MATHEMATICAL Model beyond the Master Electrochemical mechanism (ECrevEC’) under conditions of Protein-Film Voltammetry- *Surface ECrevEC’ mechanism under Butler-Volmer formalism*

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Abstract

The surface-confined two-step ECrevEC′ mechanistic framework linked with two different chemical reactions provides a rigorous mathematical basis for interpreting complex redox transformations in protein-film cyclic voltammetry. In this model, all electroactive species are strongly adsorbed on the electrode surface, and their temporal evolution is governed by a coupled system of nonlinear differential equations derived from Butler–Volmer kinetics for two sequential electron-transfer steps and first-order chemical rate laws for the intermediate transformations. The inclusion of a reversible chemical step (Crev) between intermediates and a regenerative catalytic step (C′) introduces dynamic coupling between thermodynamic equilibria and kinetic pathways, leading to rich and highly diagnostic voltammetric responses.

From a mathematical standpoint, the model captures the interplay between electron-transfer kinetics, chemical reversibility, and catalytic regeneration through dimensionless parameters that scale with the experimental time window, enabling systematic mechanistic identification. In protein-film cyclic voltammetry, this framework is particularly important because many redox enzymes—especially those containing metal centers such as Mo—undergo multi-step, surface-confined electron transfer coupled to substrate conversion. The ECrevEC′ model therefore serves as a unified platform for extracting mechanistic, kinetic, and thermodynamic information from experimentally accessible features such as peak splitting, peak symmetry, and the appearance of multiple redox waves. Ultimately, this approach advances the quantitative understanding of enzymatic electrochemistry and supports the rational design of bioelectrocatalytic systems and electrochemical biosensors.

Mathematical Description of ECrevEC'

The model below assumes a fully surface-confined system. All redox forms are strongly adsorbed at the graphite electrode surface, so there are no diffusion terms. The solution species Y acts as a substrate in the regenerative chemical step.

Reaction scheme

$$E_1 \text{ step: } \text{Red} \rightleftharpoons \text{Int1} + e^- \qquad (k_{s,1}, \alpha_1)$$

This first electron-transfer step converts the adsorbed reduced form Red into the first adsorbed intermediate Int1.

$$C_{\text{rev}} \text{ step: } \text{Int1} \rightleftharpoons \text{Int2} \qquad (k_f,\ k_b;\ K_{eq} = k_f/k_b\ ,\ k_{chem} = k_f + k_b)$$

This is a reversible chemical rearrangement between the two adsorbed intermediates.

$$E_2 \text{ step: } \text{Int2} \rightleftharpoons \text{Ox} + e^- \qquad (k_{s,2}, \alpha_2)$$

This second electron-transfer step converts Int2 into the oxidized adsorbed form Ox.

$$C' \text{regenerative step: } \text{Ox} + Y \rightarrow \text{Int2} \qquad (k_c)$$

This regenerative chemical step converts Ox back into Int2 in the presence of substrate Y.

Surface coverages and mass conservation law

$$\Gamma_{Red}(t),\ \Gamma_{Int1}(t),\ \Gamma_{Int2}(t),\ \Gamma_{Ox}(t)$$

These quantities denote the time-dependent surface coverages of the adsorbed species.

$$\Gamma^* = \Gamma_{Red} + \Gamma_{Int1} + \Gamma_{Int2} + \Gamma_{Ox}$$

The total surface coverage is constant because all redox forms remain confined to the electrode surface and only interconvert.

Butler-Volmer rate expressions

For the first electron-transfer step:

$$\nu_1 = k_{s,1}\exp\left(\frac{(1-\alpha_1)F}{RT}(E - E_1^{0\prime})\right)\Gamma_{Red} - k_{s,1}\exp\left(-\frac{\alpha_1 F}{RT}(E - E_1^{0\prime})\right)\Gamma_{Int1}$$

The first term is the anodic direction Red $\rightarrow$ Int1 $+ e^-$, while the second term is the cathodic reverse contribution.

For the second electron-transfer step:

$$\nu_2 = k_{s,2}\exp\left(\frac{(1-\alpha_2)F}{RT}(E - E_2^{0\prime})\right)\Gamma_{Int2} - k_{s,2}\exp\left(-\frac{\alpha_2 F}{RT}(E - E_2^{0\prime})\right)\Gamma_{Ox}$$

Again, the first term is the anodic contribution and the second term is the reverse cathodic contribution.

If the concentration of Y is constant, the regenerative step can be written in pseudo-first-order form as

$$k_c{}' = k_c\, c(Y)$$

which simplifies the differential equations below.

Differential equations

$$\frac{d\Gamma_{Red}}{dt} = -\nu_1$$

The coverage of Γ_{Red} decreases when the first oxidation step proceeds and increases when the reverse reduction occurs.

$$\frac{d\Gamma_{Int1}}{dt} = \nu_1 - k_f\Gamma_{Int1} + k_b\Gamma_{Int2}$$

The first intermediate is formed electrochemically, consumed in the forward chemical step, and regenerated in the backward chemical step.

$$\frac{d\Gamma_{Int2}}{dt} = k_f\Gamma_{Int1} - k_b\Gamma_{Int2} - \nu_2 + k_c{}'\Gamma_{Ox}$$

The second intermediate is produced from Int1, consumed in the second electron-transfer step, and regenerated by the catalytic chemical step.

$$\frac{d\Gamma_{Ox}}{dt} = \nu_2 - k_c{}'\Gamma_{Ox}$$

The oxidized form is created by the second electrode step and consumed by the regenerative chemical reaction.

Total current

$$i(t) = FA(\nu_1 + \nu_2)$$

The measured current is the sum of the faradaic contributions from the two electron-transfer steps.

Initial conditions

For the most common case, the entire adsorbed film is initially in the reduced state:

$$\Gamma_{Red}(0) = \Gamma^*$$

Initially, all adsorbed protein molecules are in the reduced form.

$$\Gamma_{Int1}(0) = 0$$

No molecules are initially present in the first intermediate state.

$$\Gamma_{Int2}(0) = 0$$

No molecules are initially present in the second intermediate state.

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

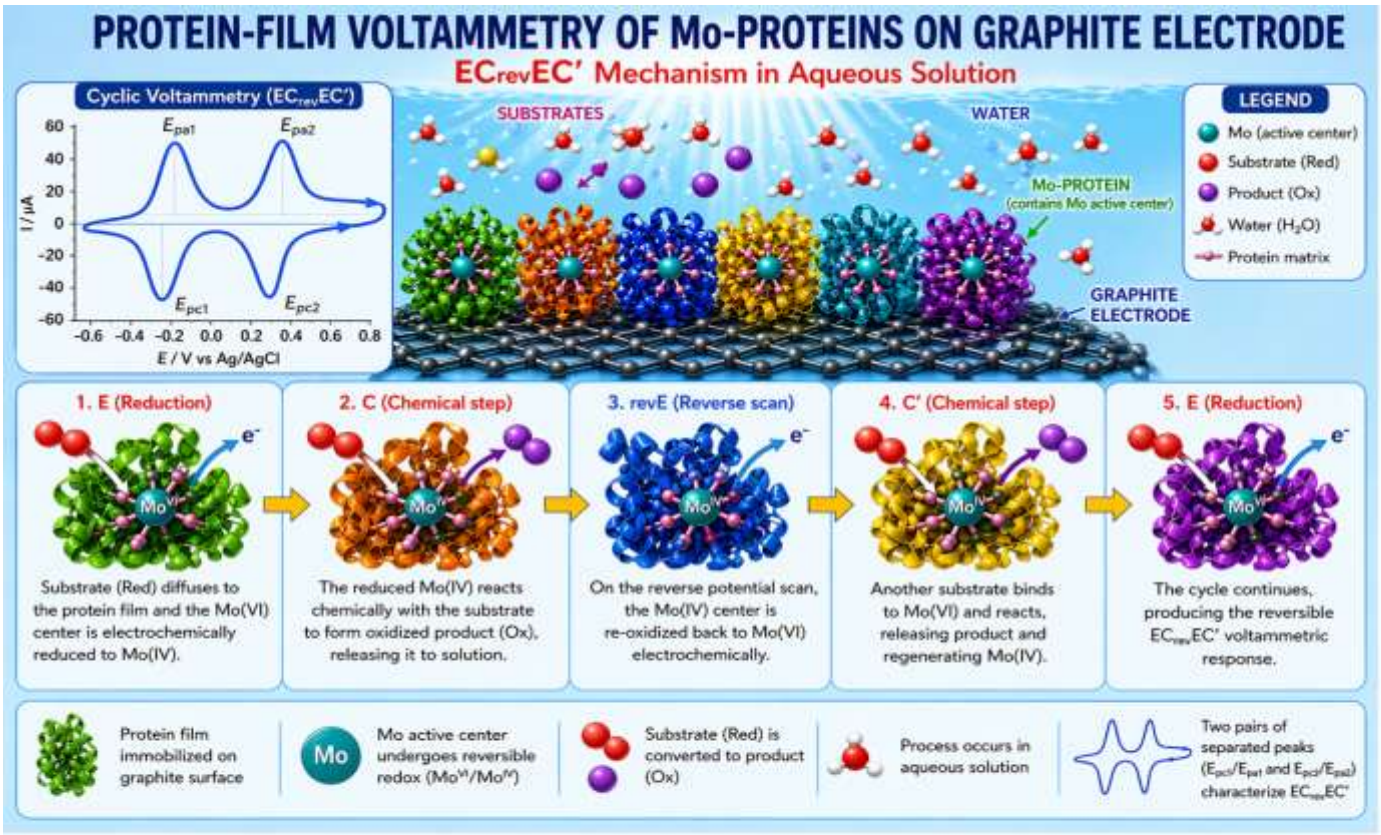
No oxidized adsorbed form is present at the beginning of the experiment.

Potential program

$$E = E(t)$$

The potential varies with time according to the voltammetric waveform, and therefore the kinetic factors in the Butler-Volmer expressions also change continuously during the experiment.

The entire original MATHCAD simulation protocol of this mechanism in cyclic voltammetry is provided for free on the platform of repository of the Goce Delcev University, Stip, Macedonia, for free.



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