Mathematics behind Protein-Film Voltammetry of a Surface CirrECirr Mechanism Coupled with Irreversible Preceding and Irreversible Follow-up Chemical Reactions under Butler-Volmer Kinetics

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Abstract

This study presents a theoretical treatment of a surface CirrECirr mechanism relevant to protein-film voltammetry. The mechanism involves an irreversible preceding chemical step, A(ads) → Red(ads), a Butler–Volmer-controlled electron-transfer reaction Red(ads) ⇌ Ox(ads), and an irreversible follow-up chemical transformation Ox(ads) + Z(ads) → Y(ads). A system of kinetic differential equations is derived to describe the temporal redistribution of all adsorbed species participating in the overall mechanism. The model explicitly accounts for the competition between electrochemical generation of Ox(ads) and its irreversible chemical consumption, which significantly affects the backward component of the voltammetric response. Analytical and numerical formulations are developed to evaluate the influence of kinetic parameters, transfer coefficients, and experimental time scale on the observed current. The proposed mathematical framework provides a useful tool for investigating surface-confined redox systems coupled with irreversible chemical transformations in protein-film voltammetry.

Reaction scheme and definition of the surface model

The surface mechanism considered here consists of an irreversible preceding chemical transformation of an initially adsorbed precursor into the reduced electroactive form, a one-electron surface electrode reaction between the reduced and oxidized forms, and an irreversible follow-up chemical reaction consuming the electrochemically generated oxidized form. The mechanism can be written as:

$$\mathrm{A(ads)} \overset{k_p}{\rightarrow} \mathrm{Red(ads)}$$

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

$$\mathrm{Ox(ads)} + \mathrm{Z(ads)} \overset{k_f}{\rightarrow} \mathrm{Y(ads)}$$

The first chemical reaction is irreversible and precedes the electrode step. It is characterized by the first-order surface chemical rate constant k_p. This step generates the reduced electroactive form Red(ads) from the adsorbed precursor A(ads). The second step is the electron-transfer reaction and is described by the Butler-Volmer formalism. The third step is an irreversible follow-up chemical reaction, in which the oxidized form Ox(ads) is

consumed by reaction with an adsorbed or interfacially available species Z(ads), producing the chemically transformed surface product Y(ads).

For a strictly surface-confined film, the total amount of adsorbed material participating in the mechanism is conserved. Thus:

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

where Γ_T is the total surface concentration of all adsorbed forms, while Γ_A, Γ_{Red}, Γ_{Ox}, and Γ_Y are the surface concentrations of A(ads), Red(ads), Ox(ads), and Y(ads), respectively. This condition is fundamental for protein-film voltammetry, because the reacting redox centers remain immobilized at the electrode surface and the voltammetric response originates from redistribution of the surface population among chemically and electrochemically connected forms.

If Z(ads) is present in large excess, or if its interfacial concentration remains constant on the experimental time scale, the follow-up reaction can be written in pseudo-first-order form:

$$k_c = k_f \Gamma_Z$$

and therefore:

$$\text{Ox(ads)} \xrightarrow{k_c} \text{Y(ads)}$$

In this formulation, k_c is the apparent first-order rate constant of the irreversible follow-up chemical step. This approximation is especially useful in protein-film voltammetry when the co-reactant Z(ads) is continuously available at the film/solution interface or when its concentration does not change significantly during one voltammetric scan.

Butler-Volmer kinetics of the surface electron-transfer step

The potential-dependent oxidation rate constant for the transformation of Red(ads) into Ox(ads) is:

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

The potential-dependent reduction rate constant for the reverse transformation of Ox(ads) into Red(ads) is:

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

In these equations, E is the applied electrode potential, E^0 is the formal potential of the immobilized Red/Ox redox couple, k_s is the standard heterogeneous electron-transfer rate constant, α is the electron-transfer coefficient, F is the Faraday constant, R is the gas constant, and T is the absolute temperature. The exponential dependence of k_{ox} and k_{red} on the applied potential is the central feature that connects the dynamic surface concentrations with the measured voltammetric current.

The value of k_s determines the kinetic regime of the surface electrode reaction. Large values of k_s produce nearly reversible voltammetric behavior, whereas small values of k_s cause quasireversible or irreversible features such as peak broadening, peak displacement, and suppression of the backward current component. The transfer coefficient α controls the symmetry of the activation barrier. When $\alpha = 0.5$, the potential affects oxidation and reduction symmetrically. When α differs from 0.5, the anodic and cathodic branches respond asymmetrically to the same potential perturbation.

Differential equations for the CirrECirr surface mechanism

For the pseudo-first-order formulation of the follow-up chemical reaction, the time evolution of the four surface species is described by the following differential equations:

$$\frac{d\Gamma_A}{dt} = -k_p\Gamma_A$$

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

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

$$\frac{d\Gamma_Y}{dt} = k_c\Gamma_{Ox}$$

The first equation describes the irreversible consumption of A(ads) and its conversion into Red(ads). The second equation describes the formation of Red(ads) from A(ads), its electrochemical oxidation into Ox(ads), and its regeneration by electrochemical reduction of Ox(ads). The third equation describes the formation of Ox(ads) through oxidation of Red(ads), its electrochemical reduction back to Red(ads), and its irreversible chemical consumption into Y(ads). The fourth equation describes the accumulation of the chemically transformed product Y(ads).

By adding all four differential equations, one obtains:

$$\frac{d\Gamma_A}{dt} + \frac{d\Gamma_{Red}}{dt} + \frac{d\Gamma_{Ox}}{dt} + \frac{d\Gamma_Y}{dt} = 0$$

or equivalently:

$$\frac{d\Gamma_T}{dt} = 0$$

This confirms that the total amount of adsorbed material remains constant during the voltammetric experiment. Therefore, the mechanism is surface-confined, even though the individual surface forms are continuously transformed by chemical and electrochemical steps.

Full second-order form of the follow-up chemical step

If the concentration of Z(ads) cannot be considered constant, the irreversible follow-up reaction must be treated in its full second-order form:

$$\mathrm{Ox(ads)} + \mathrm{Z(ads)} \overset{k_f}{\rightarrow} \mathrm{Y(ads)}$$

In this case, the kinetic equations become:

$$\frac{d\Gamma_A}{dt} = -k_p\Gamma_A$$

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

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

$$\frac{d\Gamma_Z}{dt} = -k_f\Gamma_{Ox}\Gamma_Z$$

$$\frac{d\Gamma_Y}{dt} = k_f\Gamma_{Ox}\Gamma_Z$$

This more general formulation is useful when Z(ads) is part of the finite surface population and is consumed during the experiment. However, for most practical protein-film voltammetric simulations, the pseudo-first-order approximation is simpler and more convenient, because it allows the chemical follow-up reaction to be described by the single apparent rate constant k_c.

Initial conditions

If the voltammetric experiment starts from an initial state in which the adsorbed film consists only of the precursor form A(ads), the initial conditions are:

$$\Gamma_A(0) = \Gamma_T$$

$$\Gamma_{Red}(0) = 0$$

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

$$\Gamma_Y(0) = 0$$

These initial conditions correspond to a situation in which the electroactive Red/Ox pair is generated only after the preceding irreversible chemical step begins. This is the characteristic feature of a CirrECirr surface mechanism. If the film is partially converted before the voltammetric experiment begins, more general initial conditions can be used:

$$\Gamma_A(0) = a_0\Gamma_T$$

$$\Gamma_{Red}(0) = r_0\Gamma_T$$

$$\Gamma_{Ox}(0) = o_0\Gamma_T$$

$$\Gamma_Y(0) = y_0\Gamma_T$$

with:

$$a_0 + r_0 + o_0 + y_0 = 1$$

In most theoretical simulations, the fully precursor-based initial state is the most useful starting point, because it clearly reveals the effect of the preceding irreversible chemical reaction on the shape and intensity of the voltammetric response.

Analytical expression for the preceding irreversible chemical step

The first differential equation can be solved directly:

$$\frac{d\Gamma_A}{dt} = -k_p\Gamma_A$$

Integration gives:

$$\Gamma_A(t) = \Gamma_A(0)\exp(-k_p t)$$

If $\Gamma_A(0) = \Gamma_T$, then:

$$\Gamma_A(t) = \Gamma_T\exp(-k_p t)$$

This expression shows that the amount of precursor A(ads) decreases exponentially with time. The rate of this decay is controlled by k_p. When k_p is large, Red(ads) is generated rapidly and the mechanism approaches a classical ECirr mechanism. When k_p is small, Red(ads) is generated slowly, and the voltammetric response can be strongly delayed or suppressed because the electroactive form is not available in sufficient amount during the potential scan.

By substituting this expression into the equation for Red(ads), one obtains:

$$\frac{d\Gamma_{Red}}{dt} = k_p\Gamma_T\exp(-k_p t) - k_{ox}\Gamma_{Red} + k_{red}\Gamma_{Ox}$$

This equation explicitly demonstrates how the preceding irreversible chemical step acts as a time-dependent source term for Red(ads). Thus, the electrochemical current is not governed only by the Butler-Volmer electron-transfer kinetics, but also by the rate at which the electroactive reduced form is produced inside the immobilized film.

Incorporation into the Butler-Volmer current equation

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

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

where $n = 1$ for the one-electron Red/Ox transformation, A is the electrode area, and the two terms inside the parentheses represent the anodic and cathodic electron-transfer rates, respectively. The anodic component is:

$$I_{ox} = nFAk_{ox}\Gamma_{Red}$$

and the cathodic component is:

$$I_{red} = nFAk_{red}\Gamma_{Ox}$$

Substituting the Butler-Volmer expressions for k_{ox} and k_{red} gives:

$$I = nFA\left\{k_s\exp\left[\frac{(1-\alpha)F(E-E^0)}{RT}\right]\Gamma_{Red} - k_s\exp\left[-\frac{\alpha F(E-E^0)}{RT}\right]\Gamma_{Ox}\right\}$$

or:

$$I = nFAk_s\left\{\Gamma_{Red}\exp\left[\frac{(1-\alpha)F(E-E^0)}{RT}\right] - \Gamma_{Ox}\exp\left[-\frac{\alpha F(E-E^0)}{RT}\right]\right\}$$

This is the central Butler-Volmer current equation for the surface CirrECirr mechanism. The surface concentrations Γ_{Red} and Γ_{Ox} are not independent equilibrium quantities; they are generated dynamically by the coupled differential equations. Therefore, the preceding irreversible chemical reaction controls the availability of Red(ads), while the irreversible follow-up chemical reaction controls the lifetime of Ox(ads). Both chemical reactions are directly reflected in the measured current through the time-dependent values of Γ_{Red} and Γ_{Ox}.

Stationary concentration relations at a fixed potential

At a fixed potential, the Butler-Volmer rate constants are constant. Under quasi-stationary conditions for Red(ads) and Ox(ads), one may write:

$$\frac{d\Gamma_{Red}}{dt} \approx 0$$

$$\frac{d\Gamma_{Ox}}{dt} \approx 0$$

The stationary equation for Ox(ads) is:

$$k_{ox}\Gamma_{Red} - (k_{red} + k_c)\Gamma_{Ox} = 0$$

from which:

$$\Gamma_{Ox} = \frac{k_{ox}}{k_{red} + k_c}\Gamma_{Red}$$

This relation shows that the amount of Ox(ads) is decreased by the irreversible follow-up reaction. When k_c increases, Ox(ads) is consumed more rapidly, and the cathodic component

of the voltammetric response becomes smaller. This gives the voltammogram a more irreversible character, even when the electron-transfer step is not intrinsically slow.

Using the stationary equation for Red(ads):

$$k_p\Gamma_A - k_{ox}\Gamma_{Red} + k_{red}\Gamma_{Ox} = 0$$

and substituting $\Gamma_{Ox} = \frac{k_{ox}}{k_{red}+k_c}\Gamma_{Red}$ gives:

$$k_p\Gamma_A - k_{ox}\Gamma_{Red} + k_{red}\frac{k_{ox}}{k_{red}+k_c}\Gamma_{Red} = 0$$

or:

$$k_p\Gamma_A = \frac{k_{ox}k_c}{k_{red}+k_c}\Gamma_{Red}$$

Therefore:

$$\Gamma_{Red} = \frac{k_p\Gamma_A(k_{red}+k_c)}{k_{ox}k_c}$$

and:

$$\Gamma_{Ox} = \frac{k_p\Gamma_A}{k_c}$$

These stationary expressions are useful for interpreting limiting behavior at a fixed potential. They show that the precursor A(ads) provides a chemical source of Red(ads), while the irreversible follow-up reaction removes Ox(ads). However, for dynamic voltammetric techniques such as square-wave voltammetry and cyclic staircase voltammetry, the complete time-dependent differential equations should be used instead of stationary approximations.

Current expression using stationary concentration relations

By inserting the stationary concentration relation into the Butler-Volmer current expression, one obtains:

$$I = nFA\left(k_{ox}\Gamma_{Red} - k_{red}\frac{k_{ox}}{k_{red}+k_c}\Gamma_{Red}\right)$$

or:

$$I = nFAk_{ox}\Gamma_{Red}\left(1 - \frac{k_{red}}{k_{red}+k_c}\right)$$

After simplification:

$$I = nFAk_{ox}\Gamma_{Red}\frac{k_c}{k_{red}+k_c}$$

This expression shows that the irreversible follow-up chemical reaction suppresses the backward reduction pathway by consuming Ox(ads). When $k_c = 0$, the stationary net current under these assumptions becomes zero because no follow-up chemical removal of Ox(ads) occurs. When k_c is large, the fraction $k_c/(k_{red}+k_c)$ approaches unity, and the current approaches:

$$I \approx nFAk_{ox}\Gamma_{Red}$$

Thus, a fast irreversible follow-up reaction strongly favors anodic current and suppresses the reverse component. In the complete CirrECirr mechanism, however, the magnitude of this current also depends on how rapidly Red(ads) is supplied by the preceding irreversible transformation of A(ads).

Finite-difference numerical algorithm for voltammetric simulations

For numerical simulations of dynamic voltammetric techniques, the differential equations are solved stepwise. At a given time increment Δt, the potential is E_j, and the Butler-Volmer rate constants are recalculated according to:

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

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

The surface concentrations are then updated as:

$$\Gamma_{A,j+1} = \Gamma_{A,j} - k_p\Gamma_{A,j}\Delta t$$

$$\Gamma_{Red,j+1} = \Gamma_{Red,j} + \left(k_p\Gamma_{A,j} - k_{ox,j}\Gamma_{Red,j} + k_{red,j}\Gamma_{Ox,j}\right)\Delta t$$

$$\Gamma_{Ox,j+1} = \Gamma_{Ox,j} + \left(k_{ox,j}\Gamma_{Red,j} - k_{red,j}\Gamma_{Ox,j} - k_c\Gamma_{Ox,j}\right)\Delta t$$

$$\Gamma_{Y,j+1} = \Gamma_{Y,j} + k_c\Gamma_{Ox,j}\Delta t$$

After each concentration update, the current is calculated from:

$$I_j = nFA\left(k_{ox,j}\Gamma_{Red,j} - k_{red,j}\Gamma_{Ox,j}\right)$$

This recursive algorithm is suitable for square-wave voltammetry, cyclic staircase voltammetry, and related pulse techniques. In square-wave voltammetry, the potential changes rapidly between forward and backward pulses. Therefore, $k_{ox,j}$ and $k_{red,j}$ must be recalculated at every potential sub-step, and the corresponding forward, backward, and net currents are evaluated from the updated surface concentrations.

Algorithmic sequence for square-wave voltammetry

For square-wave voltammetry, the computational procedure can be written as the following sequence:

$$E_j = E_{start} + j\Delta E + E_{SW}$$

for the forward pulse, and:

$$E_j = E_{start} + j\Delta E - E_{SW}$$

for the backward pulse. At each pulse potential, one calculates:

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

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

then updates:

$$\Gamma_{A,j}, \quad \Gamma_{Red,j}, \quad \Gamma_{Ox,j}, \quad \Gamma_{Y,j}$$

and finally calculates:

$$I_{f,j} = nFA\left(k_{ox,f}\Gamma_{Red,f} - k_{red,f}\Gamma_{Ox,f}\right)$$

$$I_{b,j} = nFA\left(k_{ox,b}\Gamma_{Red,b} - k_{red,b}\Gamma_{Ox,b}\right)$$

The net square-wave current is:

$$\Delta I_j = I_{f,j} - I_{b,j}$$

This form is especially important for protein-film voltammetry because the response is determined not only by the formal potential and electron-transfer kinetics, but also by the competition between the chemical formation of Red(ads) and the chemical consumption of Ox(ads). Consequently, the forward and backward current components may become strongly asymmetric.

Boundary conditions and surface constraints

Since all electroactive species are immobilized at the electrode surface, no diffusional boundary condition is required for A(ads), Red(ads), Ox(ads), or Y(ads). The essential surface condition is conservation of the total adsorbed population:

$$\Gamma_A(t) + \Gamma_{Red}(t) + \Gamma_{Ox}(t) + \Gamma_Y(t) = \Gamma_T$$

If Z(ads) is treated as an excess surface or interfacial reagent, then:

$$\Gamma_Z(t) = \Gamma_Z^* = \text{constant}$$

and:

$$k_c = k_f \Gamma_Z^*$$

If Z(ads) is explicitly included as a finite surface species, then the additional condition is:

$$\Gamma_Z(t) + \Gamma_Y(t) = \Gamma_Z(0)$$

provided that the only consumption pathway of Z(ads) is its reaction with Ox(ads). The choice between pseudo-first-order and full second-order formulations depends on the physical situation and on whether the concentration of Z(ads) changes significantly during the voltammetric time window.

Limiting cases of the model

If the preceding chemical step is absent or extremely slow:

$$k_p \to 0$$

then A(ads) is not efficiently converted into Red(ads). Under this condition, the amount of electroactive Red(ads) remains small and the voltammetric response is strongly suppressed.

If the preceding chemical step is very fast:

$$k_p \to \infty$$

then A(ads) is rapidly transformed into Red(ads), and the mechanism approaches a classical surface ECirr mechanism:

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

$$\text{Ox(ads)} \overset{k_c}{\to} \text{Y(ads)}$$

If the follow-up chemical reaction is absent:

$$k_c = 0$$

then the model reduces to a surface $C_{irr}E$ mechanism:

$$\text{A(ads)} \overset{k_p}{\to} \text{Red(ads)}$$

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

Under this condition, Ox(ads) is not chemically consumed, and the backward component of the voltammetric response may remain significant if electron transfer is sufficiently fast.

If the follow-up reaction is very fast:

$$k_c \to \infty$$

then Ox(ads) is rapidly converted into Y(ads). This decreases the amount of Ox(ads) available for electrochemical reduction and suppresses the backward current. As a result,

the voltammetric response becomes more irreversible and is dominated by the anodic formation and chemical consumption of Ox(ads).

If the electron transfer is very fast:

$$k_s \to \infty$$

then Red(ads) and Ox(ads) tend to follow the applied potential rapidly, while the two chemical steps determine the supply of Red(ads) and the removal of Ox(ads). In this case, the response is primarily shaped by k_p and k_c.

If the electron transfer is slow:

$$k_s \to 0$$

then the formation of Ox(ads) becomes limited by heterogeneous electron transfer. Under this condition, even a fast follow-up chemical reaction may have a weak observable effect, because Ox(ads) is produced slowly.

Mechanistic interpretation

The surface CirrECirr mechanism describes a protein-film voltammetric system in which the electroactive reduced form is not initially present in its final active state, but is generated by an irreversible preceding surface chemical reaction. After the electrochemical oxidation step, the generated oxidized form is removed by an irreversible follow-up chemical reaction. Therefore, the current is controlled by three coupled kinetic processes: formation of Red(ads), Butler-Volmer electron transfer between Red(ads) and Ox(ads), and chemical consumption of Ox(ads).

This mechanism can produce voltammetric responses that differ strongly from those of a simple surface-confined redox couple. A slow preceding step decreases the available amount of Red(ads) and reduces the peak current. A fast follow-up step suppresses the backward reduction current by removing Ox(ads). The combined action of these two irreversible chemical steps can shift the peak potential, broaden the signal, decrease the backward component, and create an apparently irreversible voltammetric profile even when the heterogeneous electron transfer is moderately fast.

The most useful mathematical form for simulation is the complete set of coupled differential equations combined with the Butler-Volmer current expression. In this way, the surface concentrations of Red(ads) and Ox(ads) are evaluated dynamically and then incorporated directly into the electron-transfer current. This approach is suitable for constructing MATHCAD, MATLAB, Python, or other numerical protocols for simulating cyclic voltammetry, staircase voltammetry, and square-wave voltammetry of surface-confined protein films.

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