Mathematical Model beyond a Surface EEC’ Mechanism under Butler-Volmer Kinetics in Protein-Film Voltammetry

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Abstract

This work presents a theoretical model for a surface-confined EEC′ mechanism under conditions of protein-film voltammetry. The mechanism consists of two consecutive one-electron transfer reactions, Red(ads) ⇌ Int(ads) ⇌ Ox(ads), followed by a regenerative catalytic step in which Ox(ads) reacts with a co-reactant Y(ads) to regenerate the intermediate state Int(ads). The model is formulated within the Butler–Volmer kinetic framework, allowing simultaneous treatment of heterogeneous electron-transfer kinetics and catalytic regeneration. Differential equations describing the temporal evolution of the surface concentrations of all electroactive species are derived together with the corresponding current expressions. The theoretical formalism provides a quantitative basis for analyzing the influence of electron-transfer rates, catalytic turnover, transfer coefficients, and experimental time scale on the voltammetric response. The developed algorithm can be directly implemented for numerical simulations of square-wave and cyclic voltammetric experiments involving adsorbed redox proteins and catalytic surface-confined systems.

Reaction scheme and definition of the model

The surface-confined EEC’ regenerative mechanism considered here consists of two consecutive one-electron electrode reactions followed by a catalytic chemical regeneration step. The reacting redox forms are immobilized at the electrode surface; therefore, the model is written in terms of surface concentrations rather than bulk concentrations.

$$\mathrm{Red(ads)} \underset{k_{\mathrm{red},1}}{\overset{k_{\mathrm{ox},1}}{\rightleftharpoons}} \mathrm{Int(ads)} + e^-$$

$$\mathrm{Int(ads)} \underset{k_{\mathrm{red},2}}{\overset{k_{\mathrm{ox},2}}{\rightleftharpoons}} \mathrm{Ox(ads)} + e^-$$

$$\mathrm{Ox(ads)} + \mathrm{Y(ads)} \overset{k_{\mathrm{cat}}}{\rightarrow} \mathrm{Int(ads)}$$

In this notation, Γ_{Red}, Γ_{Int}, and Γ_{Ox} are the surface concentrations of the reduced, intermediate, and oxidized forms of the immobilized redox-active protein. The first electron-transfer step converts $\mathrm{Red(ads)}$ into $\mathrm{Int(ads)}$, while the second electron-transfer step converts $\mathrm{Int(ads)}$ into $\mathrm{Ox(ads)}$. The catalytic regenerative step consumes the oxidized form and converts it chemically back into the intermediate form.

If the co-reactant Y is present in large excess, or if its interfacial concentration remains constant during the experiment, the catalytic step may be treated as pseudo-first-order with respect to $\mathrm{Ox(ads)}$:

$$k_{\mathrm{c}} = k_{\mathrm{cat}} \mathit{\Gamma}_Y$$

Under this assumption, the catalytic regeneration is written as:

$$\mathrm{Ox(ads)} \xrightarrow{k_{\mathrm{c}}} \mathrm{Int(ads)}$$

The use of Eq. (5) is appropriate for protein-film voltammetry when the catalytic co-reactant is continuously available at the electrode interface. In that case, the dynamic model contains only the three surface concentrations of the immobilized redox system: $\mathit{\Gamma}_{\mathrm{Red}}$, $\mathit{\Gamma}_{\mathrm{Int}}$, and $\mathit{\Gamma}_{\mathrm{Ox}}$.

Conservation condition for the immobilized redox film

Because the protein is confined to the electrode surface, there is no diffusional supply or loss of the immobilized redox material. The total surface concentration is therefore conserved:

$$\mathit{\Gamma}_{\mathrm{T}} = \mathit{\Gamma}_{\mathrm{Red}} + \mathit{\Gamma}_{\mathrm{Int}} + \mathit{\Gamma}_{\mathrm{Ox}}$$

Here, $\mathit{\Gamma}_{\mathrm{T}}$ is the total amount of electroactive protein immobilized on the electrode surface. Equation (6) is not a coverage transformation, but only the mass balance for the surface concentrations. It must be satisfied at every potential and at every time step of the voltammetric experiment.

Differentiation of Eq. (6) gives:

$$\frac{d\mathit{\Gamma}_{\mathrm{T}}}{dt} = \frac{d\mathit{\Gamma}_{\mathrm{Red}}}{dt} + \frac{d\mathit{\Gamma}_{\mathrm{Int}}}{dt} + \frac{d\mathit{\Gamma}_{\mathrm{Ox}}}{dt} = 0$$

Equation (7) confirms that the mathematical model must redistribute the surface population among $\mathrm{Red(ads)}$, $\mathrm{Int(ads)}$, and $\mathrm{Ox(ads)}$ without changing the total amount of immobilized material.

Butler-Volmer rate constants for the first electron-transfer step

The first electrode reaction is the transformation between $\mathrm{Red(ads)}$ and $\mathrm{Int(ads)}$. Its potential-dependent oxidation and reduction rate constants are described by Butler-Volmer kinetics:

$$k_{\mathrm{ox,1}}(E) = k_{\mathrm{s,1}} \exp\left[\frac{(1-\alpha_1)F(E-E_1^0)}{RT}\right]$$

$$k_{\mathrm{red,1}}(E) = k_{\mathrm{s,1}} \exp\left[-\frac{\alpha_1 F(E-E_1^0)}{RT}\right]$$

In Eqs. (8) and (9), $k_{\mathrm{s,1}}$ is the standard heterogeneous electron-transfer rate constant of the first electron-transfer step, E_1^0 is the formal potential of the $\mathrm{Red/Int}$ surface couple, and α_1 is the electron-transfer coefficient. The applied potential is denoted by E, while F, R, and T have their usual electrochemical meanings.

The net rate of the first electron-transfer step is:

$$v_1 = k_{\mathrm{ox},1}\Gamma_{\mathrm{Red}} - k_{\mathrm{red},1}\Gamma_{\mathrm{Int}}$$

This term is positive during oxidation of $\mathrm{Red(ads)}$ into $\mathrm{Int(ads)}$ and negative when the reverse reduction of $\mathrm{Int(ads)}$ into $\mathrm{Red(ads)}$ dominates.

Butler-Volmer rate constants for the second electron-transfer step

The second electrode reaction is the transformation between $\mathrm{Int(ads)}$ and $\mathrm{Ox(ads)}$. Its potential-dependent oxidation and reduction rate constants are:

$$k_{\mathrm{ox},2}(E) = k_{\mathrm{s},2}\exp\left[\frac{(1-\alpha_2)F(E-E_2^0)}{RT}\right]$$

$$k_{\mathrm{red},2}(E) = k_{\mathrm{s},2}\exp\left[-\frac{\alpha_2 F(E-E_2^0)}{RT}\right]$$

Here, $k_{\mathrm{s},2}$ is the standard heterogeneous electron-transfer rate constant of the second electron-transfer step, E_2^0 is the formal potential of the $\mathrm{Int/Ox}$ surface couple, and α_2 is the electron-transfer coefficient for this transformation.

The net rate of the second electron-transfer step is:

$$v_2 = k_{\mathrm{ox},2}\Gamma_{\mathrm{Int}} - k_{\mathrm{red},2}\Gamma_{\mathrm{Ox}}$$

This term describes the oxidation of the intermediate form into the oxidized form and the reverse reduction of the oxidized form back to the intermediate form.

Catalytic regeneration rate

Under pseudo-first-order conditions, the regenerative catalytic reaction has the rate:

$$v_{\mathrm{c}} = k_{\mathrm{c}}\Gamma_{\mathrm{Ox}}$$

The catalytic term consumes $\mathrm{Ox(ads)}$ and regenerates $\mathrm{Int(ads)}$. Therefore, it enters the differential equation for Γ_{Ox} with a negative sign and the differential equation for Γ_{Int} with a positive sign.

If the co-reactant Y is not constant, the more general second-order expression is:

$$v_{\mathrm{cat}} = k_{\mathrm{cat}}\Gamma_{\mathrm{Ox}}\Gamma_{Y}$$

In the present algorithm, the pseudo-first-order form in Eq. (14) is used because it gives the simplest surface EEC’ model for protein-film voltammetry.

Differential equations of the surface EEC’ mechanism

The complete kinetic model is obtained by combining the two Butler-Volmer electron-transfer rates with the catalytic regeneration rate:

$$\frac{d\Gamma_{\mathrm{Red}}}{dt} = -k_{\mathrm{ox},1}\Gamma_{\mathrm{Red}} + k_{\mathrm{red},1}\Gamma_{\mathrm{Int}}$$

$$\frac{d\Gamma_{\mathrm{Int}}}{dt} = k_{\mathrm{ox},1}\Gamma_{\mathrm{Red}} - k_{\mathrm{red},1}\Gamma_{\mathrm{Int}} - k_{\mathrm{ox},2}\Gamma_{\mathrm{Int}} + k_{\mathrm{red},2}\Gamma_{\mathrm{Ox}} + k_{\mathrm{c}}\Gamma_{\mathrm{Ox}}$$

$$\frac{d\Gamma_{\mathrm{Ox}}}{dt} = k_{\mathrm{ox},2}\Gamma_{\mathrm{Int}} - k_{\mathrm{red},2}\Gamma_{\mathrm{Ox}} - k_{\mathrm{c}}\Gamma_{\mathrm{Ox}}$$

Equation (16) describes the decrease of $\mathrm{Red(ads)}$ by the first oxidation step and its recovery by reduction of $\mathrm{Int(ads)}$. Equation (17) describes the intermediate state. This species is formed by oxidation of $\mathrm{Red(ads)}$, consumed by reduction back to $\mathrm{Red(ads)}$, consumed by the second oxidation step, regenerated by reduction of $\mathrm{Ox(ads)}$, and additionally regenerated by the catalytic chemical reaction. Equation (18) describes the oxidized state, which is formed by oxidation of $\mathrm{Int(ads)}$ and consumed by both electrochemical reduction and catalytic regeneration.

By adding Eqs. (16), (17), and (18), one obtains:

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

Equation (19) confirms that the proposed system of differential equations satisfies the surface mass balance in Eq. (6).

Matrix form of the kinetic model

For numerical work, Eqs. (16)-(18) may be written in compact matrix form:

$$\frac{d}{dt}\begin{bmatrix}\Gamma_{\mathrm{Red}}\\ \Gamma_{\mathrm{Int}}\\ \Gamma_{\mathrm{Ox}}\end{bmatrix} = \begin{bmatrix}-k_{\mathrm{ox},1} & k_{\mathrm{red},1} & 0\\ k_{\mathrm{ox},1} & -\left(k_{\mathrm{red},1} + k_{\mathrm{ox},2}\right) & k_{\mathrm{red},2} + k_{\mathrm{c}}\\ 0 & k_{\mathrm{ox},2} & -\left(k_{\mathrm{red},2} + k_{\mathrm{c}}\right)\end{bmatrix}\begin{bmatrix}\Gamma_{\mathrm{Red}}\\ \Gamma_{\mathrm{Int}}\\ \Gamma_{\mathrm{Ox}}\end{bmatrix}$$

This form is useful because the potential-dependent rate constants can be recalculated at every potential step, while the same algebraic structure of the kinetic matrix is preserved throughout the simulation.

Initial conditions

If the experiment starts at a sufficiently negative potential, the immobilized film is assumed to be fully reduced:

$$\Gamma_{\mathrm{Red}}(0) = \Gamma_{\mathrm{T}}, \qquad \Gamma_{\mathrm{Int}}(0) = 0, \qquad \Gamma_{\mathrm{Ox}}(0) = 0$$

These initial conditions are appropriate when the starting potential stabilizes the reduced form of the adsorbed protein. If the starting potential is located between the two formal potentials, partial formation of the intermediate state may be considered:

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

with the condition:

$$\Gamma_{\mathrm{Red},0} + \Gamma_{\mathrm{Int},0} + \Gamma_{\mathrm{Ox},0} = \Gamma_{\mathrm{T}}$$

Boundary conditions for protein-film voltammetry

For a strictly surface-confined film, no diffusion boundary condition is required for $\mathrm{Red(ads)}$, $\mathrm{Int(ads)}$, or $\mathrm{Ox(ads)}$. Instead, the essential condition is conservation of the immobilized surface population:

$$\Gamma_{\mathrm{Red}}(t) + \Gamma_{\mathrm{Int}}(t) + \Gamma_{\mathrm{Ox}}(t) = \Gamma_{\mathrm{T}}$$

If Y is present in large excess, its interfacial amount is treated as constant:

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

and therefore:

$$k_{\mathrm{c}} = k_{\mathrm{cat}}\Gamma_Y^* = \text{constant}$$

Equations (24)-(26) are the boundary conditions that distinguish the present protein-film model from a diffusion-controlled solution model.

Incorporation of surface concentrations into the two Butler-Volmer current equations

The first electron-transfer step contributes the partial faradaic current:

$$I_1 = FA\left(k_{\mathrm{ox},1}\Gamma_{\mathrm{Red}} - k_{\mathrm{red},1}\Gamma_{\mathrm{Int}}\right)$$

By inserting the Butler-Volmer expressions from Eqs. (8) and (9), the current of the first electron-transfer step becomes:

$$I_1 = FA\left\{k_{\mathrm{s},1}\exp\left[\frac{(1-\alpha_1)F(E-E_1^0)}{RT}\right]\Gamma_{\mathrm{Red}} - k_{\mathrm{s},1}\exp\left[-\frac{\alpha_1 F(E-E_1^0)}{RT}\right]\Gamma_{\mathrm{Int}}\right\}$$

Equation (28) is the first Butler-Volmer current equation of the surface EEC’ mechanism. It shows that the first electron-transfer current is controlled by the dynamic concentrations Γ_{Red} and Γ_{Int} obtained from the differential equations.

The second electron-transfer step contributes the partial faradaic current:

$$I_2 = FA\left(k_{\mathrm{ox},2}\Gamma_{\mathrm{Int}} - k_{\mathrm{red},2}\Gamma_{\mathrm{Ox}}\right)$$

After incorporation of Eqs. (11) and (12), this current becomes:

$$I_2 = FA\left\{k_{\mathrm{s},2}\exp\left[\frac{(1-\alpha_2)F(E-E_2^0)}{RT}\right]\Gamma_{\mathrm{Int}} - k_{\mathrm{s},2}\exp\left[-\frac{\alpha_2 F(E-E_2^0)}{RT}\right]\Gamma_{\mathrm{Ox}}\right\}$$

Equation (30) is the second Butler-Volmer current equation of the surface EEC’ mechanism. The catalytic regeneration step does not enter the current expression directly, because it is not an electrode reaction. Its effect is indirect but essential: it changes Γ_{Int} and Γ_{Ox} through Eqs. (17) and (18).

The total faradaic current is the sum of the two partial electron-transfer currents:

$$I = I_1 + I_2$$

or explicitly:

$$I = FA\left(k_{\mathrm{ox},1}\Gamma_{\mathrm{Red}} - k_{\mathrm{red},1}\Gamma_{\mathrm{Int}} + k_{\mathrm{ox},2}\Gamma_{\mathrm{Int}} - k_{\mathrm{red},2}\Gamma_{\mathrm{Ox}}\right)$$

After full incorporation of the two Butler-Volmer expressions, the total current is:

$$\begin{aligned} I = FA\{ \quad & k_{\mathrm{s},1}\exp\left[\frac{(1-\alpha_1)F(E-E_1^0)}{RT}\right]\Gamma_{\mathrm{Red}} - k_{\mathrm{s},1}\exp\left[-\frac{\alpha_1 F(E-E_1^0)}{RT}\right]\Gamma_{\mathrm{Int}} \\ & + k_{\mathrm{s},2}\exp\left[\frac{(1-\alpha_2)F(E-E_2^0)}{RT}\right]\Gamma_{\mathrm{Int}} - k_{\mathrm{s},2}\exp\left[-\frac{\alpha_2 F(E-E_2^0)}{RT}\right]\Gamma_{\mathrm{Ox}}\} \end{aligned}$$

Equation (33) is the central working current equation for the surface EEC’ mechanism. It must be evaluated using the instantaneous surface concentrations obtained from Eqs. (16)-(18).

Stationary solution at a fixed potential

At a fixed potential, all rate constants are constant. The stationary state is obtained by setting the time derivatives equal to zero:

$$\frac{d\Gamma_{\mathrm{Red}}}{dt} = 0, \qquad \frac{d\Gamma_{\mathrm{Int}}}{dt} = 0, \qquad \frac{d\Gamma_{\mathrm{Ox}}}{dt} = 0$$

From Eq. (16), one obtains:

$$k_{\mathrm{ox},1}\Gamma_{\mathrm{Red}} = k_{\mathrm{red},1}\Gamma_{\mathrm{Int}}$$

or:

$$\Gamma_{\mathrm{Int}} = \frac{k_{\mathrm{ox},1}}{k_{\mathrm{red},1}}\Gamma_{\mathrm{Red}}$$

From Eq. (18), the stationary relation between Γ_{Ox} and Γ_{Int} is:

$$k_{\mathrm{ox},2}\Gamma_{\mathrm{Int}} = \left(k_{\mathrm{red},2} + k_{\mathrm{c}}\right)\Gamma_{\mathrm{Ox}}$$

or:

$$\Gamma_{\mathrm{Ox}} = \frac{k_{\mathrm{ox},2}}{k_{\mathrm{red},2} + k_{\mathrm{c}}}\Gamma_{\mathrm{Int}}$$

Substitution of Eqs. (36) and (38) into the mass balance gives:

$$\Gamma_{\mathrm{T}} = \Gamma_{\mathrm{Red}}\left[1 + \frac{k_{\mathrm{ox},1}}{k_{\mathrm{red},1}} + \frac{k_{\mathrm{ox},1}k_{\mathrm{ox},2}}{k_{\mathrm{red},1}\left(k_{\mathrm{red},2} + k_{\mathrm{c}}\right)}\right]$$

Therefore, the stationary surface concentration of the reduced form is:

$$\Gamma_{\mathrm{Red}} = \frac{\Gamma_{\mathrm{T}}}{1 + \frac{k_{\mathrm{ox},1}}{k_{\mathrm{red},1}} + \frac{k_{\mathrm{ox},1}k_{\mathrm{ox},2}}{k_{\mathrm{red},1}\left(k_{\mathrm{red},2} + k_{\mathrm{c}}\right)}}$$

The stationary concentration of the intermediate form is:

$$\Gamma_{\mathrm{Int}} = \frac{\frac{k_{\mathrm{ox},1}}{k_{\mathrm{red},1}}\Gamma_{\mathrm{T}}}{1 + \frac{k_{\mathrm{ox},1}}{k_{\mathrm{red},1}} + \frac{k_{\mathrm{ox},1}k_{\mathrm{ox},2}}{k_{\mathrm{red},1}\left(k_{\mathrm{red},2} + k_{\mathrm{c}}\right)}}$$

The stationary concentration of the oxidized form is:

$$\Gamma_{\mathrm{Ox}} = \frac{\frac{k_{\mathrm{ox},1}k_{\mathrm{ox},2}}{k_{\mathrm{red},1}\left(k_{\mathrm{red},2} + k_{\mathrm{c}}\right)}\Gamma_{\mathrm{T}}}{1 + \frac{k_{\mathrm{ox},1}}{k_{\mathrm{red},1}} + \frac{k_{\mathrm{ox},1}k_{\mathrm{ox},2}}{k_{\mathrm{red},1}\left(k_{\mathrm{red},2} + k_{\mathrm{c}}\right)}}$$

Equations (40)-(42) show the direct effect of the catalytic regeneration reaction. An increase in k_{c} decreases the stationary amount of $\mathrm{Ox(ads)}$ and increases the relative importance of the intermediate form. This is the characteristic regenerative feature of the EEC’ mechanism.

Stationary current with incorporated Butler-Volmer concentrations

The stationary current is obtained by inserting Eqs. (40)-(42) into Eq. (32):

$$I_{\mathrm{st}} = FA\left(k_{\mathrm{ox},1}\Gamma_{\mathrm{Red}} - k_{\mathrm{red},1}\Gamma_{\mathrm{Int}} + k_{\mathrm{ox},2}\Gamma_{\mathrm{Int}} - k_{\mathrm{red},2}\Gamma_{\mathrm{Ox}}\right)$$

At the stationary state, Eq. (35) gives $k_{\mathrm{ox},1}\Gamma_{\mathrm{Red}} = k_{\mathrm{red},1}\Gamma_{\mathrm{Int}}$. Consequently, the first electron-transfer contribution is balanced:

$$I_{1,\mathrm{st}} = FA\left(k_{\mathrm{ox},1}\Gamma_{\mathrm{Red}} - k_{\mathrm{red},1}\Gamma_{\mathrm{Int}}\right) = 0$$

The stationary catalytic current arises from the second electron-transfer step because $\mathrm{Ox(ads)}$ is continuously consumed by the regenerative chemical reaction:

$$I_{\mathrm{st}} = FA\left(k_{\mathrm{ox},2}\Gamma_{\mathrm{Int}} - k_{\mathrm{red},2}\Gamma_{\mathrm{Ox}}\right)$$

Using Eq. (37), this becomes:

$$I_{\mathrm{st}} = FAk_{\mathrm{c}}\Gamma_{\mathrm{Ox}}$$

and after inserting Eq. (42):

$$I_{\mathrm{st}} = FA\frac{k_{\mathrm{c}}\frac{k_{\mathrm{ox},1}k_{\mathrm{ox},2}}{k_{\mathrm{red},1}\left(k_{\mathrm{red},2} + k_{\mathrm{c}}\right)}\Gamma_{\mathrm{T}}}{1 + \frac{k_{\mathrm{ox},1}}{k_{\mathrm{red},1}} + \frac{k_{\mathrm{ox},1}k_{\mathrm{ox},2}}{k_{\mathrm{red},1}\left(k_{\mathrm{red},2} + k_{\mathrm{c}}\right)}}$$

Equation (47) shows that the regenerative EEC’ current depends simultaneously on the kinetics of both electron-transfer steps and on the catalytic regeneration rate.

Numerical finite-difference algorithm

For voltammetric simulations, the potential changes with time. Therefore, the rate constants must be recalculated at each potential point. For a time increment Δt, the potential at the j-th step is E_j:

$$E = E_j$$

At this potential, calculate:

$$k_{\mathrm{ox},1,j} = k_{\mathrm{s},1}\exp\left[\frac{(1-\alpha_1)F\left(E_j - E_1^0\right)}{RT}\right]$$

$$k_{\mathrm{red},1,j} = k_{\mathrm{s},1}\exp\left[-\frac{\alpha_1 F\left(E_j - E_1^0\right)}{RT}\right]$$

$$k_{\mathrm{ox},2,j} = k_{\mathrm{s},2}\exp\left[\frac{(1-\alpha_2)F\left(E_j - E_2^0\right)}{RT}\right]$$

$$k_{\mathrm{red},2,j} = k_{\mathrm{s},2}\exp\left[-\frac{\alpha_2 F\left(E_j - E_2^0\right)}{RT}\right]$$

The surface concentrations are updated according to:

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

$$D_{\mathrm{Int},j} = k_{\mathrm{ox},1,j}\Gamma_{\mathrm{Red},j} - k_{\mathrm{red},1,j}\Gamma_{\mathrm{Int},j} - k_{\mathrm{ox},2,j}\Gamma_{\mathrm{Int},j} + k_{\mathrm{red},2,j}\Gamma_{\mathrm{Ox},j} + k_{\mathrm{c}}\Gamma_{\mathrm{Ox},j}$$

$$\Gamma_{\mathrm{Int},j+1} = \Gamma_{\mathrm{Int},j} + D_{\mathrm{Int},j}\Delta t$$

$$\Gamma_{\mathrm{Ox},j+1} = \Gamma_{\mathrm{Ox},j} + \left(k_{\mathrm{ox},2,j}\Gamma_{\mathrm{Int},j} - k_{\mathrm{red},2,j}\Gamma_{\mathrm{Ox},j} - k_{\mathrm{c}}\Gamma_{\mathrm{Ox},j}\right)\Delta t$$

After every update, the total surface concentration should be checked:

$$\Gamma_{\mathrm{Red},j+1} + \Gamma_{\mathrm{Int},j+1} + \Gamma_{\mathrm{Ox},j+1} = \Gamma_{\mathrm{T}}$$

The partial currents at the same potential step are:

$$I_{1,j} = FA\left(k_{\mathrm{ox},1,j}\Gamma_{\mathrm{Red},j} - k_{\mathrm{red},1,j}\Gamma_{\mathrm{Int},j}\right)$$

$$I_{2,j} = FA\left(k_{\mathrm{ox},2,j}\Gamma_{\mathrm{Int},j} - k_{\mathrm{red},2,j}\Gamma_{\mathrm{Ox},j}\right)$$

and the total simulated current is:

$$I_j = I_{1,j} + I_{2,j}$$

This procedure gives a direct numerical algorithm for cyclic voltammetry, cyclic staircase voltammetry, and square-wave voltammetry of a surface-confined EEC’ mechanism.

Implementation under square-wave voltammetry

In square-wave voltammetry, each staircase potential contains a forward and a backward pulse. Therefore, the same finite-difference algorithm is applied separately to the forward and backward parts of the pulse. For the forward pulse:

$$E_{j,\mathrm{f}} = E_j + \frac{E_{\mathrm{sw}}}{2}$$

For the backward pulse:

$$E_{j,\mathrm{b}} = E_j - \frac{E_{\mathrm{sw}}}{2}$$

At $E_{j,\mathrm{f}}$, Eqs. (49)-(55) are used to update the concentrations and calculate the forward current:

$$I_{j,\mathrm{f}} = I_{1,j,\mathrm{f}} + I_{2,j,\mathrm{f}}$$

At $E_{j,\mathrm{b}}$, the rate constants are recalculated and the backward current is obtained:

$$I_{j,\mathrm{b}} = I_{1,j,\mathrm{b}} + I_{2,j,\mathrm{b}}$$

The net square-wave current is then:

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

Equations (60)-(64) represent the essential algorithmic step for simulating the square-wave response of the surface EEC’ mechanism. The catalytic reaction modifies the net current by changing the availability of $\mathrm{Int(ads)}$ and $\mathrm{Ox(ads)}$ between the forward and backward pulses.

Limiting cases

If the catalytic regeneration is absent:

$$k_{\mathrm{c}} = 0$$

then the mechanism reduces to a simple sequential two-step surface EE mechanism:

$$\mathrm{Red(ads)} \rightleftharpoons \mathrm{Int(ads)} \rightleftharpoons \mathrm{Ox(ads)}$$

If the catalytic regeneration is very fast:

$$k_{\mathrm{c}} \gg k_{\mathrm{red},2}$$

then the oxidized form is rapidly converted back into the intermediate form. Under this condition, the backward current of the second electron-transfer step is strongly affected because $\mathit{\Gamma}_{\mathrm{Ox}}$ becomes small, while $\mathit{\Gamma}_{\mathrm{Int}}$ is continuously replenished.

If the first electron-transfer step is slow:

$$k_{\mathrm{s},1} \ll 1$$

then the formation of $\mathrm{Int(ads)}$ is kinetically limited, and the catalytic regeneration may have a weak observable effect because $\mathrm{Ox(ads)}$ cannot be efficiently produced.

If the second electron-transfer step is slow:

$$k_{\mathrm{s},2} \ll 1$$

then the conversion of $\mathrm{Int(ads)}$ into $\mathrm{Ox(ads)}$ limits the regenerative catalytic cycle.

If both electron-transfer steps are fast:

$$k_{\mathrm{s},1} \gg 1, \qquad k_{\mathrm{s},2} \gg 1$$

then the distribution of the surface concentrations follows the potential rapidly, and the catalytic regeneration rate becomes one of the main factors controlling the shape and magnitude of the voltammetric response.

Final mathematical algorithm

The complete simulation algorithm for the surface EEC’ mechanism can be summarized as follows:

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1. Define $\Gamma_\mathrm{T}, E_1^0, E_2^0, k_{\mathrm{s},1}, k_{\mathrm{s},2}, \alpha_1, \alpha_2, k_\mathrm{c}, T, A$.
2. Set initial values $\Gamma_\mathrm{Red}(0), \Gamma_\mathrm{Int}(0), \Gamma_\mathrm{Ox}(0)$.
3. For each potential $E_j$, calculate $k_{\mathrm{ox},1,j}, k_{\mathrm{red},1,j}, k_{\mathrm{ox},2,j}, k_{\mathrm{red},2,j}$.
4. Update $\Gamma_\mathrm{Red}, \Gamma_\mathrm{Int}, \Gamma_\mathrm{Ox}$ using Eqs. (53)-(56).
5. Calculate $I_{1,j}, I_{2,j}$, and $I_j$.
6. For square-wave voltammetry, calculate $I_\mathrm{f}, I_\mathrm{b}$, and $\Delta I = I_\mathrm{f} - I_\mathrm{b}$.
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This final algorithm contains only the surface concentrations of $\mathrm{Red(ads)}$, $\mathrm{Int(ads)}$, and $\mathrm{Ox(ads)}$, together with the two Butler-Volmer electron-transfer equations and the regenerative catalytic chemical step. No coverage transformation is required.

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