Mathematical Algorithm of Protein-Film Voltammetry of a Surface CirrECrev Mechanism Coupled with an Irreversible Preceding Chemical Step and a Homogeneous Reversible Follow-up Chemical Reaction

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Abstract

A comprehensive mathematical model is proposed for a surface CirrECrev mechanism under conditions of protein-film voltammetry. The reaction sequence consists of an irreversible preceding chemical step, A(ads) → Red(ads), followed by a reversible electron-transfer process Red(ads) ⇌ Ox(ads) and a reversible chemical reaction Ox(ads) ⇌ Y(ads), characterized by forward and backward rate constants and an equilibrium constant, Keq. The model is formulated using Butler–Volmer kinetics and incorporates both kinetic and equilibrium descriptions of the coupled chemical transformation. Differential equations governing the evolution of surface concentrations are derived together with analytical relationships linking the equilibrium constant to the distribution of adsorbed species. The developed formalism enables systematic evaluation of the effects of electron-transfer kinetics, chemical equilibrium, and precursor conversion on voltammetric behavior. The algorithm is particularly suitable for simulating square-wave and cyclic voltammetric responses of adsorbed proteins and other surface-confined redox systems coupled with reversible chemical reactions.

Reaction scheme and model

The surface CirrECrev mechanism considered in this model is composed of three coupled steps. The first step is an irreversible preceding chemical transformation of an adsorbed precursor into the electroactive reduced form. The second step is a reversible one-electron electrode reaction described by Butler-Volmer kinetics. The third step is a reversible follow-up chemical reaction of the electrochemically generated oxidized form with an adsorbed or interfacially available chemical species denoted as Z(ads). The reaction scheme is written as:

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

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

$$\mathrm{Ox(ads)} + \mathrm{Z(ads)} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{Y(ads)}$$

In this scheme, A(ads) is an adsorbed precursor state, Red(ads) and Ox(ads) are the electroactive reduced and oxidized forms of the immobilized protein or redox-active surface-confined molecule, and Y(ads) is the product of the reversible follow-up chemical reaction. The rate constant kp describes the irreversible preceding chemical conversion of A(ads) into

Red(ads). The heterogeneous electron-transfer step is characterized by the standard electron-transfer rate constant ks, the transfer coefficient α, and the formal potential E0. The follow-up reversible chemical step is described by the forward rate constant kf, the backward rate constant kb, and the equilibrium constant Keq.

The equilibrium constant of the follow-up reversible chemical reaction is defined as:

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

When the adsorbed or interfacial concentration of Z is explicitly included, the forward chemical rate is proportional to ΓOxΓZ. If Z is present in large excess or its surface concentration remains effectively constant during the experiment, the forward chemical reaction can be treated as pseudo-first-order with respect to Ox(ads), and the apparent forward rate constant is:

$$k_{f,app} = k_f \Gamma_Z$$

Under this condition, the reversible follow-up chemical step is written as:

$$\mathrm{Ox(ads)} \underset{k_b}{\overset{k_{f,app}}{\rightleftharpoons}} \mathrm{Y(ads)}$$

and the equilibrium constant used in the pseudo-first-order surface model becomes:

$$K_{eq} = \frac{k_{f,app}}{k_b} = \frac{k_f \Gamma_Z}{k_b}$$

For numerical simulations in protein-film voltammetry, this pseudo-first-order formulation is usually the most convenient form, because it keeps the model focused on the surface concentrations of A, Red, Ox, and Y.

Conservation condition for the surface-confined film

Since the redox-active system is immobilized at the electrode surface, the total amount of adsorbed material is conserved. The total surface concentration is therefore:

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

Here, ΓT is the total surface concentration of the immobilized material, while ΓA, ΓRed, ΓOx, and ΓY are the surface concentrations of A(ads), Red(ads), Ox(ads), and Y(ads), respectively. This conservation condition is central for surface-confined protein-film voltammetry, because no diffusional supply of the protein from the solution phase is considered. The current originates only from redistribution of the finite surface population among the adsorbed states.

If the concentration of Z(ads) is not constant, the general conservation equation may also include ΓZ. However, in the usual catalytic or ligand-excess formulation, ΓZ is treated as constant and is incorporated into kf,app. In the following derivation, the pseudo-first-order form is used.

Butler-Volmer kinetics for the electrode step

The reversible electron-transfer reaction between Red(ads) and Ox(ads) is described by the Butler-Volmer formalism. The potential-dependent oxidation rate constant is:

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

The potential-dependent reduction rate constant is:

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

In these equations, E is the applied electrode potential, E0 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 ks defines the standard heterogeneous electron-transfer rate constant at E=E0, while α defines the symmetry of the electron-transfer activation barrier.

When ks is large, the surface redox couple follows the applied potential almost reversibly. When ks is small, the electrode reaction becomes quasireversible or irreversible, producing peak broadening, peak displacement, and suppression of the backward current component.

Differential equations of the CirrECrev surface mechanism

The kinetic model is obtained by writing the rate balance for each surface species. For the pseudo-first-order follow-up chemical step, the differential equations are:

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

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

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

$$\frac{d\Gamma_Y}{dt} = k_{f,app}\Gamma_{Ox} - k_b\Gamma_Y$$

The first equation describes the irreversible disappearance of the adsorbed precursor A(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 consumption by reduction back to Red(ads), and its reversible chemical conversion into Y(ads). The fourth equation describes the formation and consumption of the follow-up chemical product Y(ads).

By adding all four differential equations, one obtains:

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

Therefore:

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

This confirms that the model is internally consistent and conserves the total amount of adsorbed material during the voltammetric experiment.

Explicit incorporation of the equilibrium constant

For the reversible follow-up chemical step:

$$\text{Ox(ads)} \underset{k_b}{\overset{k_{f,app}}{\rightleftharpoons}} \text{Y(ads)}$$

chemical equilibrium gives:

$$K_{eq} = \frac{\Gamma_Y}{\Gamma_{Ox}} = \frac{k_{f,app}}{k_b}$$

Thus:

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

This relation shows that the equilibrium constant directly controls the distribution between Ox(ads) and Y(ads). A large value of Keq shifts the surface population toward Y(ads), decreasing the concentration of electrochemically reducible Ox(ads). A small value of Keq favors Ox(ads), allowing stronger electrochemical reduction during the reverse pulse or cathodic scan.

At chemical equilibrium, the total concentration of the species participating in the follow-up chemical step is:

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

and therefore:

$$\Gamma_{Ox} = \frac{\Gamma_{Ox} + \Gamma_Y}{1 + K_{eq}}$$

$$\Gamma_Y = \frac{K_{eq}(\Gamma_{Ox} + \Gamma_Y)}{1 + K_{eq}}$$

These expressions are useful for interpreting the effect of the reversible follow-up chemical reaction on the voltammetric response. The larger the value of Keq, the smaller the fraction of the oxidized form that remains available for electrochemical reduction.

Differential equations with Keq explicitly included

Because:

$$k_{f,app} = K_{eq} k_b$$

one may rewrite the kinetic model as:

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

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

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

$$\frac{d\Gamma_Y}{dt} = K_{eq} k_b \Gamma_{Ox} - k_b \Gamma_Y$$

This form is particularly convenient when the equilibrium constant Keq is selected as an independent mechanistic parameter in numerical simulations. In this formulation, kb controls how rapidly the reversible chemical step approaches equilibrium, while Keq controls the final equilibrium distribution between Ox(ads) and Y(ads).

Analytical solution for the preceding irreversible chemical step

The first differential equation can be solved independently:

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

with the initial condition:

$$\Gamma_A(0) = \Gamma_{A,0}$$

The solution is:

$$\Gamma_A(t) = \Gamma_{A,0} \exp\left(-k_p t\right)$$

If the entire surface population is initially present as A(ads), then:

$$\Gamma_{A,0} = \Gamma_T$$

and:

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

The rate of formation of the electroactive reduced form from the precursor is then:

$$R_p(t) = k_p \Gamma_A(t) = k_p \Gamma_T \exp\left(-k_p t\right)$$

This term enters directly into the differential equation for ΓRed as a source term. Therefore, the preceding irreversible chemical reaction controls how rapidly the electroactive form becomes available for electron transfer.

Current equation for the surface-confined electrode step

Only the electrode reaction between Red(ads) and Ox(ads) contributes directly to the faradaic current. The current is therefore proportional to the net rate of electron transfer:

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

Here, n=1 for the one-electron transformation, F is the Faraday constant, and A is the electrode area. The first term represents the anodic oxidation rate of Red(ads) into Ox(ads), while the second term represents the cathodic reduction rate of Ox(ads) into Red(ads).

By substituting the Butler-Volmer expressions into the current equation, one obtains:

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

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 expression is the central Butler-Volmer current equation for the surface CirrECrev mechanism. The surface concentrations ΓRed and ΓOx are not independent equilibrium quantities. They are dynamically controlled by the preceding irreversible conversion of A(ads), the electron-transfer reaction, and the reversible follow-up chemical conversion of Ox(ads) into Y(ads).

Incorporation of the follow-up reversible chemical equilibrium into the current

When the follow-up chemical step is sufficiently fast relative to the voltammetric time scale, the equilibrium relation:

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

can be used together with the surface conservation equation:

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

Substitution gives:

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

Thus, the concentration of the oxidized electroactive form can be written as:

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

Inserting this expression into the Butler-Volmer current equation gives:

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

After substituting the Butler-Volmer rate constants explicitly:

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

This expression shows directly how the reversible follow-up chemical step affects the current. Increasing Keq decreases the amount of free Ox(ads) available for reduction. Consequently, the cathodic component becomes smaller, and the voltammetric response may appear more irreversible even when the electron-transfer kinetics are not intrinsically slow.

Numerical algorithm for dynamic voltammetric simulations

For cyclic voltammetry, cyclic staircase voltammetry, or square-wave voltammetry, the potential changes with time. Therefore, the kinetic equations must be solved step by step. At a given time step j, the applied potential is E_j. The Butler-Volmer rate constants are recalculated at every potential step:

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

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

The surface concentrations are then updated by finite-difference expressions:

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

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

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

$$\Gamma_{Y,j+1} = \Gamma_{Y,j} + \left(k_{f,app}\Gamma_{Ox,j} - k_b\Gamma_{Y,j}\right)\Delta t$$

or, when Keq is used explicitly:

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

$$\Gamma_{Y,j+1} = \Gamma_{Y,j} + \left(K_{eq}k_b\Gamma_{Ox,j} - k_b\Gamma_{Y,j}\right)\Delta t$$

After each concentration update, the faradaic current is calculated from:

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

This finite-difference algorithm is especially important for square-wave voltammetry. During a square-wave experiment, the potential alternates rapidly between forward and backward pulses. Therefore, kox and kred must be recalculated for every pulse, while the surface concentrations must be updated continuously according to the coupled kinetic model.

Initial conditions

The initial conditions depend on the starting potential and on the initial chemical state of the immobilized film. If the experiment starts before the preceding chemical reaction has occurred, the entire surface population may be present as the precursor:

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

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

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

$$\Gamma_Y(0) = 0$$

These conditions are appropriate when A(ads) is the initially immobilized state and the electroactive form Red(ads) is generated only during the experiment by the irreversible preceding chemical reaction.

If the preceding chemical reaction has already partly occurred before the voltammetric experiment, a mixed initial condition may be used:

$$\Gamma_A(0) = \Gamma_{A,0}$$

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

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

$$\Gamma_Y(0) = \Gamma_{Y,0}$$

with:

$$\Gamma_{A,0} + \Gamma_{Red,0} + \Gamma_{Ox,0} + \Gamma_{Y,0} = \Gamma_T$$

If the starting potential is sufficiently negative, the initially electroactive part of the film is usually assumed to be in the reduced form. If the starting potential is positive, a fraction of the film may already be oxidized or chemically converted into Y(ads).

Limiting cases of the surface CirrECrev mechanism

If the preceding chemical reaction is absent:

$$k_p = 0$$

then A(ads) is not converted into Red(ads), and no electroactive material is generated from the precursor. If the initial concentrations of Red(ads) and Ox(ads) are zero, the faradaic current is also zero.

If the preceding chemical reaction is very fast:

$$k_p \to \infty$$

then A(ads) is rapidly converted into Red(ads), and the mechanism approaches a surface ECrev mechanism with the initial population mainly present as Red(ads).

If the reversible follow-up chemical reaction is absent:

$$k_{f,app} = 0$$

and:

$$k_b = 0$$

then the mechanism reduces to a surface CirrE mechanism, where the voltammetric response is controlled by the irreversible generation of Red(ads) and by the Butler-Volmer electrode reaction only.

If the follow-up chemical reaction is strongly shifted toward Y(ads):

$$K_{eq} \gg 1$$

then most of the generated Ox(ads) is converted into Y(ads). Under these conditions, the backward electrochemical reduction of Ox(ads) is suppressed because the concentration of free Ox(ads) becomes small.

If the follow-up chemical reaction is shifted toward Ox(ads):

$$K_{eq} \ll 1$$

then only a small fraction of Ox(ads) is converted into Y(ads), and the voltammetric response remains closer to that of a simple surface-confined reversible electron-transfer reaction preceded by an irreversible chemical step.

If the electron transfer is fast:

$$k_s \to \infty$$

then the distribution between Red(ads) and Ox(ads) follows the applied potential rapidly, while the preceding and follow-up chemical reactions determine how much electroactive material is available and how much Ox(ads) remains free for reduction.

If the electron transfer is slow:

$$k_s \to 0$$

then the electrode reaction becomes rate-limiting. In this case, even a fast chemical follow-up reaction may have a limited observable effect, because Ox(ads) is produced slowly.

Mechanistic interpretation

The surface CirrECrev mechanism combines two important chemical effects with Butler-Volmer electron-transfer kinetics. The irreversible preceding step controls the time-dependent formation of the electroactive reduced form. Therefore, the faradaic current may increase with time or depend strongly on the waiting time before the voltammetric scan. The reversible follow-up chemical step controls the fate of the oxidized form generated at the electrode. When Keq is large, Ox(ads) is removed from the electrochemical cycle by conversion into Y(ads), which suppresses the backward current. When Keq is small, the follow-up reaction has a weaker effect and the response resembles a preceding chemical reaction coupled to a reversible surface electrode process.

This model is suitable for protein-film voltammetry because all reacting species are confined to the electrode surface. The model does not require diffusional boundary conditions for the protein species. Instead, the experimentally measured current is linked directly to the time-dependent surface concentrations of Red(ads) and Ox(ads), which are controlled by the irreversible preceding chemical reaction, the Butler-Volmer electron-transfer step, and the reversible follow-up chemical equilibrium. The equations given above can be directly implemented in MATHCAD, MATLAB, Python, or similar software for simulation of cyclic voltammograms, cyclic staircase voltammograms, and square-wave voltammograms of the surface CirrECrev mechanism.

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