EDUCATIONAL VOLTAMMETRY: PART 1: Simulation of an EC(reversible) Mechanism in Cyclic Voltammetry

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Abstract

For the first time, an open and freely accessible simulation platform based on MATHCAD is introduced for educational purposes in electrochemistry. This work, *Educational Voltammetry: Part 1*, provides interactive step-by-step protocols that enable students, educators, and researchers to simulate cyclic staircase voltammograms of a diffusional EC(reversible) electrode mechanism under a variety of experimental and kinetic conditions. The approach is designed both for learning and for practical training, making it possible to explore the effects of mass transfer, electrode kinetics, and chemical coupling without requiring advanced programming skills. Upon request, the original MATHCAD files can be obtained directly from the authors. In forthcoming contributions to this series, free interactive protocols for additional important electrode mechanisms will be provided, further broadening the educational toolkit for voltammetric analysis. A 30-day free trial version of MATHCAD 15 is available at: https://support.ptc.com/products/Mathcad/Mathcad-15-0/free-trial?refid=cadventure.

This initiative aims to encourage wider adoption of theoretical modeling in electrochemical education and provide experimentalists with freely available tools for mechanistic understanding.

EC_{rev} electrode mechanism at a planar electrode of a dissolved redox couple in Cyclic Staircse Voltammetry

$$\mathbf{Red} = \mathbf{Ox} + \mathbf{e^-} \qquad (k_s, \alpha) \qquad (1)$$

$$\mathbf{Ox} = \mathbf{Y} \qquad (k_f, k_b, K_{eq}) \qquad (2)$$

$Es := -0.5$ startiung potential (in V vs. the formal potential)

$Ef := 0.5$ switching potential (in V vs. the formal potential)

$dE := 0.005$ potential step increment (in V)

$\Delta E := Ef - Es$ potential window

$v := 0.1$ potential scan rate in V/s

$\tau := \frac{dE}{v}$ duartion of a single step (in s)

$\tau = 0.05$

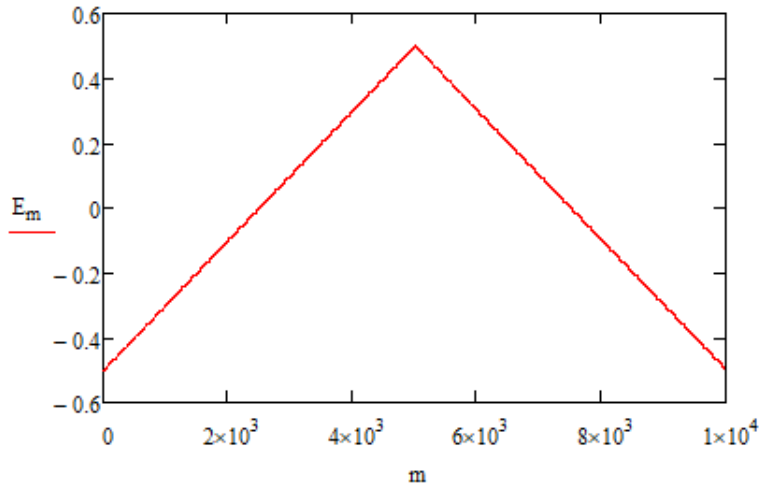
$M := 25$ numer of time increments in a single potential step

$d := \frac{\tau}{M}$ time increment (in s)

$2 \cdot \frac{\Delta E}{dE} = 400$ total number of potential steps

$m := 1 .. 2 \cdot \frac{\Delta E}{dE} \cdot 25$ serial number of time inceremnts

$$E_m := \text{if}\left[m \le \frac{\Delta E}{dE} \cdot 25, Es + \left(\text{ceil}\left(\frac{m}{25}\right) \cdot dE - dE\right), Ef - \left[\text{ceil}\left[\frac{m - \left(\frac{\Delta E}{dE} \cdot 25\right)}{25}\right] \cdot dE - dE\right]\right] \qquad \text{potential ramp} \qquad (3)$$



$F := 96485$ Farady constant

$T := 298.15$ theromodynamic temperature

$R := 8.314$ Gass constant

$n := 1$ stoichiometric number of electrons

$\Phi_m := n \cdot \frac{F}{R \cdot T} \cdot E_m$ dimensionless potential **(4)**

$D := 5 \cdot 10^{-6}$ common diffusion coefficient in cm^2/s

$ks := 0.005$ electrochemical standard rate constant in cm/s

$\alpha := 0.5$ electron transfer coeffcient

$kf := 0.010$ forward rate constant of the chemical recation in s^{-1}

$kb := 1$ backward rate constant of the chemical reaction in s^{-1}

$Keq := \frac{kf}{kb}$ equilibrium contant of the follow up chemical reaction

$K := \frac{ks \cdot \sqrt{\tau}}{\sqrt{D}}$ dimensionless electrode kinetic parameter

$Kchem := (kf + kb) \cdot \tau$ dimensioless chemical kinetic parameter

$S_m := \sqrt{m} - \sqrt{m-1}$ numerical integration parameter **(5)**

$M_m := \operatorname{erf}\left(\sqrt{Kchem \cdot \frac{m}{25}}\right) - \operatorname{erf}\left[\sqrt{Kchem \cdot \frac{(m-1)}{25}}\right]$ numerical integration parameter **(6)**

$$\Psi_1 := \frac{K \cdot e^{\alpha \cdot \Phi_1}}{1 - K \cdot e^{\alpha \cdot \Phi_1} \cdot \left[\frac{-2}{\sqrt{25\pi}} \cdot \left(\left(1 + \frac{e^{-\Phi_1}}{1 + Keq}\right)\right) - \frac{K \cdot e^{-\Phi_1} \cdot M_1}{\sqrt{Kchem} \cdot (Keq + 1)}\right]} \quad \textbf{(7)}$$

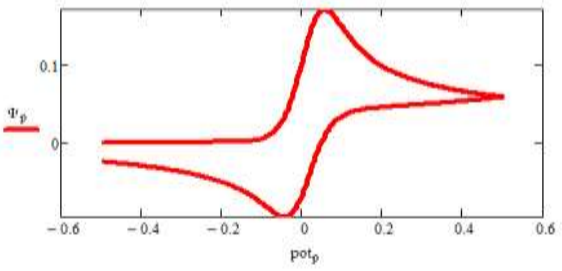
Recurent formulas for calculating the dimensioless current

$$\Psi_m := \frac{K \cdot e^{\alpha \cdot \Phi_m} \cdot \left[1 - \frac{2}{\sqrt{25\pi}} \cdot \left(1 + \frac{e^{-\Phi_m}}{1 + Keq}\right) \cdot \sum_{j=1}^{m-1} \left(\Psi_j \cdot S_{m-j+1}\right) - \frac{K \cdot e^{-\Phi_m}}{(1 + Keq) \cdot \sqrt{Kchem}} \cdot \sum_{j=1}^{m-1} \left(\Psi_j \cdot M_{m-j+1}\right)\right]}{1 - K \cdot e^{\alpha \cdot \Phi_m} \cdot \left[\frac{-2}{\sqrt{25\pi}} \cdot \left(\left(1 + \frac{e^{-\Phi_m}}{1 + Keq}\right)\right) - \frac{K \cdot e^{-\Phi_m} \cdot M_1}{\sqrt{Kchem} \cdot (Keq + 1)}\right]} \quad \textbf{(8)}$$

$p := 1 .. 2 \cdot \frac{\Delta E}{dE} - 1$ serial number of potential steps **(9)**

$\Psi_p := \Psi\left(\frac{\tau}{d \cdot 25} + p\right) \cdot 25$ dimesnioless current at the end of each potential step **(10)**

$pot_p := if\left[p \le \frac{\Delta E}{dE}, Es + p \cdot dE, Ef - \left(p - \frac{\Delta E}{dE}\right) \cdot dE\right]$ potential value of each potential step in V **(11)**



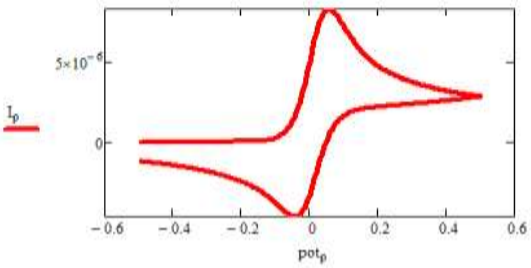
dimensionless cyclic staircase voltammogram

$S := 0.05$ electrode surface area in cm²

$c := 1 \cdot 10^{-6}$ bulk koncetntration of the electractive reactant in mol/cm³

$A := n \cdot F \cdot S \cdot c \cdot \left(\sqrt{\frac{D}{\tau}}\right)$ amperometric contsant

$I_p := \Psi_p \cdot A$ real current in A



References

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. 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. Rubin Gulaboski, V. Mirceski, Journal of Solid State Electrochemistry 28 (**2024**) 1121-1130.