Mathematical Algorithm behind Protein-Film Voltammetry of Surface Reaction Coupled with an Irreversible Preceding Chemical Step and an Irreversible Regenerative Catalytic Reaction Considered under Kinetic Conditions

Rubin Gulaboski, Pavle Apostoloski

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

Abstract

A mathematical model is developed for a surface CirrEC′ mechanism in protein-film voltammetry, consisting of an irreversible preceding chemical reaction, A(ads) → Red(ads), followed by a reversible electron-transfer step Red(ads) ⇌ Ox(ads) and an irreversible regenerative catalytic reaction Ox(ads) + Y(ads) → Red(ads). The model combines Butler–Volmer electron-transfer kinetics with kinetic equations describing the formation and regeneration of electroactive species within the surface-confined film. The resulting differential equations provide a complete description of the evolution of surface concentrations and the corresponding faradaic current. Special attention is given to the interplay between the rate of precursor conversion and catalytic regeneration, both of which strongly influence the shape and magnitude of the voltammetric response. The proposed algorithm enables quantitative simulations of protein-film voltammograms and offers mechanistic insight into catalytic systems exhibiting both chemical activation and regeneration processes at the electrode interface.

Reaction scheme and model

The surface mechanism considered here contains one irreversible preceding chemical reaction, one reversible electrode reaction, and one irreversible regenerative catalytic reaction. The reacting redox-active species are confined at the electrode surface, and therefore the model is written in terms of surface concentrations. The mechanism is denoted as a surface $C_{\mathrm{irr}}EC'$ mechanism:

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

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

$$\mathrm{Ox(ads)} + \mathrm{Y(ads)} \overset{k_c}{\rightarrow} \mathrm{Red(ads)}$$

In this scheme, A(ads) is an electrochemically inactive or precursor adsorbed form that is irreversibly transformed into the reduced electroactive form Red(ads). The parameter k_p is the rate constant of this irreversible preceding chemical step. The pair Red(ads)/Ox(ads) is the surface-confined redox couple involved in the electron-transfer process. The last reaction is the regenerative catalytic step, in which the electrochemically generated oxidized form reacts with the co-reactant Y(ads) and is converted back to Red(ads).

If Y(ads) is present in large excess, or if its interfacial concentration remains effectively constant during the experiment, the second-order regenerative reaction can be treated as a pseudo-first-order process:

$$k_c{}' = k_c \Gamma_Y$$

where Γ_Y is the effectively constant surface concentration of the co-reactant. In the following equations, $k_c{}'$ is used for the apparent pseudo-first-order catalytic rate constant. For simplicity, it may also be denoted as k_c when no ambiguity is possible.

The total surface concentration of the adsorbed protein-related species is conserved:

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

Here, Γ_T is the total surface concentration of all adsorbed protein states, while Γ_A, Γ_{Red}, and Γ_{Ox} are the surface concentrations of the precursor, reduced, and oxidized forms, respectively. This conservation equation is the main boundary condition for a strictly surface-confined protein-film system. No diffusion term is required for the adsorbed protein species because the protein does not move from the bulk solution toward the electrode surface.

Butler-Volmer electron-transfer kinetics

The electron-transfer step is described by Butler-Volmer kinetics. The potential-dependent oxidation rate constant for the transformation of Red(ads) into Ox(ads) is:

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

The corresponding reduction rate constant for the transformation of Ox(ads) into Red(ads) is:

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

In these equations, k_s is the standard heterogeneous electron-transfer rate constant, α is the electron-transfer coefficient, 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. Since k_{ox} and k_{red} depend exponentially on the applied potential, they must be recalculated at every potential step in dynamic voltammetric techniques such as square-wave voltammetry and cyclic staircase voltammetry.

The preceding chemical transformation and the regenerative catalytic reaction are not electron-transfer reactions. Therefore, they are not written with Butler-Volmer expressions. Their kinetic contributions enter the model through the differential equations for Γ_A, Γ_{Red}, and Γ_{Ox}.

Differential equations of the surface $C_{\mathrm{irr}}EC'$ mechanism

The time evolution of the surface concentration of the precursor form is governed only by the irreversible preceding chemical reaction:

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

The reduced form is generated by the preceding chemical reaction, consumed by electrochemical oxidation, regenerated by electrochemical reduction, and regenerated chemically by the catalytic reaction:

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

The oxidized form is produced by electrochemical oxidation of Red(ads) and consumed by both electrochemical reduction and catalytic regeneration:

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

Equations (8)-(10) represent the complete kinetic model for the surface-confined $C_{\mathrm{irr}}EC'$ mechanism under pseudo-first-order catalytic conditions. Addition of the three differential equations gives:

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

and therefore:

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

This confirms that the model conserves the total amount of adsorbed material. The preceding chemical step redistributes the surface population from A(ads) into Red(ads), while the electron-transfer and catalytic steps redistribute the population between Red(ads) and Ox(ads).

Explicit solution of the preceding chemical step

At a fixed time scale, the precursor concentration can be evaluated independently because equation (8) contains only Γ_A:

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

If the film is initially present only in the precursor form, then:

$$\Gamma_A(0) = \Gamma_T, \qquad \Gamma_{\mathrm{Red}}(0) = 0, \qquad \Gamma_{\mathrm{Ox}}(0) = 0$$

and therefore:

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

This expression shows that the amount of precursor decreases exponentially with time. The rate at which electroactive Red(ads) becomes available is controlled by k_p. Consequently, the preceding chemical step may delay or suppress the voltammetric response if it is slow relative to the time scale of the potential modulation.

Using equation (15), the concentration of the reduced form may also be expressed through the conservation equation:

$$\Gamma_{\text{Red}} = \Gamma_T - \Gamma_A - \Gamma_{\text{Ox}}$$

or explicitly:

$$\Gamma_{\text{Red}}(t) = \Gamma_T\big[1 - \exp\big(-k_p t\big)\big] - \Gamma_{\text{Ox}}(t)$$

Equation (17) is useful in numerical simulations because it shows that the maximum available amount of electroactive material is not immediately equal to Γ_T. Instead, it grows progressively as the precursor is converted into Red(ads).

Incorporation into the Butler-Volmer kinetic equation

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

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

where n is the number of transferred electrons and A_{el} is the electrode area. To avoid confusion between the precursor A and the electrode area, the electrode area is denoted as A_{el} in the expanded expression:

$$I = nFA_{\text{el}}(k_{\text{ox}}\Gamma_{\text{Red}} - k_{\text{red}}\Gamma_{\text{Ox}})$$

Substitution of the Butler-Volmer rate constants into equation (19) gives:

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

This is the Butler-Volmer current equation for the surface $C_{\text{irr}}EC'$ mechanism. The equation has the same electron-transfer form as a simple surface redox reaction, but the concentrations Γ_{Red} and Γ_{Ox} are not governed only by the electrode potential. They are simultaneously controlled by the irreversible preceding chemical step and by the regenerative catalytic reaction.

By using equation (16), the current can be written as:

$$I = nFA_{\text{el}}\{k_{\text{ox}}(\Gamma_T - \Gamma_A - \Gamma_{\text{Ox}}) - k_{\text{red}}\Gamma_{\text{Ox}}\}$$

After substitution of the explicit solution for $\Gamma_A(t)$, one obtains:

$$I = nFA_{\text{el}}\big\{k_{\text{ox}}\big[\Gamma_T - \Gamma_A(0)e^{-k_p t} - \Gamma_{\text{Ox}}\big] - k_{\text{red}}\Gamma_{\text{Ox}}\big\}$$

For the initially pure precursor film, equation (22) becomes:

$$I = nFA_{\mathrm{el}}\left\{k_{\mathrm{ox}}\left[\Gamma_T\left(1 - e^{-k_p t}\right) - \Gamma_{\mathrm{Ox}}\right] - k_{\mathrm{red}}\Gamma_{\mathrm{Ox}}\right\}$$

In this form, the current is explicitly linked to the time-dependent formation of the electroactive reduced form. At short times or very small k_p, the term $1 - e^{-k_p t}$ is small, so the available concentration of Red(ads) is low and the anodic current is suppressed. At long times or very large k_p, the precursor is rapidly converted into Red(ads), and the model approaches the classical surface EC′ mechanism.

Evaluation under quasi-stationary conditions for Red/Ox redistribution

At a fixed potential, k_{ox} and k_{red} are constant. If the Red/Ox redistribution is considered faster than the variation of the applied potential, equation (10) may be evaluated under the quasi-stationary condition:

$$\frac{d\Gamma_{\mathrm{Ox}}}{dt} = 0$$

Then:

$$k_{\mathrm{ox}}\Gamma_{\mathrm{Red}} = (k_{\mathrm{red}} + k_c{}')\Gamma_{\mathrm{Ox}}$$

and therefore:

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

Using the conservation condition:

$$\Gamma_{\mathrm{Red}} = \Gamma_T - \Gamma_A - \Gamma_{\mathrm{Ox}}$$

one obtains:

$$\Gamma_{\mathrm{Ox}} = \frac{k_{\mathrm{ox}}(\Gamma_T - \Gamma_A)}{k_{\mathrm{ox}} + k_{\mathrm{red}} + k_c{}'}$$

and:

$$\Gamma_{\mathrm{Red}} = \frac{(k_{\mathrm{red}} + k_c{}')(\Gamma_T - \Gamma_A)}{k_{\mathrm{ox}} + k_{\mathrm{red}} + k_c{}'}$$

If equation (13) is incorporated into equations (28) and (29), the quasi-stationary concentrations become:

$$\Gamma_{\mathrm{Ox}}(t) = \frac{k_{\mathrm{ox}}\left[\Gamma_T - \Gamma_A(0)e^{-k_p t}\right]}{k_{\mathrm{ox}} + k_{\mathrm{red}} + k_c{}'}$$

$$\Gamma_{\mathrm{Red}}(t) = \frac{(k_{\mathrm{red}} + k_c{}')\left[\Gamma_T - \Gamma_A(0)e^{-k_p t}\right]}{k_{\mathrm{ox}} + k_{\mathrm{red}} + k_c{}'}$$

These expressions show how the preceding reaction and the catalytic regeneration act simultaneously. The preceding reaction controls how much electroactive material is available, while the catalytic step controls how strongly the oxidized form is recycled back into the reduced form.

Quasi-stationary catalytic current

By inserting equations (28) and (29) into equation (19), one obtains:

$$I = nFA_{\mathrm{el}}\left[\frac{k_{\mathrm{ox}}(k_{\mathrm{red}} + k_c{}')(\Gamma_T - \Gamma_A)}{k_{\mathrm{ox}} + k_{\mathrm{red}} + k_c{}'} - \frac{k_{\mathrm{red}}k_{\mathrm{ox}}(\Gamma_T - \Gamma_A)}{k_{\mathrm{ox}} + k_{\mathrm{red}} + k_c{}'}\right]$$

After simplification:

$$I = nFA_{\mathrm{el}}\frac{k_{\mathrm{ox}}k_c{}'(\Gamma_T - \Gamma_A)}{k_{\mathrm{ox}} + k_{\mathrm{red}} + k_c{}'}$$

Using the explicit solution for the precursor concentration:

$$I(t) = nFA_{\mathrm{el}}\frac{k_{\mathrm{ox}}k_c{}'\left[\Gamma_T - \Gamma_A(0)e^{-k_p t}\right]}{k_{\mathrm{ox}} + k_{\mathrm{red}} + k_c{}'}$$

For the initially pure precursor film:

$$I(t) = nFA_{\mathrm{el}}\frac{k_{\mathrm{ox}}k_c{}'\Gamma_T\left(1 - e^{-k_p t}\right)}{k_{\mathrm{ox}} + k_{\mathrm{red}} + k_c{}'}$$

Equation (35) is the quasi-stationary catalytic current of the surface $C_{\mathrm{irr}}EC'$ mechanism. It shows that the current disappears if the regenerative step is absent, because then $k_c{}' = 0$. It also disappears at the very beginning of the experiment if the film is initially present entirely as the inactive precursor and no reduced form has yet been generated. Thus, the observed voltammetric response depends on the competition between precursor activation, electron transfer, and catalytic regeneration.

When the Butler-Volmer expression for k_{ox} and k_{red} is inserted explicitly, equation (35) becomes:

$$I(t) = nFA_{\mathrm{el}}\Gamma_T\left(1 - e^{-k_p t}\right)\frac{k_s k_c{}'\exp\left[\frac{(1-\alpha)F(E - E^0)}{RT}\right]}{k_s\exp\left[\frac{(1-\alpha)F(E - E^0)}{RT}\right] + k_s\exp\left[-\frac{\alpha F(E - E^0)}{RT}\right] + k_c{}'}$$

This final expression incorporates the partial surface concentrations into the Butler-Volmer framework. It links the measured catalytic current to the applied potential, the heterogeneous electron-transfer kinetics, the irreversible preceding chemical reaction, the irreversible regenerative catalytic reaction, the total surface concentration, and the experimental temperature.

Numerical algorithm for dynamic voltammetry

For square-wave voltammetry, cyclic staircase voltammetry, or cyclic voltammetry, the potential changes with time. Therefore, the system must be solved stepwise. At the time point t_j, the applied potential is E_j, and the Butler-Volmer rate constants are:

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

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

The surface concentrations are updated by finite-difference expressions:

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

$$\Gamma_{\mathrm{Red},j+1} = \Gamma_{\mathrm{Red},j} + \left[k_p \Gamma_{A,j} - k_{\mathrm{ox},j}\Gamma_{\mathrm{Red},j} + k_{\mathrm{red},j}\Gamma_{\mathrm{Ox},j} + k_c{}' \Gamma_{\mathrm{Ox},j}\right]\Delta t$$

$$\Gamma_{\mathrm{Ox},j+1} = \Gamma_{\mathrm{Ox},j} + \left[k_{\mathrm{ox},j}\Gamma_{\mathrm{Red},j} - k_{\mathrm{red},j}\Gamma_{\mathrm{Ox},j} - k_c{}' \Gamma_{\mathrm{Ox},j}\right]\Delta t$$

After each update, the current is calculated from:

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

The numerical algorithm consists of the following steps. First, the initial surface concentrations are defined. Second, the potential E_j is assigned according to the waveform. Third, $k_{\mathrm{ox},j}$ and $k_{\mathrm{red},j}$ are calculated from the Butler-Volmer equations. Fourth, the surface concentrations are updated using equations (39)-(41). Finally, the current is calculated using equation (42). This procedure is repeated for every potential step.

For square-wave voltammetry, the forward and backward currents are calculated at the end of the corresponding pulses:

$$I_{\mathrm{net}} = I_{\mathrm{forward}} - I_{\mathrm{backward}}$$

In this case, the preceding chemical step may influence the response differently at different frequencies. At high frequency, the time available for conversion of A(ads) into Red(ads) is short, and the current may be suppressed. At low frequency, there is more time for the precursor to generate the electroactive reduced form, and the catalytic component can become more pronounced.

Boundary and initial conditions

Because all protein-related species are adsorbed at the electrode surface, no diffusion boundary condition is applied to Γ_A, Γ_{Red}, or Γ_{Ox}. The essential surface condition is conservation of the total adsorbed amount:

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

If the co-reactant Y is present in excess, its surface concentration is treated as constant:

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

and therefore:

$$k_c{}' = k_c\Gamma_Y^* = \text{constant}$$

A common initial condition for the pure precursor film is:

$$\Gamma_A(0) = \Gamma_T, \qquad \Gamma_{\text{Red}}(0) = 0, \qquad \Gamma_{\text{Ox}}(0) = 0$$

If the experiment begins after partial conversion of the precursor, a more general initial condition can be used:

$$\Gamma_A(0) = \Gamma_{A,0}, \qquad \Gamma_{\text{Red}}(0) = \Gamma_{\text{Red},0}, \qquad \Gamma_{\text{Ox}}(0) = \Gamma_{\text{Ox},0}$$

with:

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

Limiting cases

If the preceding chemical reaction is absent or extremely slow:

$$k_p \to 0$$

then the precursor is not efficiently converted into the reduced electroactive form. If the film is initially present as A(ads), the voltammetric signal is strongly suppressed because very little Red(ads) is available for oxidation.

If the preceding chemical reaction is very fast:

$$k_p \to \infty$$

then A(ads) is rapidly transformed into Red(ads), and the mechanism approaches the surface EC′ catalytic mechanism:

$$\text{Red(ads)} - e^- \rightleftharpoons \text{Ox(ads)}, \qquad \text{Ox(ads)} + \text{Y(ads)} \to \text{Red(ads)}$$

If the catalytic regenerative reaction is absent:

$$k_c{}' \to 0$$

then the mechanism reduces to an irreversible preceding chemical reaction followed by a simple surface electron-transfer reaction. Under this condition, no catalytic amplification occurs.

If the catalytic regenerative reaction is very fast:

$$k_c{}' \to \infty$$

then Ox(ads) is rapidly converted back into Red(ads). This maintains a high population of the reduced form at the electrode surface and enhances the anodic current.

If the heterogeneous electron transfer is very fast:

$$k_s \to \infty$$

then the Red/Ox distribution tends to follow the applied potential almost reversibly, and the observed current is mainly controlled by the preceding chemical activation and by catalytic regeneration.

If the heterogeneous electron transfer is slow:

$$k_s \to 0$$

then the generation of Ox(ads) becomes kinetically limited. In that case, even a fast regenerative catalytic reaction may have a weaker observable effect because the oxidized form is produced slowly.

Mechanistic interpretation

The surface $C_{\mathrm{irr}}EC'$ model describes a protein-film voltammetric system in which the electroactive reduced form is not initially available, but is produced by an irreversible preceding surface reaction. After formation, Red(ads) undergoes Butler-Volmer electron transfer to produce Ox(ads). The oxidized form is then regenerated chemically back into Red(ads) through an irreversible catalytic reaction with Y(ads).

The preceding chemical step controls the availability of the electroactive species, whereas the catalytic step controls the recycling of the oxidized state. Therefore, the voltammetric response is controlled by three kinetic parameters: k_p, k_s, and $k_c{}'$. A slow preceding step delays the onset of current, a slow electron-transfer step broadens and shifts the voltammetric response, and a fast catalytic step amplifies the anodic current by continuously regenerating Red(ads).

This model is suitable for numerical simulations of surface-confined protein-film voltammetry under cyclic voltammetric, cyclic staircase, or square-wave voltammetric conditions. In all cases, the key requirement is that the partial differential equations for Γ_A, Γ_{Red}, and Γ_{Ox} are solved together with the Butler-Volmer equations for k_{ox} and k_{red} at every potential step.

Entire MATHCAD simulation protocols of this mechanism, ready for simulating square-wave and cyclic voltammograms, can be implemented using the differential equations and finite-difference expressions given above. Under conditions of cyclic voltammetry, the corresponding simulation Mathcad file is available at:

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