

# **Educational Voltammetry, Part VIII: Electrochemical reaction coupled with an irreversible regenerative chemical reaction (the EC' or electrochemical-catalytic mechanism) at stationary planar electrode under conditions of square-wave voltammetry**

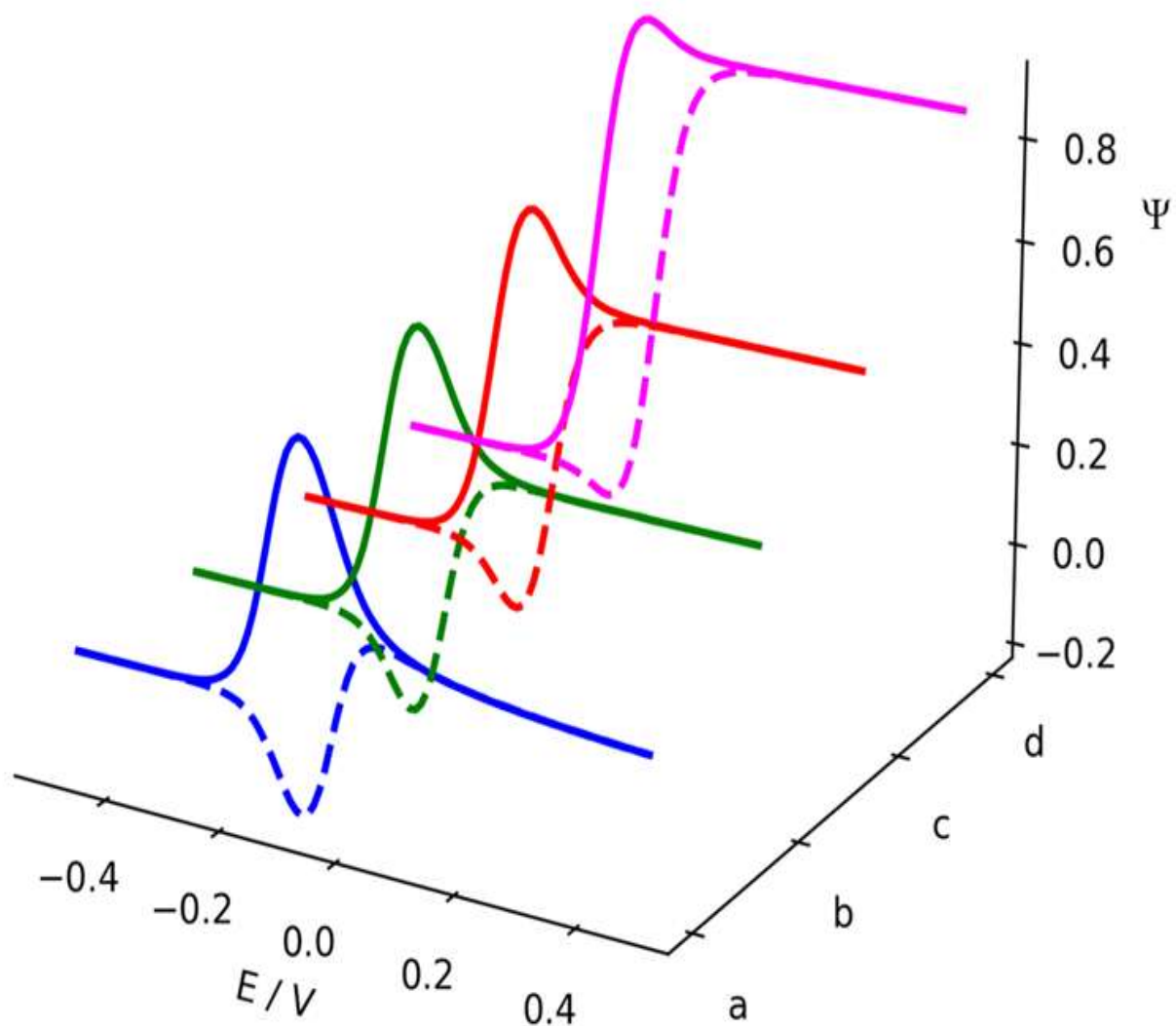
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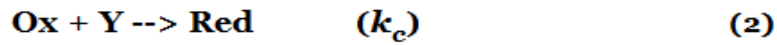
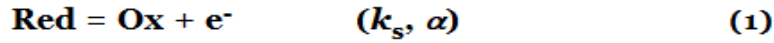
## **Abstract**

Square-wave voltammetry (SWV) offers unique advantages for mechanistic studies because its waveform combines a staircase ramp with rapid potential oscillations and it provides sensitivity to kinetic regimes through adjustable parameters (step increment, amplitude and frequency). In this instalment, we analyze, simulate and interpret voltammetric responses for the EC' mechanism i.e. an electrochemical reaction where the oxidised species reacts irreversibly with a co-reactant to regenerate the starting redox form, producing catalytic current amplification. The study is carried out at a stationary planar electrode under purely diffusional transport, using the Butler–Volmer formalism for electron transfer and a pseudo-first-order rate for the regenerative chemical step. We derive the dimensionless kinetic parameters that govern the response ( $K$  for electron transfer and  $K_{chem}$  and use numerical recursive formulas to compute forward, reverse and net currents. A step-by-step Mathcad protocol is provided so students and researchers can reproduce square-wave voltammograms, explore how scan rate and catalytic rate constant shape the voltammetric profile, and recognize diagnostic features that distinguish EC' mechanisms from simple EC or CE pathways. This resource bridges theory and practice and serves as an accessible introduction to simulating catalytic electrochemical processes with SWV.



**Figure 1.** Effect of chemical rate parameter ( $K_{chem}$ ) to the features of forward and backward current components of an  $EC'$  electrochemical-catalytic mechanism characterized with  $K$  of 0.1,  $n = 1$ ,  $\alpha = 0.5$ . Magnitude of  $K_{chem}$  is set to 0.0002 (a); 0.075 (b); 0.5 (c) and 1 (d).  $E_{sw}=50$  mV,  $dE = 10$  mV and  $f = 10$  Hz.

## EC' (electrochemical-catalytic) electrode mechanism at a planar electrode of a dissolved redox couple in Cyclic Staircase Voltammetry



$E_s := -0.5$  starting potential (in V vs. the formal potential)

$dE := 0.01$  potential step increment (in V)

$\Delta E := 1$  potential window (in V)

$f := 10$  frequency in Hz

$E_{sw} := 0.05$  amplitude in V

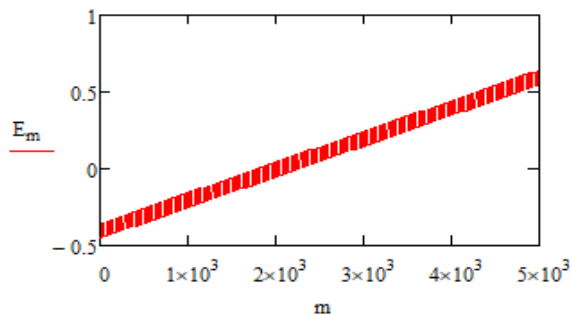
$m := 1.. \frac{\Delta E}{dE} \cdot 50$  serial number of time increments

$$U_m := \left( \text{ceil}\left(\frac{m}{25} \cdot \frac{1}{2}\right) \cdot dE + \text{if}\left(\frac{\text{ceil}\left(\frac{m}{25}\right)}{2} = \text{ceil}\left(\frac{m}{25} \cdot \frac{1}{2}\right), 1, -1\right) \cdot E_{sw} + E_{sw} \right) - dE$$

$$E_m := (E_s + E_{sw}) + U_m$$

(3)

potential



$F := 96485$  Farady constant

$T := 298.15$  thermodynamic temperature (K)

$R := 8.314$  Gass constant (J/mol K)

$n := 1$  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<sup>2</sup>/s

$k_s := 0.05$  electrochemical standard rate constant in cm/s

$\alpha := 0.5$  electron transfer coefficient

$kc := 10$  rate constant of the chemical regenerative recation in s<sup>-1</sup>

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

$K_{chem} := \frac{(kc)}{f}$  dimensionless chemical kinetic parameter

$K_{chem} = 1$

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$$M_m := \operatorname{erf}\left(\sqrt{K_{chem} \cdot \frac{m}{50}}\right) - \operatorname{erf}\left[\sqrt{K_{chem} \cdot \frac{(m-1)}{50}}\right] \quad \text{numerical integration parameter} \quad (6)$$

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$$\Psi_1 := \frac{K \cdot e^{\alpha \cdot \Phi_1}}{1 + \frac{K \cdot e^{\alpha \cdot \Phi_1} \cdot M_1 (1 + e^{-\Phi_1})}{\sqrt{K_{chem}}}} \quad (7)$$

**Recurent formulas for calculating the dimensionless current**

$$\Psi_m := \frac{K \cdot e^{\alpha \cdot \Phi_m} \left[ 1 - \frac{1 + e^{-\Phi_m}}{\sqrt{K_{chem}}} \cdot \sum_{j=1}^{m-1} (\Psi_j \cdot M_{m-j+1}) \right]}{1 + \frac{K \cdot e^{\alpha \cdot \Phi_m} \cdot M_1 (1 + e^{-\Phi_m})}{\sqrt{K_{chem}}}} \quad (8)$$

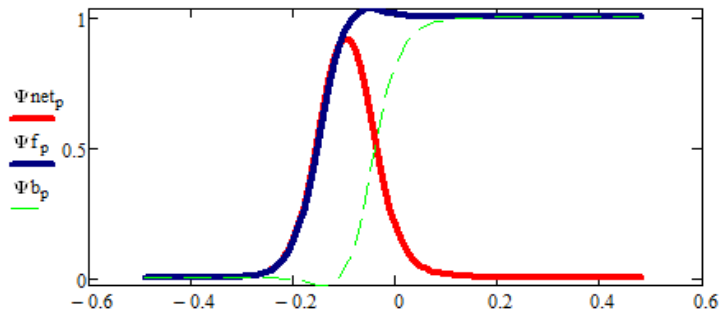
$$p := 1.. \frac{\Delta E}{dE} - 2 \quad \text{serial number of potential pulses} \quad (9)$$

$$\Psi_{f_p} := \Psi_{(p+1) \cdot 50} \quad \text{dimensionless current at the end of forward potential pulses} \quad (10)$$

$$\Psi_{b_p} := \Psi_{50 \cdot p + 25} \quad \text{dimensionless current at the end of backward potential pulses} \quad (11)$$

$$\Psi_{net_p} := \Psi_{f_p} - \Psi_{b_p} \quad \text{dimensionless "net" current} \quad (12)$$

$$pot_p := Es + (p) \cdot dE \quad \text{potential value of each potential pulse in V} \quad (13)$$



dimensionless SW voltammogram

$$S_{\text{eff}} := 0.05 \quad \text{electrode surface area in cm}^2$$

$$c_{\text{eff}} := 1 \cdot 10^{-6} \quad \text{bulk concentration of the electroactive reactant in mol/cm}^3$$

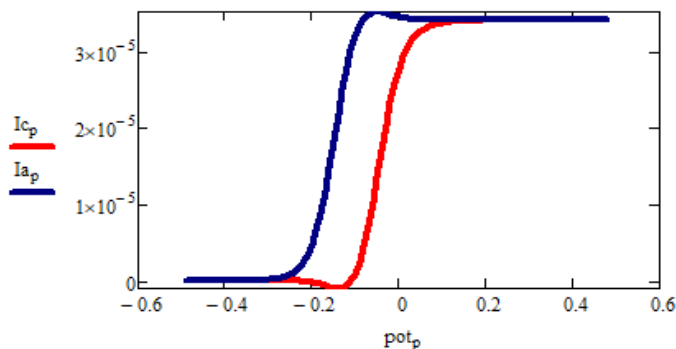
$$A_{\text{eff}} := n \cdot F \cdot S_{\text{eff}} \cdot c_{\text{eff}} \cdot (\sqrt{D \cdot f}) \quad \text{amperometric constant}$$

$$I_p := \Psi_p \cdot A_{\text{eff}} \quad \text{real current in A}$$

$$I_{a_p} := \Psi_{f_p} \cdot A_{\text{eff}}$$

$$I_{c_p} := \Psi_{b_p} \cdot A_{\text{eff}}$$

$$I_{net_p} := I_{a_p} - I_{c_p}$$



## 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.