
S and L-numerical integration factors
F-Faraday constant
R-universal gas constant
T-Thermodynamic temperature
Φ - dimensionless potential
j and k-number of potential SW steps
kf and kb-rate constants of forward and backward chemical steps
Ψ is dimensionless current
Es-strating potential
ΔE-potential windows

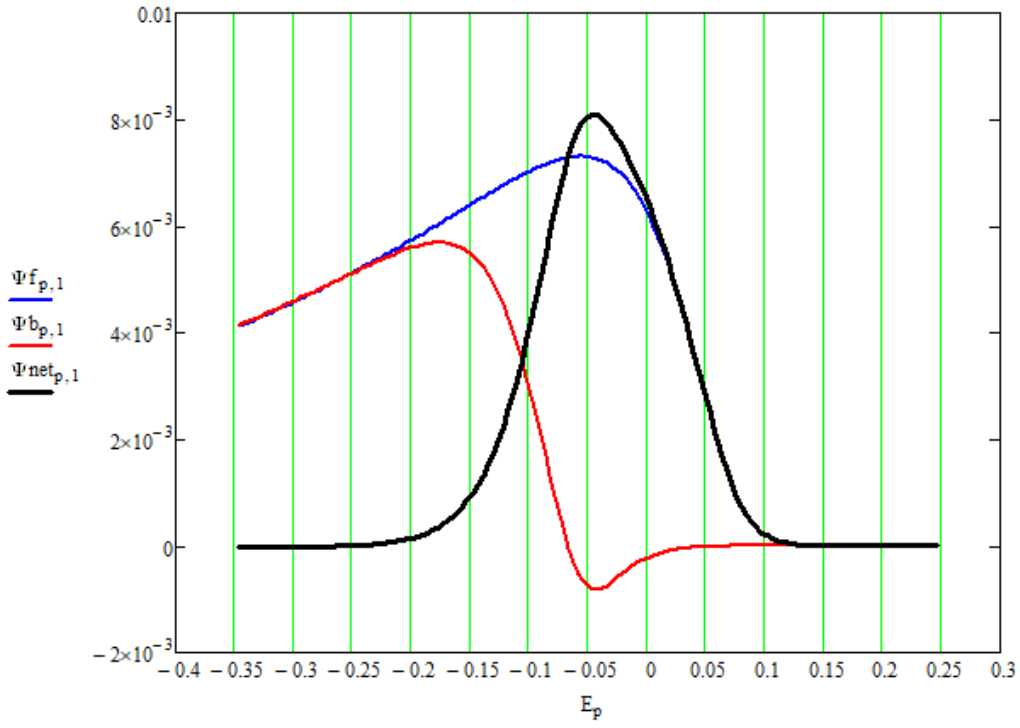
$$\Psi_{1,r} := \frac{\left[\frac{\lambda_r \cdot e^{-\alpha\cdot\Phi_1}\cdot K}{1+K}\cdot(1-0)-\left[(z)^{-1}\cdot\lambda_r\cdot\left(\frac{1}{1+K}\right)\cdot(-1)\cdot e^{-\alpha\cdot\Phi_1}\cdot 0-\frac{\lambda_r}{50}\cdot e^{\Phi_1\cdot(1-\alpha)}\cdot 0\right]\right]-\lambda_r\cdot\frac{U}{1+U}\cdot\frac{1}{b}\cdot e^{\Phi_1\cdot(1-\alpha)}\cdot 0+\frac{b}{1+U}\cdot e^{\Phi_1\cdot(1-\alpha)}\cdot 0}{\left(\frac{\lambda_r\cdot e^{-\alpha\cdot\Phi_1}\cdot K}{1+K}\cdot\frac{1}{50}\right)+1+(z)^{-1}\cdot\lambda_r\cdot(-1)\cdot\left(\frac{1}{1+K}\right)\cdot S_1\cdot e^{-\alpha\cdot\Phi_1}+\frac{\lambda_r}{50}\cdot e^{\Phi_1\cdot(1-\alpha)}-\lambda_r\cdot\frac{U}{1+U}\cdot\frac{1}{b}\cdot e^{\Phi_1\cdot(1-\alpha)}+\frac{b}{1+U}\cdot e^{\Phi_1\cdot(1-\alpha)}}$$

$$\Psi_{k,r} := \frac{\frac{\lambda_r\cdot e^{-\alpha\cdot\Phi_k}\cdot K}{1+K}\cdot\left(1-\frac{1}{50}\cdot\sum_{j=1}^{k-1}\Psi_{j,r}\right)-(z)^{-1}\cdot\lambda_r\cdot\left(\frac{1}{1+K}\right)\cdot(-1)\cdot e^{-\alpha\cdot\Phi_k}\cdot\sum_{j=1}^{k-1}\left(\Psi_{j,r}\cdot S_{k-j+1}\right)-\frac{\lambda_r}{50}\cdot e^{\Phi_k\cdot(1-\alpha)}\cdot\sum_{j=1}^{k-1}\Psi_{j,r}-\frac{\lambda_r}{50}\cdot\frac{U}{(1+U)}\cdot\frac{1}{b}\cdot e^{\Phi_k\cdot(1-\alpha)}\cdot(-1)\cdot\sum_{j=1}^{k-1}\left(\Psi_{j,r}\cdot L_{k-j+1}\right)+\frac{b}{(1+U)}\cdot(1)\cdot e^{\Phi_k\cdot(1-\alpha)}\cdot\left[\sum_{j=1}^{k-1}\left(\Psi_{j,r}\cdot L_{k-j+1}\right)\right]}{\frac{\lambda_r\cdot e^{-\alpha\cdot\Phi_k}\cdot K}{(1+K)}\cdot\frac{1}{50}+1+(z)^{-1}\cdot\lambda_r\cdot(-1)\cdot\left(\frac{1}{1+K}\right)\cdot S_1\cdot e^{-\alpha\cdot\Phi_k}+\frac{\lambda_r}{50}\cdot e^{\Phi_k\cdot(1-\alpha)}-\frac{\lambda_r}{50}\cdot\frac{U}{(1+U)}\cdot\frac{1}{b}\cdot e^{\Phi_k\cdot(1-\alpha)}\cdot L_1\cdot(-1)-\frac{b}{(1+U)}\cdot e^{\Phi_k\cdot(1-\alpha)}\cdot L_1\cdot(1)}$$

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

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

$$E_p := Es - p\cdot dE$$



References

1. V. Mirceski, S. Komorsky-Lovric, M. Lovric, *Square-wave voltammetry. Theory and application* (F. Scholz, ed.), Springer, Berlin, Germany, **2007**.
2. R. G. Compton, C. E. Banks, *Understanding voltammetry*, 2nd edition, Imperial College Press, London, UK, **2011**.
3. A. J. Bard, L. R. Faulkner, *Electrochemical methods. Fundamentals and applications*, 3rd edition, John Wiley & Sons, Inc., **2004**.
4. A. Molina, J. Gonzales, *Pulse voltammetry in physical electrochemistry and electroanalysis*, in *Monographs in electrochemistry* (F. Scholz, ed.), Berlin Heidelberg, Springer, **2016**.
5. R. Gulaboski, V. Mirceski, *Maced. J. Chem. Chem. Eng*. **2020**, *39*, 153.
6. R. Gulaboski, V. Mirceski, I. Bogeski, *J. Solid State Electrochem*. **2012**, *16*, 2315.
7. V. Mirceski, R. Gulaboski, M. Lovric, I. Bogeski, R. Kappl, M. Hoth, *Electroanal*. **2013**, *25*, 2411.
8. V. Mirceski, R. Gulaboski, *Maced. J. Chem. Chem. Eng*. **2014**, *33*, 1.
9. P. N. Barlett, *Bioelectrochemistry-Fundamentals, experimental techniques and application*, Wiley, Chichester, **2008**.
10. M. Saveant, *Elements of molecular and biomolecular electrochemistry: An electrochemical approach to electron transfer chemistry*, Hoboken, NJ, Wiley, **2006**.
11. R. Gulaboski, V. Mirceski, M. Lovric, *J. Solid State Electrochem*. **2019**, *23*, 2493.
12. F. A. Armstrong, *Voltammetry of proteins* In: *Encyclopaedia of electrochemistry* (A. J. Bard, M. Stratmann, G. S. Wilson (eds)), vol. 9, Wiley VCH, Weinheim, **2002**.
13. C. Leger, P. Bertrand, *Chem. Rev*. **2007**, *108*, 2379
14. P. Kokoskarova, R. Gulaboski, *Electroanal*. **2020**, *32*, 333.
15. R. Gulaboski, V. Mirceski, M. Lovric, I. Bogeski, *Electrochem. Commun*. **2005**, *7*, 515.
16. R. Gulaboski, *Electroanal*. **2019**, *31*, 545.

17. R. Gulaboski, *J. Solid State Electrochem*. **2009**, *13*, 1015.
18. R. Gulaboski, M. Janeva, V. Maksimova, *Electroanal*. **2019**, *31*, 946.
19. R. Gulaboski, P. Kokoskarova, S. Petkovska, *Croat. Chem. Acta* **2018**, *91*, 377.
20. R. Gulaboski, P. Kokoskarova, S. Risafova, *J. Electroanal. Chem*. **2020**, *866* https://doi.org/10.1016/j.jelechem.2020.114189
21. R. Gulaboski, V. Mirceski, *Electrochim. Acta*, **2015**, *167*, 219.
22. M. Lopez-Tenes, E. Laborda, A. Molina, R. G. Compton, *Anal. Chem*. **2019**, *91*, 6072.
23. M. Rafiee, D. Nematollahi, H. Salehzadeh, *Electrochim. Acta* **2011**, *56*, 9946.
24. O. Nekrassova, N. S. Lawrence, R. G. Compton, *Electroanal*. **2003**, *15*, 1501.
25. H. Salehzadeh, D. Nematollahi, *Electrochim. Acta* **2013**, *111*, 909.
26. M. T. Carter, M. Rodriguez, A. J. Bard, *J. Am. Chem. Soc*. **1989**, *111*, 8901.
27. V. Pierroz, T. Joshi, A. Leonidova, C. Mari, J. Schur, I. Ott, L. Spiccia, S. Ferrari, G. Gasser, *J. Am. Chem Soc*. **2012**, *134*, 20376.
28. Ch. Batchelor-McAuley, Q. Li, S. M. Dapin, R. G. Compton, *J. Phys. Chem. B* **2010**, 114, 4094.
29. A. De Rache, T. Doneux, C. Buess-Herman, *Anal. Chem*. **2014**, *86*, 8057.
30. J. A. Ribeiro, C. M. Pereira, F. Silva, *Electrochim. Acta* **2015**, *180*, 687.
31. V. Mirceski, M. Lovric, *Electroanal*. **1997**, *9*, 1283.
32. R. Gulaboski, M. Lovric, V. Mirceski, I. Bogeski, M. Hoth, *Biophys. Chem.* **2008**, *138*, 130.