SUPPLEMENTARY MATERIAL: MATHCAD FILE for TWO-STEP SURFACE EECrev MECHANSIM

(Es − standard)potentials

$f := 10$ f is SW feequency

$r := 1..1$

$kf := 0.1$ $ks1 := 10$ ks1 is the standard rate constant of first electrode step

$kb := 0.1$ $ks2 := 10$ ks2 is the standard rate constant of second electrode step

$EsI := 0.2$ $\Delta E := 0.8$ $dE := 0.004$ $Esw := 0.05$ $EsII := 0.6$

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

$KI_r := \left(\frac{ks1 \cdot r}{f}\right)$

$\gamma := \frac{(kf + kb)}{f}$ kf and kb are forward and backward constant of chemical reaction
γ is the dimensionless chemical kinetic parameter

$KII := \frac{ks2}{f}$

$U := \frac{kf}{kb}$ U is the equilibrium constant of follow up chemical reaction

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

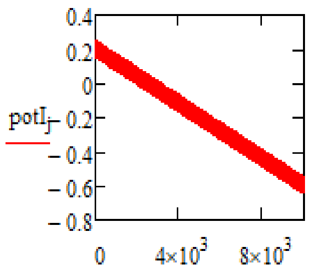
$\alpha 1 := 0.5$ $\alpha 2 := 0.5$

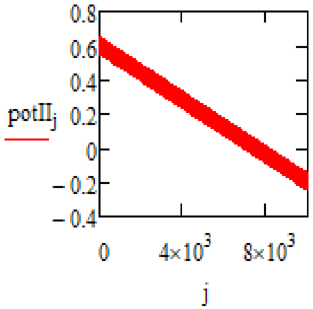
KI is dimensionless kinetic parameter of first electrode step

KII is dimensionless kinetic parameter of second electrode step

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

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





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

$M_j := e^{-\gamma \cdot \frac{j}{50}} - e^{-\gamma \cdot \frac{j+1}{50}}$ M is numerical integration factor

$x := 0.001$

These are the recurrent formulas for calculating dimensionless currents

$$\Psi I_{1,r} := \mathrm{root}\left[\left[1 + \frac{KI_r \cdot e^{-\alpha 1 \cdot \Phi I_1}}{50} \cdot \left(1 + e^{\Phi I_1}\right)\right] \cdot x - \frac{KI_r}{50} \cdot e^{(1-\alpha 1) \cdot \Phi I_1} \cdot \left[\frac{x \cdot \frac{KII \cdot e^{-\alpha 2 \cdot \Phi II_1}}{50}}{1 + \frac{KII \cdot e^{-\alpha 2 \cdot \Phi II_1}}{50} \cdot \left(1 + e^{\Phi II_1}\right)} \right] - KI_r \cdot e^{-\alpha 2 \cdot \Phi I_1}, x \right]$$

$$\Psi II_{1,r} := \frac{1KII \cdot e^{-\alpha 2 \cdot \Phi II_1}}{50 + 1KII \cdot e^{-\alpha 2 \cdot \Phi II_1} \cdot \left(1 + e^{\Phi II_1}\right)} \cdot \Psi I_{1,r} + \frac{\frac{UKII}{1+U} \cdot e^{(-\alpha 2) \cdot \Phi II_1} - \frac{KII \cdot e^{-\alpha 2 \cdot \Phi II_1}}{1} \cdot 0}{50 + KII \cdot e^{-\alpha 2 \cdot \Phi II_1} \cdot \left(1 + e^{\Phi II_1}\right) + \frac{U \cdot KII}{(1+U) \cdot 50} \cdot e^{(1-\alpha 2) \cdot \Phi II_1} \cdot M_1} + \frac{\frac{1\gamma}{1+U} \cdot e^{(1-\alpha 2) \cdot \Phi II_1} \cdot 0}{50 + KII \cdot e^{-\alpha 2 \cdot \Phi II_1} \cdot \left(1 + e^{\Phi II_1}\right) + \frac{\gamma}{1+U} \cdot e^{(1-\alpha 2) \cdot \Phi II_1} \cdot M_1}$$

$$x := 0.001$$

$$\Psi I_{j,r} := \mathrm{root}\left[x - KI_r \cdot e^{-\alpha 1 \cdot \Phi I_j} \cdot \left[1 - \left[\frac{1}{50} \cdot \left(1 + e^{\Phi I_j}\right) \cdot \left(x + \sum_{i=1}^{j-1} \Psi I_{i,r} \right) + \frac{e^{\Phi I_j}}{50} \cdot \left[\frac{1}{1 + e^{\Phi II_j}} \cdot \left(x + \sum_{i=1}^{j-1} \Psi I_{i,r} \right) - \frac{50}{KII \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot \left(1 + e^{\Phi II_j}\right)} \cdot \left[KII \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot \left[\frac{1}{50} \cdot \left(x + \sum_{i=1}^{j-1} \Psi I_{i,r} \right) - \frac{1}{50} \cdot \left(1 + e^{\Phi II_j}\right) \cdot \left[\frac{50 \cdot x}{KI_r \cdot e^{(1-\alpha 1) \cdot \Phi I_j}} - 50 \cdot e^{-\Phi I_j} \cdot \left[1 - \frac{1}{50} \cdot \left(1 + e^{\Phi I_j}\right) \cdot \left(x + \sum_{i=1}^{j-1} \Psi I_{i,r} \right) \right] \right] \right] \right] \right] \right] \right], x \right]$$

$$\Psi II_{j,r} := \frac{0.02KII \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot 1}{1 + 1\frac{KII}{50} \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot 1 \cdot \left(1 + e^{\Phi II_j}\right)} \cdot \sum_{i=1}^{j} \Psi I_{i,r} + \frac{0.02KII \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot 1 - \frac{\frac{1KII}{50} \cdot e^{(-\alpha 2) \cdot \Phi II_j} \cdot 1}{1} \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot 1\right) - \frac{\frac{1UKII}{\gamma \cdot (1+U)} \cdot e^{(1-\alpha 2) \cdot \Phi II_j} \cdot 1}{1} \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot M_i\right) - \frac{1\gamma}{1+U} \cdot e^{(1-\alpha 2) \cdot \Phi II_j} \cdot 1 \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot M_i\right)}{1 + \frac{1KII}{50} \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot 1 + \frac{1UKII}{\gamma(1+U)} \cdot e^{(1-\alpha 2) \cdot \Phi II_j} \cdot M_1 + \frac{\gamma}{1+U} \cdot e^{(1-\alpha 2) \cdot \Phi II_j} \cdot M_1 \cdot 1} \cdot 1$$

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

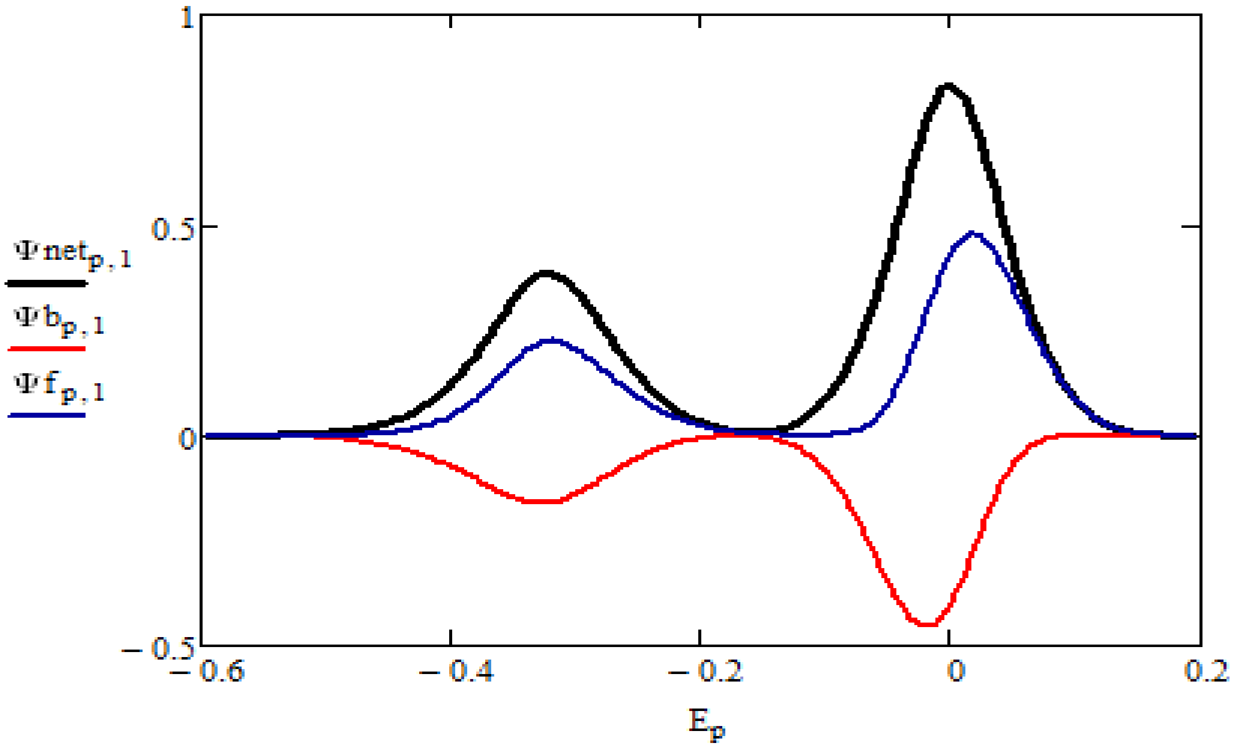
$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$

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

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

$\Psi b_{p,r} := \Psi_{50\cdot p+25,r}$ $\Psi f_{p,r} := \Psi_{(p+1)\cdot 5(}$ $\Psi net_{p,r} := \Psi f_{p,r} - \Psi b_{p,r}$

$E_p := EsI - p\cdot dE$



References

1. A. J. Bard, L. R. Faulkner, *Electrochemical methods. Fundamentals and applications*, 3rd edition, John Wiley & Sons, Inc. **2004**.
2. A. Molina, J. Gonzales, *Pulse voltammetry in physical electrochemistry and electroanalysis*, in *Monographs in electrochemistry* (F. Scholz, ed.), Berlin Heidelber, Springer, **2016**.
3. V. Mirceski, S. Komorsky-Lovric, M. Lovric, *Square-wave voltammetry, Theory and application*, Springer, Berlin, Germany, 2007.
4. R. Gulaboski, V. Mirceski, I. Bogeski, M. Hoth, *J. Solid State Electrochem*. **2012**, *16*, 2315.
5. C. Léger, P. Bertrand, *Chem. Rev*. **2008**, 108, 2379.
6. F. A. Armstrong, *Voltammetry of Proteins*. In: A.J. Bard, M. Stratmann, G.S. Wilson (eds) *Encyclopedia of Electrochemistry*, vol. 9, Wiley VCH, Weinheim, **2002**.
7. R. G. Compton, C. E. Banks, *Understanding voltammetry*, 2nd Edition, Imperial College Press, London, UK, **2011**
8. P. N. *Barlett*, *Bioelectrochemistry-Fundamentals, Experimental Techniques and Application*, Wiley, Chichester, **2008**.
9. V. Mirceski, R. Gulaboski, M. Lovric, I. Bogeski, R. Kappl, M. Hoth, *Electroanalyis* **2013**, *25*, 2411.
10. J. G. Osteryoung, J. J. O'Dea, *Square-Wave Voltammetry, Electroanalytical chemistry: a series of advances*. Marcel Dekker, Inc: New York, **1986**.
11. E. Laborda. J. Gonzales, A. Molina, *Electrochem. Commun*. **2014**, *43*, 25.
12. A. Molina, J. Gonzales, M. Henstridge, R. G. Compton, *Electrochim. Acta* **2011**, *56*, 4589.
13. A. Molina, R. G. Compton, C. Serna, F. Martinez-Ortiz, E. Laborda, *Electrochim. Acta* **2009**, *54*, 2320.
14. R. Gulaboski, *J. Solid State Electrochem*. **2009**, *13*, 1015.
15. R. Gulaboski, L. Mihajlov, *Biophys. Chem*. **2011**, *155*, 1.
16. P. Kokoskarova, V. Maksimova, M. Janeva, R. Gulaboski *Electroanalysis*, **2019**, *31*, 1454.
17. M. Lovric, "Square-wave voltammetry," in *Electroanalytical Methods*, F. Scholz, Ed. Springer, Berlin, Germany, 2nd edition, **2010**.
18. R. Gulaboski, P. Kokoskarova, S. Mitrev, *Electrochim. Acta* **2012**, *69*, 86.

19. E. Laborda, M. Henstridge, A. Molina F. Martinez-Ortiz, R. G. Compton, *J. Electroanal. Chem*. **2011**, *660*, 169.
20. F. Garay, M. Lovric, *J. Electroanal. Chem*. **2002**, *518*, 91.
21. R. Gulaboski**,** V. Mirceski, M. Lovric, I. Bogeski, *Electrochem. Commun*. **2005**, *7*, 515
22. V. Mirceski, R. Gulaboski, *Electroanalysis*, **2001**, *13*, 1326.
23. R. Gulaboski, P. Kokoskarova, S. Petkovska, *Croat. Chem. Acta* **2018**, *91*, 377.
24. R. Gulaboski, V. Mirceski, *Electrochim. Acta* **2015**, *167*, 219.
25. R. Gulaboski, V. Mirceski, M. Lovric. *J. Solid State Electrochem*. **2019**, *23*, 2493.
26. V. Mirceski, R. Gulaboski, J. Solid State Electrochem. **2003**, *7*, 157.
27. V. Mirceski, R. Gulaboski, *Maced. J. Chem. Chem. Eng.* **2014**, *33*, 1.
28. A. A. El Maali, Bioelectrochem. **2004**, *64*, 99.
29. A. Molina, J. M. Gomez-Gil, J. Gonzalez, E. Laborda, J. Electroanal. Chem. **2019**, *847*, 113097. doi.org/10.1016/j.jelechem.2019.04.057
30. M. L. Olmstead, R. G. Hamilton, R. S. Nicholson, *Anal. Chem*. **1969**, *41*, 260.
31. J.M. Savéant, *Elements of Molecular and Biomolecular Electrochemistry: An Electrochemical Approach to Electron Transfer Chemistry*, Hoboken, NJ, Wiley, **2006**.
32.
33. R. Gulaboski, M. Lovric, V. Mirceski, I. Bogeski, M. Hoth, *Biophys. Chem*. **2008**, *137*, 49.
34. R. Gulaboski**,** M. Lovric, V. Mirceski, I. Bogeski, M. Hoth, *Biophys. Chem*. **2008**, *138*, 130.
35. M. Lovric, J. Osteryoung, *Electrochim. Acta* **1982**, *27*, 963.
36. M. Lovric, J. J. O'Dea, J. Osteryoung, *Anal. Chem*. **1983**, *55*, 704.
37. C. Serna, A. Molina, *J. Electroanal. Chem*. **1999**, *466*, 8.
38. A. Molina, F. Martinez-Ortiz, E. Laborda, R. G. Compton, *Electrochim. Acta* **2010**, *55*, 5163.
39. F. Garay, C. A. Barbero, *Anal. Chem*. **2006**, *78*, 6740.
40. A. Molina, F. Martinez-Ortiz, E. Laborda, R. G. Compton, *J. Electroanal. Chem.* **2010**, *648*, 67.
41. M. Lovric, *Electroanal*ysis **1999**, *11*, 1089.
42. A. Molina, C. Serna. L. Camacho, *J. Electroanal. Chem.* **1995**, *394*, 1.
43. V. Mirceski, D. Guzijewski, K. Lisichkov, *Electrochim. Acta* **2013**, *114*, 667.
44. D. Guziejewski, V. Mirceski, D. Jadresko, *Electroanalysis* **2015**, *27*, 67.
45. R. Gulaboski, *Electroanalysis* **2019**, *31*, 545.
46. R. Gulaboski, M. Janeva, V. Maksimova, *Electroanalysis* **2019**, *31*, 946.
47. V. Mirceski, M. Lovric, *Electroanal*ysis **1997**, *9*, 1283.
48. M. Lovric, *J. Electroanal. Chem.* **1983**, *153*, 1.

49. R. Meunier-Prest, E. Laviron, *J. Electroanal. Chem*. **1996**, *410*, 133.
50. A. B. Miler, R. G. Compton, *J. Phys. Chem. B* **2000**, *104*, 5331.
51. J. J. O'Dea, J. G. Osteryoung, *Anal. Chem.* **1997**, *69*, 650.
52. A. Molina, C. Serna, M. López-Tenés, M. M. Moreno, *J. Electroanal. Chem.* **2005**, *576*, 9.
53. J. Galvez, R. Saura, A. Molina, T. Fuente, *J. Electroanal. Chem.* **1982**, *139*, 15.
54. J. Osteryoung, J. J. O'Dea, *Square-wave voltammetry, in Electroanalytical Chemistry*, A. J. Bard, Ed. Marcel Dekker, New York, NY, USA, **1986**, 14, 209.
55. E. Laborda, J. Gonzales, A. Molina, *Electrochim. Acta* **2014**, *43*, 25.
56. J. J. O'Dea, J. G. Osteryoung, *Anal. Chem*. **1993**, *65*, 3090.
57. J. J. O'Dea, J. Osteryoung, R. A. Osteryoung, *Anal. Chem*. **1981**, *53*, 695.
58. M. Lovric, D. Jadresko, Electrochim. Acta, **2010**, *55*, 948.
59. V. Mirceski, M. Lovric, R. Gulaboski, *J. Electroanal. Chem*. **2001**, *515*, 91.
60. J. Galvez, M. L. Alcaraz, S. M. Park, *J. Electroanal. Chem.* **1989**, *266*, 1.
61. M. Lovric, S. Komorsky-Lovric, *Intern. J. Electrochem*. **2012**, http://dx.doi.org/10.1155/2012/596268
62. S. Komorsky-Lovric, M. Lovric, *J. Electroanal. Chem*. **2011**, *660*, 22.
63. P. Song, A. C. Fisher, J. D. Wadhawan, J. J. Cooper, H. J. Ward, N. S. Lawrence, *RSC Advances* **2016**, *6*, 70237.
64. V. Mirceski, E. Laborda, D. Guziejewski, R. Compton, *Anal. Chem*. **2013**, *85*, 5586.
65. V. Mirceski, D. Guzijewski, M. Bozem, I. Bogeski, *Electrochim. Acta* **2016**, *213*, 520.
66. C. Batchelor-McAuley, E. Katelhon, E. O. Barnes, R. G. Compton, E. Laborda, A. Molina, *Chemistry Open* **2015**, *4*, 224.
67. P. N. Barlett, *Bioelectrochemistry*: *Fundamentals, experimental techniques and application*, Wiley, Chichester, **2008**.
68. C. Leger, P. Bertrand, *Chem. Rev*. **2008**, *108*, 2379.
69. F. A. Arsmstrong, *Electrifying metalloenzymes* in*: Metalloproteins: Theory, calculations and experiments* (A. E. Cho, W. A. Goddar III, eds), CRC Press, Taylor&Francis Group, London, New York, **2015**.
70. F. A. Armstrong, *Applications of voltammetric methods for probing the chemistry of redox proteins* In: *Bioelectrochemistry: Principles and practice* (G. Lenaz, G. Milazz eds), Birkhauser Verlag AG, Basel, **1997**.
71. H. Salehzadeh, D. Nematollahi, *Electrochim. Acta* **2013**, *111*, 909.
72. M. Rafiee, D. Nematollahi, H. Salehzadeh, *Electrochim. Acta* **2011**, *56*, 9946.
73. D. Nematollahi, S. Hosseinzadeh, B. Dadpou, *J. Electroanal. Chem*. **2015**, *759*, 144.
74. M. L. Olmstead, R. G. Hamilton, R. S. Nicholson, *Anal. Chem*. **1969**, *41*, 260.
75. V. Mirceski, R. Gulaboski, I. Kuzmanovski, *Bull. Chem. Technol. Macedonia* **1999**, *18*, 57.
76. R. Gulaboski, M. Lovrić, V. Mirčeski, I. Bogeski, M. Hoth, Biophys. Chem., 137 (2008) 49-55.

77. R. Gulaboski, J. Solid State Electrochem. 13 (2009) 1015-1024

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78. R. Gulaboski, V. Mirceski, I. Bogeski, M. Hoth, J. Solid State Electrochem. 16 (2012) 2315-2328
79. V. Mirceski, R. Gulaboski, J. Solid State Electrochem. 7 (2003) 157-165
80. R. Gulaboski, P. Kokoskarova, S. Mitrev, Electrochim. Acta 69 (2012) 86-96.
81. R.G. Compton, C.E. Banks, Cyclic voltammetry: Coupled homogeneous kinetics and adsorption in Understanding Voltammetry, Willey, 2007, pp. 233-284,
82. R. Gulaboski, L. Mihajlov, Biophys. Chem. 159 (2011) 1-9
83. V. Mirceski, S. Komorsky-Lovrić, M. Lovrić, Square-Wave Voltammetry: Theory and Application, (Scholz, F., Ed.) 2nd edn., Berlin, Springer, 2007.
84. V. Mirceski, R. Gulaboski, M. Lovric, I. Bogeski, R. Kappl. M. Hoth, Electroanal. 25 (2013) 2411-2422.
85. T.M. Saccucci, J.F. Rusling, J. Phys. Chem. B, 105 (2001) 6142-6147.
86. R. Gulaboski, V. Mirceski, Electrochim. Acta 167 (2015) 219-225.
87. S.E. Creager, T.T. Wooster, Anal. Chem. 70 (1998) 4257-4263.
88. J. Wang, Analytical Electrochemistry, 2nd edn., Wiley VCH, 2000.
89. V.D. Parker, Chapter 3- Linear sweep and cyclic voltammetry, Comprehensive Chemical Kinetics, 26 (1986) 145-202.
90. L.K. Bieniasz, J. Gonzalez, A. Molina, E. Laborda, Electrochim. Acta 56 (2010) 543-552.
91. S. Komorsky-Lovrić, M. Lovric, Anal. Chim. Acta, 305 (1995) 248-255.
92. D. Jadresko, D. Guzijewski, V. Mirceski, Chem. Electrochem. 5 (2018) 187-194.
93. V. Mirceski, D. Guzijewski, M. Bozem, I. Bogeski, Electrochim. Acta 213 (2016) 520-528.

94. V. Mirceski, E. Laborda, D. Gruzijewski, R.G. Compton, Anal. Chem. 85 (2013) 5586-5594.

95. R.I. Masel, Principles of Adsorption and Reaction on Solid Surfaces, Wiley, New York, 1996.

96. K. Christmann, Introduction to Surface Physical Chemistry, Steinkopff-Verlag, Darmstadt, Germany, 1991.

97. G. Ertl, J. Küppers, Low-energy electrons and surface chemistry, 2. Auflage, Verlag Chemie, Weinheim, 1985.

98. R. Gulaboski, S. Petkovska, Anal. Bioanal. Electrochem. 10 (2018) 566-575.