Modeling Protein-Film Voltammetry of Surface $C_{rev}E$ Mechanism under Butler-Volmer Kinetics

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Protein-film voltammetry is simple electrochemical methodology designed to get access to direct electrochemical conversion of redox-active species immobilized at the electrode surface. In this case, the reacting molecules do not diffuse from the bulk solution toward the electrode. Instead, the entire electrochemical response is controlled by the amount of adsorbed material, the rate of heterogeneous electron transfer, and possible coupled chemical transformations inside the surface-confined film.

The surface mechanism considered here, i.e. the surface CrevE mechanism, is a reversible one-electron transformation between the adsorbed reduced and oxidized forms of a protein, preceded by a reversible chemical conversion of the oxidized form into another adsorbed state:

$$\mathrm{Y(ads)} \rightleftharpoons \mathrm{R(ads)} \qquad \text{(I)}$$

$$\mathrm{Red(ads)} \rightleftharpoons \mathrm{Ox(ads)} + e^{-} \qquad \text{(II)}$$

The first reaction (I) is the chemical reaction. This chemical step is a surface-confined reversible chemical reaction, described by the forward rate constant k_f, the backward rate constant k_b, and the equilibrium constant K_{eq} equal to $K_{eq} = k_f/k_b$.

The second reaction (II) is electrochemical step, characterized by electron transfer coefficient alpha, and standard rate constant of electron transfer ks.

The total surface concentration of all adsorbed forms is conserved:

$$\Gamma_T = \Gamma_{Red} + \Gamma_{Ox} + \Gamma_Y$$

In last equation, Γ_T is the total surface coverage, while Γ_{Red}, Γ_{Ox}, and Γ_Y are the surface concentrations of the reduced, oxidized, and chemically transformed adsorbed species. This condition is essential for surface-confined protein-film voltammetry, because no mass transport from the solution is involved. All changes in the voltammetric signal originate from redistribution of the fixed surface population among the three adsorbed states.

As mentioned, the reversible chemical step is defined by:

$$K_{eq} = \frac{k_f}{k_b}$$

When the chemical step is sufficiently fast compared with the time scale of the voltammetric experiment, the chemical equilibrium condition can be written as:

$$\Gamma_Y = K_{eq}\Gamma_{Red}$$

By substituting this relation into the total surface conservation equation, one obtains:

$$\Gamma_T = \Gamma_{Red} + \Gamma_{Ox} + K_{eq}\Gamma_{Red}$$

or:

$$\Gamma_T = \Gamma_{Ox} + \left(1 + K_{eq}\right)\Gamma_{Red}$$

From this expression, the surface concentration of the reduced form can be evaluated as:

$$\Gamma_{Red} = \frac{\Gamma_T - \Gamma_{Ox}}{1 + K_{eq}}$$

Similarly, the surface concentration of the oxidized form can be expressed as:

$$\Gamma_{Ox} = \Gamma_T - \left(1 + K_{eq}\right)\Gamma_{Red}$$

When K_{eq} is high, a larger fraction of the reduced state is generated from Y(ads), and therefore the concentration of free Y(ads) becomes smaller. As a result, the cathodic component of the voltammetric response can be suppressed even when the electron-transfer reaction itself is not slow.

The electron-transfer kinetics are described by the Butler-Volmer formalism. The potential-dependent oxidation rate constant is:

$$k_{ox} = k_s \exp\left[\frac{\alpha F(E - E^0)}{RT}\right]$$

The potential-dependent reduction rate constant is:

$$k_{red} = k_s \exp\left[-\frac{(1 - \alpha)F(E - E^0)}{RT}\right]$$

In these equations, E is the applied electrode potential, E^0 is the formal potential of the surface redox couple, F is the Faraday constant, R is the gas constant, and T is the absolute temperature. The parameter k_s determines how fast the adsorbed protein exchanges electrons with the electrode at the formal potential. A large k_s produces nearly reversible voltammetric behavior, whereas a small k_s leads to quasireversible or irreversible features, such as peak broadening, peak displacement, and decrease of the backward component.

The parameter α describes the symmetry of the activation barrier. When $\alpha = 0.5$, the effect of the applied potential on oxidation and reduction is symmetric. If α differs from 0.5, the oxidation and reduction branches respond differently to the same potential perturbation, which can lead to asymmetric voltammetric peaks.

For a surface-confined system, the faradaic current is proportional to the net rate of electron transfer between the electrode and the adsorbed film:

$$I = nFA(k_{ox}\Gamma_{Red} - k_{red}\Gamma_{Ox})$$

where n is the number of transferred electrons and A is the electrode area. The first term, $k_{ox}\Gamma_{Red}$, represents the anodic oxidation flux of Red(ads) into Ox(ads). The second term, $k_{red}\Gamma_{Ox}$, represents

the cathodic reduction flux of Ox(ads) back to Red(ads). Therefore, the measured current is the difference between the forward and backward electron-transfer rates.

Using the equilibrium expression for the chemically coupled step, the current can be written only in terms of Γ_{Red} and the total surface coverage:

$$I = nFA\left[k_{ox}\Gamma_{Red} - k_{red}\left(\frac{\Gamma_T - \Gamma_{Ox}}{1 + K_{eq}}\right)\right]$$

This form is useful because it explicitly shows how the chemical equilibrium modifies the Butler-Volmer current. If K_{eq} increases, the denominator $(1 + K_{eq})$ increases, and the effective concentration of Ox(ads) available for reduction decreases. Consequently, the backward current becomes smaller. This effect can make the voltammogram appear more irreversible, even if the heterogeneous electron transfer is relatively fast.

Alternatively, the current can be written in terms of Γ_{Ox}:

$$I = nFA\left[k_{ox}\left(\Gamma_T - (1 + K_{eq})\Gamma_{Red}\right) - k_{red}\Gamma_{Ox}\right]$$

This expression emphasizes the opposite viewpoint: formation of Ox(ads) during oxidation is immediately influenced by its chemical conversion to Y(ads). The larger the value of K_{eq}, the more strongly the total surface population is shifted away from Ox(ads), which changes both the peak current and the shape of the voltammetric response.

If the chemical reaction is not sufficiently fast to maintain equilibrium, the full kinetic model must be used. The time evolution of the surface concentrations is then described by the following differential equations:

$$\frac{d\Gamma_{Red}}{dt} = k_f\Gamma_Y - k_b\Gamma_{Red} - k_{ox}\Gamma_{Red} + k_{red}\Gamma_{Ox}$$

$$\frac{d\Gamma_{Ox}}{dt} = k_{ox}\Gamma_{Red} - k_{red}\Gamma_{Ox}$$

The first equation describes the gain of Red(ads) via regeneration from Y and its oxidation to Ox(ads). The second equation describes the formation and consumption of Ox(ads) through the electron-transfer step.

At the beginning of the experiment, the initial condition is often selected so that the protein film is fully reduced:

$$\Gamma_{Red}(t = 0)/\Gamma_Y = Keq$$

$$\Gamma_{Ox}(t = 0) = 0$$

These initial conditions are appropriate when the starting potential is sufficiently negative to keep the surface-confined redox protein in its reduced state. If the experiment starts from a more positive potential, different initial surface distributions may be required.

Several limiting cases can be obtained from the same model. If the chemical reaction is absent, then:

$$k_f = 0 \quad \text{and} \quad k_b = 0$$

and the mechanism reduces to a simple surface-confined electron-transfer reaction:

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

Under this condition, the voltammetric response is controlled only by k_s, α, and the total surface coverage. This is the simplest protein-film voltammetric model.

If the chemical step is irreversible, then:

$$k_f > 0 \quad \text{and} \quad k_b = 0$$

In this case, Red(ads) is continuously createdo form Y(ads). The backward current decreases because less Red(ads) is available for electrochemical reduction. This limiting case corresponds to a surface CE mechanism with irreversible chemical follow-up reaction.

If both chemical rate constants are nonzero:

$$k_f > 0 \quad \text{and} \quad k_b > 0$$

then the chemical step is reversible. The degree to which the chemical equilibrium influences the voltammetric response depends on the values of k_f, k_b, and K_{eq} relative to the experimental time scale. Fast chemical kinetics produce an equilibrium-controlled response, whereas slow chemical kinetics produce a kinetically controlled response.

When k_s is very large, the electron transfer is fast and the surface concentrations of Red(ads) and Ox(ads) tend to follow the applied potential almost reversibly. In this case, the chemical reaction becomes the dominant factor shaping the voltammogram. When k_s is small, electron transfer itself becomes the limiting process, and the chemical reaction may have a weaker observable effect because Ox(ads) is generated slowly.

Thus, the considered surface CrevE mechanism treated with Butler-Volmer kinetics provides a flexible theoretical framework for protein-film voltammetry. It allows the simultaneous evaluation of electron-transfer kinetics, surface concentration redistribution, and chemically coupled conformational or ligand-binding processes. The most important feature of this formalism is that the experimentally measured current is directly linked to the dynamic surface concentrations of Red(ads) and Ox(ads), which are themselves controlled by both the electrode potential and the coupled chemical equilibrium.

Entire MATHCAD simulation protocols of surface CrevE mechanism (ready for simulating square-wave and cyclic voltammograms) related to this mechanism are given in Repository of Goce Delcev University, Stip, for free.

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.