The ECrevEC′ Mechanism as a Universal Model for Simulating Common Electrode Processes in Cyclic Voltammetry

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Abstract

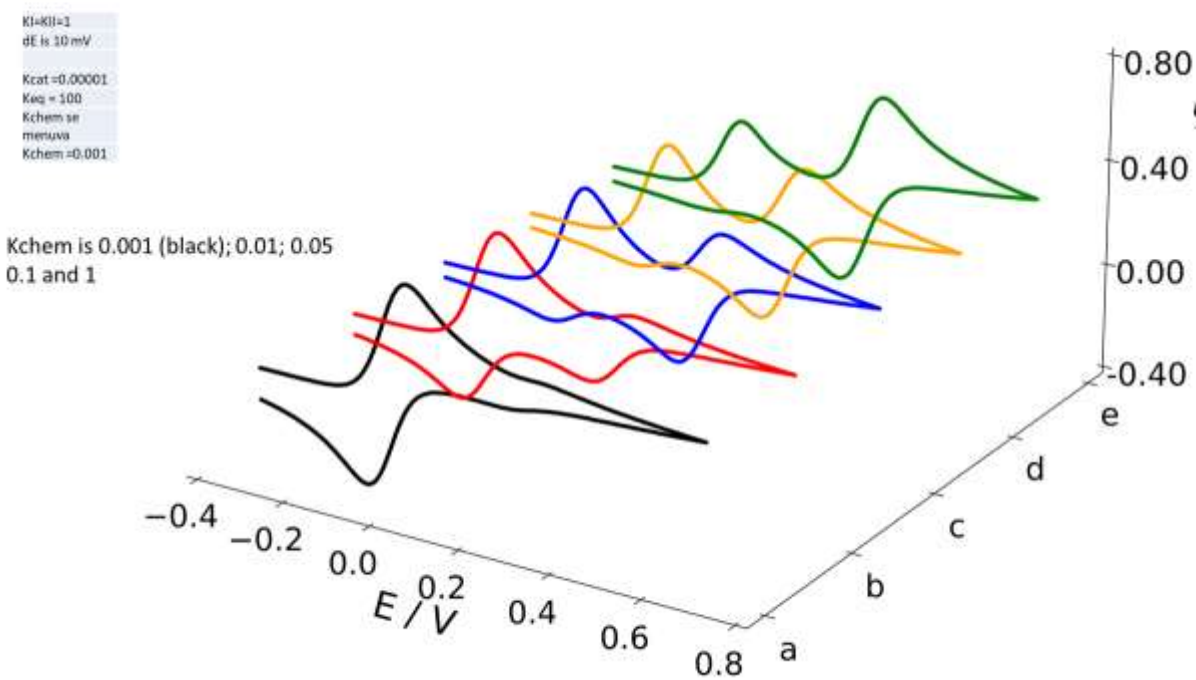
Theoretical models in voltammetry are traditionally developed for specific electrode mechanisms, requiring separate mathematical treatments for simple electron-transfer reactions, catalytic processes, chemical follow-up reactions, regenerative pathways, and adsorption-controlled systems. In this work, we demonstrate that the reversible ECrevEC′ reaction scheme can serve as a unified theoretical framework capable of reproducing the voltammetric behavior of a broad spectrum of commonly encountered electrode mechanisms. Using systematic numerical simulations under cyclo voltammetric conditions, we show that appropriate limiting values of the kinetic and thermodynamic parameters transform the parent ECrevEC′ mechanism into numerous classical reaction pathways, including reversible and quasireversible electron transfer, EC, CE, catalytic EC′, regenerative ECEC′, and related mechanisms. The simulations reveal continuous transitions between mechanistic regimes and establish direct relationships among apparently distinct electrode processes. The proposed approach enables interpretation of diverse voltammetric responses within a single theoretical formalism, reducing the need for multiple independent mechanistic models. Beyond its pedagogical value, the framework provides a practical tool for mechanistic analysis, parameter estimation, and exploration of complex reaction pathways. The results suggest that the ECrevEC′ mechanism represents a versatile parent model from which many conventional electrode mechanisms can be derived as special limiting cases, offering a new perspective toward a unified theory of voltammetric processes. In addition, in the previous work, we gave all important figures, and the entire theoretical model in MATHCAD.

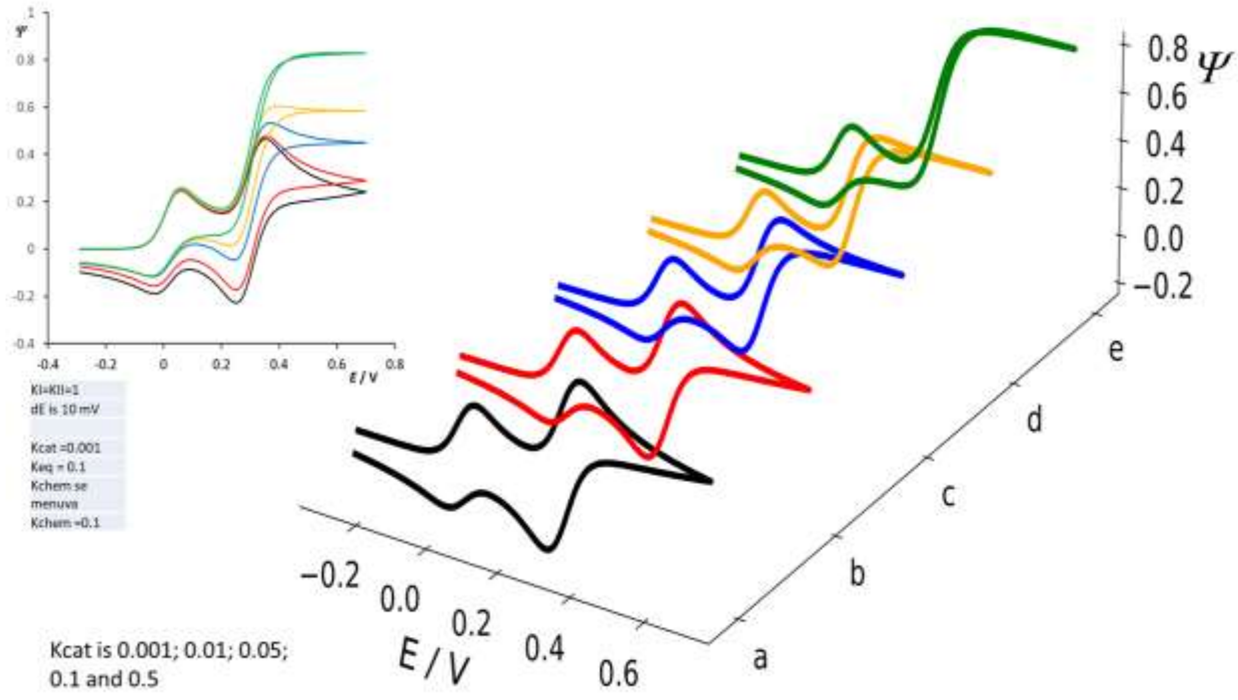
$$\mathbf{E}_1: \quad \mathrm{R} \underset{k_{s,1}^{-1}}{\overset{k_{s,1}}{\rightleftharpoons}} \mathrm{Ox} + e^-$$

$$\mathbf{C}_{\text{rev}}: \quad \mathrm{Ox} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{Int} \qquad (K_{\text{eq}} = k_f/k_b)$$

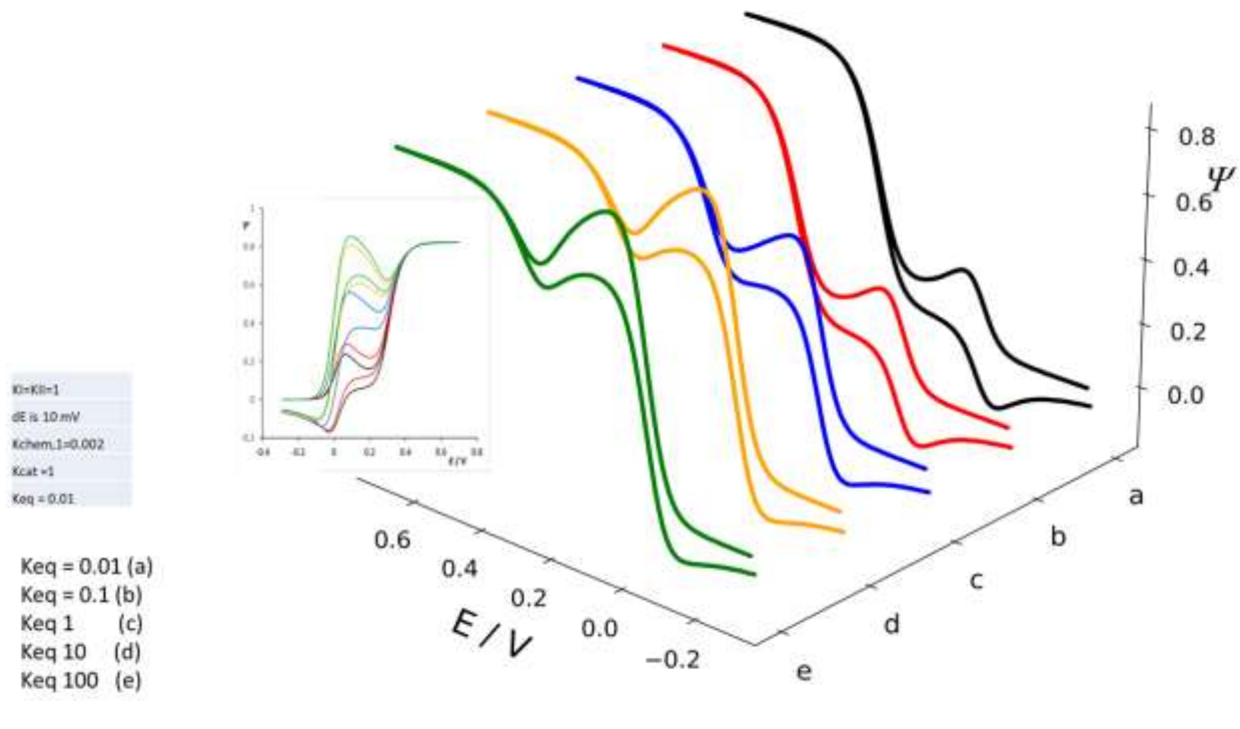
$$\mathbf{E}_2: \quad \mathrm{Int} \underset{k_{s,2}^{-1}}{\overset{k_{s,2}}{\rightleftharpoons}} \mathrm{Red} + e^-$$

$$\mathbf{C}'\,(\text{regenerative}): \quad \mathrm{Red} + \mathrm{Y} \xrightarrow{k_c} \mathrm{R}$$

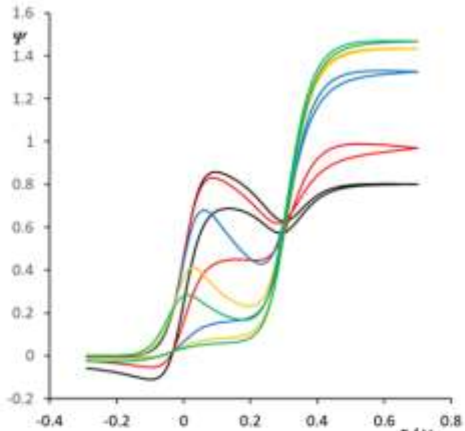


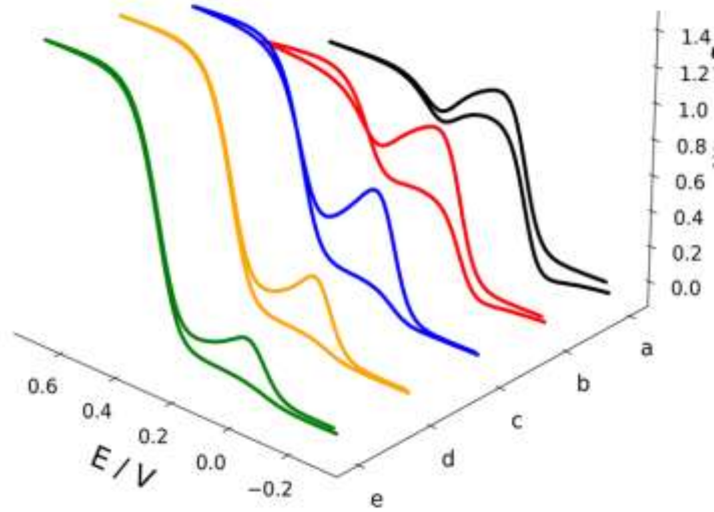


Kcat is 0.001; 0.01; 0.05; 0.1 and 0.5



Keq = 0.01 (a)
Keq = 0.1 (b)
Keq 1 (c)
Keq 10 (d)
Keq 100 (e)





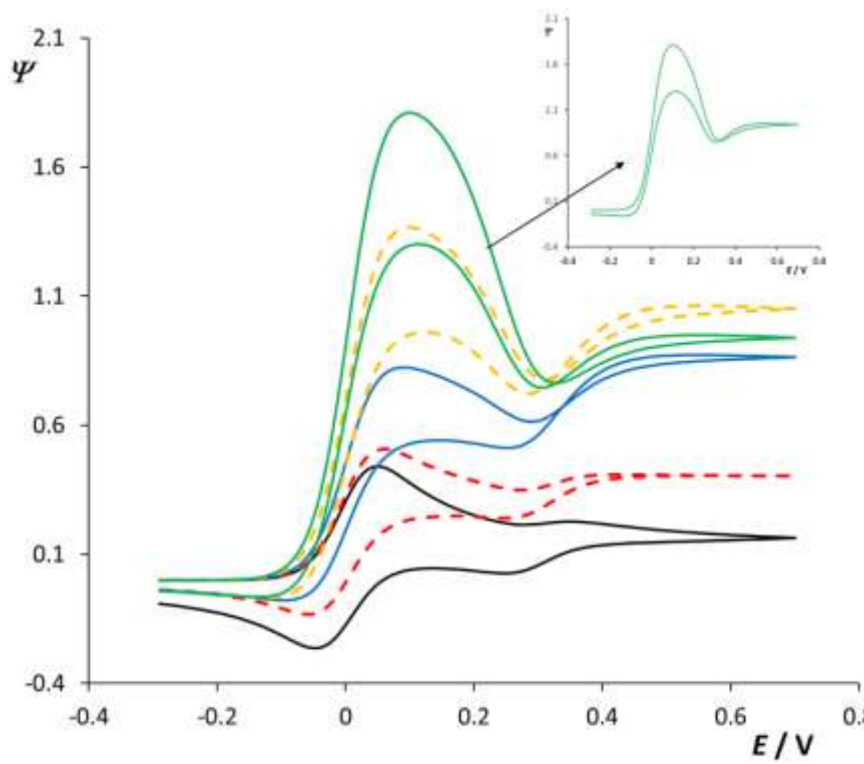
KI=KII=1
dE is 10 mV

Kcat =1
Keq = 100
Kchem se menuva
Kchem =0.001

Kchem 10 (green), 1, 0.1; 0.01 and 0.001 (black)

KI=KII=1
dE is 10 mV

Kcat =0.001
Keq = 0.1
Kchem se menuva
Kchem =0.1



Kcat is 0.001 (black)
0.1 (red)...
1 (blue)
10 (yellow)
100 (green)

Keq is 100
Kchem is 0.005

Kcat vlijae I na prv
Proces pri ovie uslovi

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.