Mathematical Modeling of Surface-Confined EC′E Mechanism in Protein-Film Voltammetry (Electrode Reaction Scheme of two-step Consecutive Redox Mechanism featuring Intermediate Regenerative Step, with all Redox Forms Present in Adsorbed State)

Sanja Lazarova, Milkica Janeva, Rubin Gulaboski

Faculty of Medical Sciences, Goce Delcev University, Stip, Macedonia

Abstract

A comprehensive theoretical framework for the analysis of a surface-confined EC′E mechanism is presented, describing a two-step consecutive redox process involving an intermediate regenerative chemical step, where all participating redox forms are immobilized on the electrode surface. The model is developed under conditions of complete surface confinement, neglecting mass transport effects, and is based on a system of coupled differential equations formulated within the Butler–Volmer kinetic formalism.

The regenerative chemical reaction, treated under pseudo-first-order conditions, introduces catalytic feedback that significantly alters the dynamic distribution of surface species and the resulting electrochemical response. Numerical simulations are performed for various kinetic regimes of the electron-transfer steps and the chemical regeneration, revealing distinct voltammetric signatures characteristic of the interplay between consecutive electron transfers and catalytic cycling. The model demonstrates that the relative rates of the two electron-transfer steps and the regenerative reaction govern the shape, position, and magnitude of the voltammetric peaks, enabling mechanistic discrimination and kinetic parameter evaluation. Under limiting conditions, the proposed framework converges to simpler surface-confined mechanisms, including EE, EC′E, E, and single-step EC′ systems, highlighting its versatility as a unified modeling platform.

The presented theoretical approach is particularly relevant for interpreting voltammetric responses of surface-immobilized redox systems, such as protein-film electrochemistry and catalytic interfaces, where intermediate species undergo rapid regenerative transformations. This work provides a robust basis for mechanistic analysis and quantitative evaluation of complex surface-confined electrochemical systems.

1. Description of the Reaction Scheme

The EC′E mechanism for a redox transformations assuming all participants in adsorbed states is defined as:

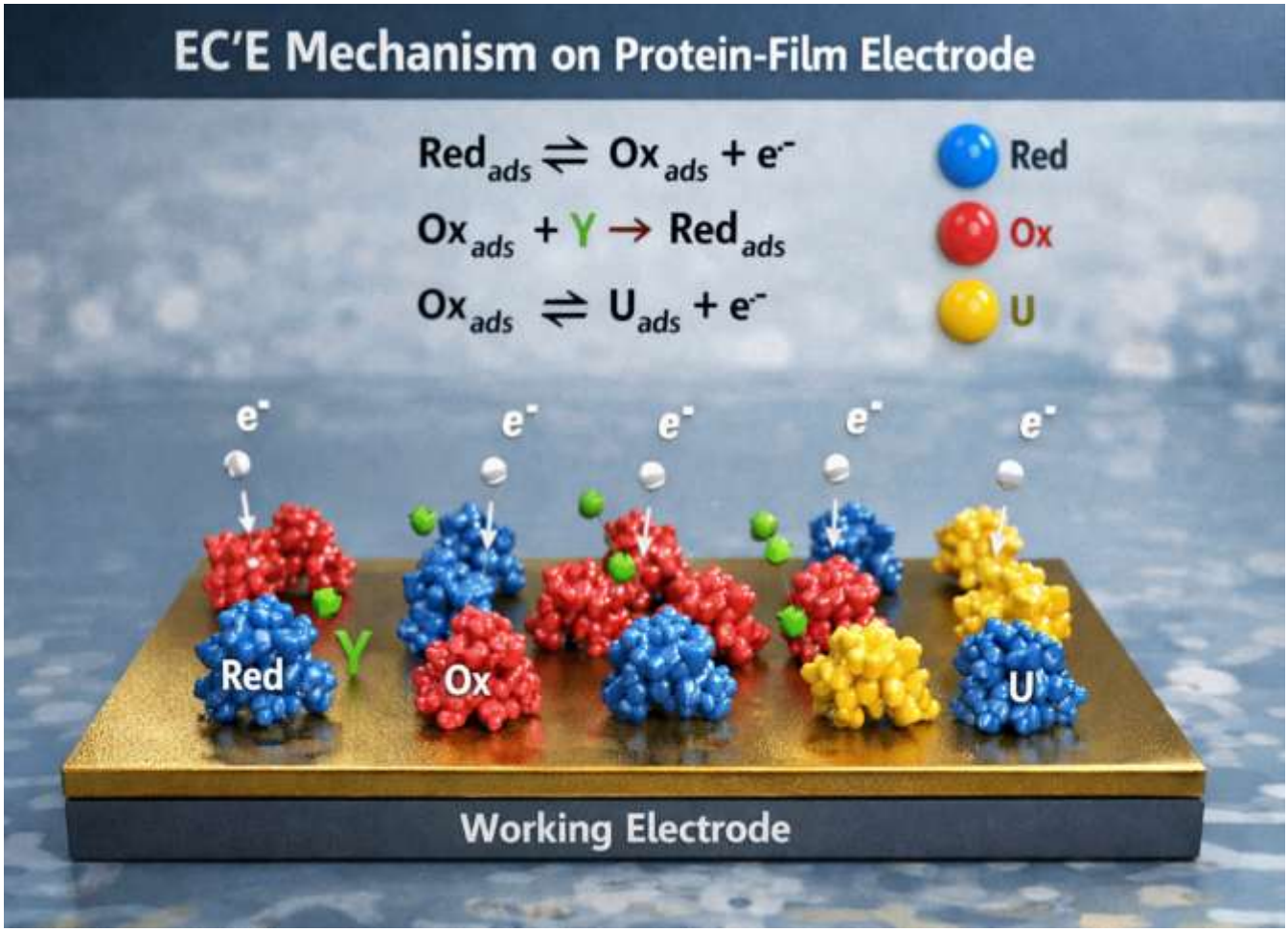
$Red(ads) \rightleftharpoons Ox(ads) + e^-$

$Ox(ads) + Y \rightarrow Red(ads)$

$Ox(ads) \rightleftharpoons U(ads) + e^-$

Assuming Y is in large excess, the chemical step is pseudo-first-order, i.e.,:

$kc' = kc \cdot c(Y)$



2. Differential Equations (Mass Balance)

The time evolution of surface concentrations (Γ) is governed by:

Differential Equation for Red:

$d\Gamma(Red)/dt = -I_1/(nFS) + kc' \cdot \Gamma(Ox)$

Red is consumed in the first electron-transfer step and regenerated via the catalytic reaction.

Differential Equation for Ox:

$d\Gamma(Ox)/dt = I_1/(nFS) - kc' \cdot \Gamma(Ox) - I_2/(nFS)$

Ox is formed from Red, consumed by catalytic regeneration, and further oxidized to F.

Differential Equation for U:

$d\Gamma(U)/dt = I_2/(nFS)$

Final redox form "U" is formed in the second electron-transfer step and does not participate in further reactions.

3. Kinetic Expressions (Butler–Volmer Form)

Electron-transfer rates are described using Butler–Volmer kinetics:

Butler-VOlmer formalism applied to First electron-transfer step (Red ⇌ Ox):

$$\mathbf{I_1(nFS) = k\_s,1 \cdot exp[(1 - \alpha1)\cdot F/(R\cdot T)\cdot (E - E1°')] \cdot \Gamma Red - k\_s,1 \cdot exp[-\alpha1\cdot F/(R\cdot T)\cdot (E - E1°')] \cdot \Gamma(Ox)}$$

Butler-VOlmer formalism applied to Second electron-transfer step (Ox ⇌ U):

$$\mathbf{I_2/(nFS) = k\_s,2 \cdot exp[(1 - \alpha2)\cdot F/(R\cdot T)\cdot (E - E2°')] \cdot \Gamma(Ox) - k\_s,2 \cdot exp[-\alpha2\cdot F/(R\cdot T)\cdot (E - E2°')] \cdot \Gamma(U)}$$

4. Initial Conditions

At t = 0, the system is assumed to be fully reduced:

$\Gamma\_Red(0) = \Gamma^*$

$\Gamma\_Ox(0) = 0$

$\Gamma\_U(0) = 0$

5. Conditions for t > 0

During the experiment, the following conditions apply:

Mass Conservation of total surface concentration of all redox active species:

$\Gamma\_Red(t) + \Gamma\_Ox(t) + \Gamma\_U(t) = \Gamma^*$

Meaning of the symbols:

Γ -symbol of surface concentration

t-time

E = E(t)- time-dependent potential

F-Faraday Constant

T-Thermodynamic temperature

S-electrode surface area

n-number of electrons exchanged

α-electron transfer coefficient

ks,1 and ks,2-standard rate constants of electron transfer of first and second electron transfer steps, respectively

kc'-chemical rate constant of catalytic (regenerative) reaction

I_1-current associated to the first electrode transformation

I_2-current associated to the second electrode transformation

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. V. Mirceski, M. Lovric, R. Gulaboski, Journal of Electroanalytical Chemistry 515 (2001) 91-100.

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.

40. R Gulaboski, F Borges, CM Pereira, M Cordeiro, J Garrido, AF Silva, Combinatorial chemistry & high throughput screening 10 (2007), 514-526