# Mathematical description of the diffusional "all-in-one" CrevE$_1$CirrE$_2$C' mechanism under Butler-Volmer kinetics in Square-wave voltammetry

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**Abstract**

This work defines for the first time the reaction scheme, initial conditions, diffusion-reaction equations, electrode boundary conditions, and current expression for the diffusional CrevE1CirrE2C' mechanism. All species are considered dissolved in solution; electron transfer occurs only at the electrode surface and is described by Butler-Volmer kinetics. This mathematical model provides a unified platform for studying complex diffusional electrochemical mechanisms involving chemical pre-equilibria, two electrode reactions, irreversible intermediate transformation, and catalytic regeneration. By adjusting selected kinetic constants, the model may reproduce simpler limiting mechanisms such as E, CE, EC, ECE, EC', EE, and other more complex mechanisms evaluated out of the simples one.

CrevE1CirrE2Cat mechanism DIFFUSIONAL in SWV May 09 2026

(a) Crev:

$A \rightleftharpoons Red$ ($kf_1$, kb, Keq = kf/kb)

(b) $E_1$Cirr:

$Red \rightleftharpoons Int1 + e^-$ (ks,1, $\alpha_1$)

$Int1 \rightarrow Int2$ (kc,irr)

(c) $E_2$:

$Int2 \rightleftharpoons Ox + e^-$ (ks,2, $\alpha_2$)

(d) C':

$Ox + Y \rightarrow Int2$ (kcatalytic)

1. The reaction scheme

Reversible preceding chemical step, Crev:

$$\mathrm{A} \rightleftharpoons \mathrm{Red} \quad (k_f,\ k_b,\ K_{eq} = \frac{k_f}{k_b})$$

This equilibrium defines the chemical conversion between the precursor A and the electroactive reduced species Red before the first electrode step.

First electron-transfer step followed by an irreversible chemical transformation, E1Cirr:

$$\mathrm{Red} \rightleftharpoons \mathrm{Int1} + e^- \ (k_{s,1},\ \alpha_1)$$

This step describes the first heterogeneous electron transfer at the electrode surface, where Red is converted into the first intermediate Int1.

$$\mathrm{Int1} \rightarrow \mathrm{Int2} \ \ (k_{c,irr})$$

This irreversible chemical step consumes Int1 in solution and generates Int2, thereby coupling homogeneous kinetics to the first electron-transfer process.

Second electron-transfer step, E2:

$$\mathrm{Int2} \rightleftharpoons \mathrm{Ox} + e^- \quad (k_{s,2},\ \alpha_{2)})$$

This step represents the second heterogeneous electron transfer at the electrode surface, converting Int2 into the oxidized species Ox.

Catalytic regenerative step, C':

$$\mathrm{Ox} + \mathrm{Y} \rightarrow \mathrm{Int2} \quad (k_{cat})$$

This catalytic reaction regenerates Int2 from Ox in the presence of the solution species Y and may amplify or reshape the voltammetric response.

2. Concentration notation

$$c_i = c_i(x, t), \qquad i = \mathrm{A, Red, Int1 ,Int2, Ox, Y}$$

Each concentration depends on distance from the electrode surface and time. The coordinate x is measured perpendicular to the electrode, with x = 0 at the electrode surface and x approaching infinity in the bulk solution.

$$D_i = \text{diffusion coefficient of species } i$$

The diffusion coefficient describes how rapidly each dissolved species is transported through the solution by diffusion.

3. Differential equations in solution

$$\frac{\partial c_{\mathrm{A}}}{\partial t} = D_{\mathrm{A}} \frac{\partial^2 c_{\mathrm{A}}}{\partial x^2} - k_f c_{\mathrm{A}} + k_b c_{Red}$$

This equation states that A changes by diffusion, by consumption in the forward chemical reaction, and by regeneration from Red in the backward reaction.

$$\frac{\partial c_{Red}}{\partial t} = D_{Red} \frac{\partial^2 c_{Red}}{\partial x^2} + k_f c_{\mathrm{A}} - k_b c_{Red}$$

Red is formed from A and consumed back to A in the reversible chemical equilibrium, while its electron-transfer conversion is treated only at the electrode boundary.

$$\frac{\partial c_{Int1}}{\partial t} = D_{Int1} \frac{\partial^2 c_{Int1}}{\partial x^2} - k_{c,irr} c_{Int1}$$

Int1 is depleted in solution by the irreversible chemical transformation into Int2. Its electrochemical formation is introduced through the surface flux condition.

$$\frac{\partial c_{Int2}}{\partial t} = D_{Int2} \frac{\partial^2 c_{Int2}}{\partial x^2} + k_{c,irr} c_{Int1} + k_{cat} c_{Ox} c_{\mathrm{Y}}$$

Int2 is produced by the irreversible transformation of Int1 and by catalytic regeneration from Ox and Y.

$$\frac{\partial c_{Ox}}{\partial t} = D_{Ox} \frac{\partial^2 c_{Ox}}{\partial x^2} - k_{cat} c_{Ox} c_{\mathrm{Y}}$$

Ox is consumed in solution by the catalytic reaction with Y, while its electrochemical formation is defined at the electrode surface.

$$\frac{\partial c_{\mathrm{Y}}}{\partial t} = D_{\mathrm{Y}} \frac{\partial^2 c_{\mathrm{Y}}}{\partial x^2} - k_{cat} c_{Ox} c_{\mathrm{Y}}$$

Y is consumed together with Ox in the catalytic regeneration step. If Y is present in large excess, its concentration may be treated as constant.

If Y is in present in large excess, then it holds that:

$$c_{\mathrm{Y}} \approx c_{\mathrm{Y}}^* = \text{constant}$$

$$k_{cat}{}' = k_{cat} c_{\mathrm{Y}}^*$$

$$k_{cat} c_{Ox} c_{\mathrm{Y}} \approx k_{cat}{}' c_{Ox}$$

These expressions convert the second-order catalytic step into a pseudo-first-order reaction, which simplifies numerical simulation.

4. Initial conditions

At t = 0 and for all x greater than or equal to 0:

$$c_{\mathrm{A}}(x, 0) = c_{\mathrm{A}}^*$$

The initial concentration of A is equal to its bulk value throughout the solution.

$$c_{Red}(x, 0) = c^*_{Red}$$

The initial concentration of Red is equal to its bulk value. If the preceding equilibrium is established before the experiment, cRed* is related to cA* through Keq.

$$\frac{c^*_{Red}}{c^*_{\mathrm{A}}} = K_{eq}$$

This relation expresses the initial chemical equilibrium between A and Red before the potential perturbation is applied.

$$c_{Int1}(x, 0) = 0$$

Initially, Int1 is absent because the first electron-transfer step has not yet generated it.

$$c_{Int2}(x, 0) = 0$$

Initially, Int2 is absent unless it is deliberately added before the experiment.

$$c_{Ox}(x, 0) = 0$$

Initially, Ox is absent because the second electron-transfer step has not yet produced it.

$$c_{\mathrm{Y}}(x, 0) = c^*_{\mathrm{Y}}$$

The catalytic reactant Y is initially present at its bulk concentration.

5. Bulk boundary conditions

For x approaching infinity and t greater than 0:

$$c_{\mathrm{A}}(\infty, t) = c^*_{\mathrm{A}}$$

$$c_{Red}(\infty, t) = c^*_{Red}$$

$$c_{Int1}(\infty, t) = 0$$

$$c_{Int2}(\infty, t) = 0$$

$$c_{Ox}(\infty, t) = 0$$

$$c_{\mathrm{Y}}(\infty, t) = c^*_{\mathrm{Y}}$$

These conditions express semi-infinite diffusion. Far from the electrode, the solution remains unaffected by the electrode reaction and retains the initial bulk composition.

6. Butler-Volmer kinetic formalism

The formal potentials of the two electrode steps are denoted as E1^0' and E2^0'. The overpotentials are:

$$\eta_1(t) = E(t) - E_1^{0\prime}$$

$$\eta_2(t) = E(t) - E_2^{0\prime}$$

The overpotential defines the thermodynamic driving force for each electron-transfer step at a given applied potential.

First electrode step:

$$v_1(t) = k_{s,1}\left[c_{Red}(0,t)\exp\left(\frac{(1-\alpha_1)F\eta_1(t)}{RT}\right) - c_{Int1}(0,t)\exp\left(-\frac{\alpha_1 F\eta_1(t)}{RT}\right)\right]$$

This Butler-Volmer expression gives the net heterogeneous rate of the Red/Int1 couple. Positive v1 corresponds to oxidation of Red to Int1.

Second electrode step:

$$v_2(t) = k_{s,2}\left[c_{Int2}(0,t)\exp\left(\frac{(1-\alpha_2)F\eta_2(t)}{RT}\right) - c_{Ox}(0,t)\exp\left(-\frac{\alpha_2 F\eta_2(t)}{RT}\right)\right]$$

This expression defines the net heterogeneous rate of the Int2/Ox couple. Positive v2 corresponds to oxidation of Int2 to Ox.

7. Electrode-surface flux boundary conditions

At x = 0:

$$D_{\mathrm{A}}\left.\frac{\partial c_{\mathrm{A}}}{\partial x}\right|_{x=0} = 0$$

A is not directly involved in electron transfer, so its electrode-surface flux is zero.

$$D_{Red}\left.\frac{\partial c_{Red}}{\partial x}\right|_{x=0} = v_1(t)$$

This condition couples diffusion of Red to its heterogeneous consumption or production at the electrode surface.

$$D_{Int1}\left.\frac{\partial c_{Int1}}{\partial x}\right|_{x=0} = -v_1(t)$$

Int1 has the opposite surface flux to Red because it is generated when Red is oxidized and consumed when the reverse reaction occurs.

$$D_{Int2}\left.\frac{\partial c_{Int2}}{\partial x}\right|_{x=0} = v_2(t)$$

This boundary condition links the surface concentration of Int2 to its oxidation or reduction in the second electron-transfer step.

$$D_{Ox}\left.\frac{\partial c_{Ox}}{\partial x}\right|_{x=0} = -v_2(t)$$

Ox has the opposite surface flux to Int2 because it is produced during oxidation of Int2 and consumed during the reverse process.

$$D_{\mathrm{Y}} \left.\frac{\partial c_{\mathrm{Y}}}{\partial x}\right|_{x=0} = 0$$

Y does not exchange electrons directly with the electrode, so its electrode-surface flux is zero.

8. Total Faradaic current

For one-electron transfers:

$$I(t) = FA[v_1(t) + v_2(t)]$$

The total current is the sum of the Faradaic contributions from both electrode reactions. Depending on the sign convention used in the simulation, the sign of the current may be reversed.

9. Square-wave voltammetric potential program

During square-wave voltammetry, the applied potential is pulsed around a staircase potential. A general representation is:

$$E(t) = E_{stair}(t) \pm \frac{E_{sw}}{2}$$

The square-wave amplitude Esw and the staircase increment dE define the potential perturbation, while the frequency f defines the experimental time scale.

$$\tau = \frac{1}{f}$$

The period tau determines how much time is available for diffusion, electron transfer, and homogeneous chemical reactions during each square-wave cycle.

10. Useful dimensionless kinetic parameters

$$K_{s,1} = \frac{k_{s,1}}{\sqrt{D_{Red} f}}$$

This parameter compares the rate of the first heterogeneous electron-transfer step with diffusion over the square-wave time scale.

$$K_{s,2} = \frac{k_{s,2}}{\sqrt{D_{Int2} f}}$$

This parameter compares the second heterogeneous electron-transfer rate with diffusional transport during the experiment.

$$K_{chem,1} = \frac{k_f + k_b}{f},$$

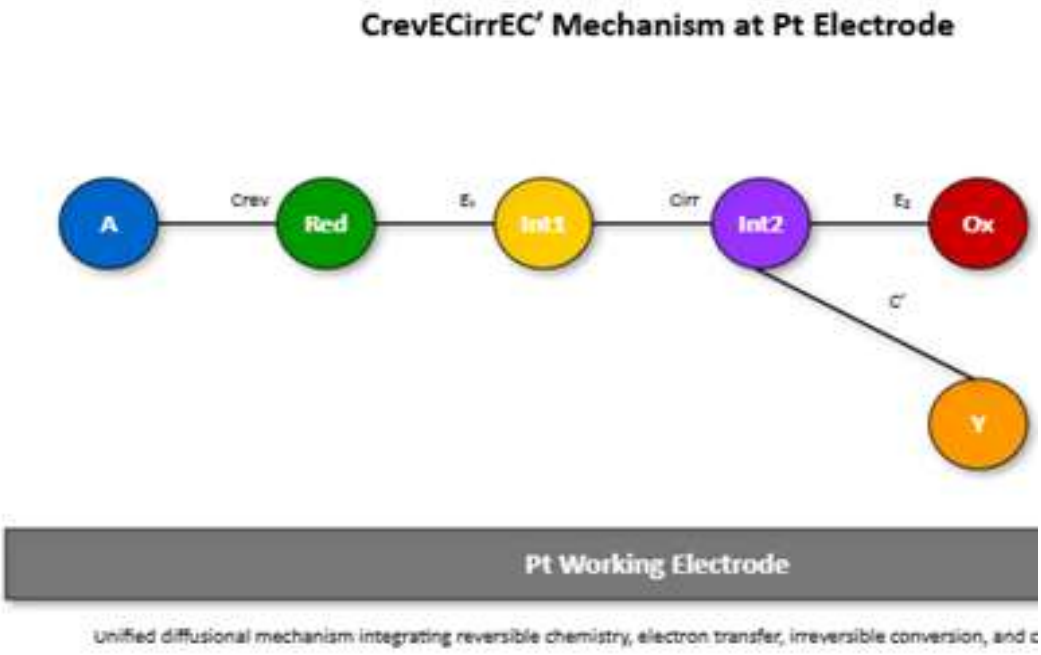
These parameters compare the reversible preceding chemical reaction rates with the frequency of the square-wave perturbation.

$$K_{c,irr} = \frac{k_{c,irr}}{f}$$

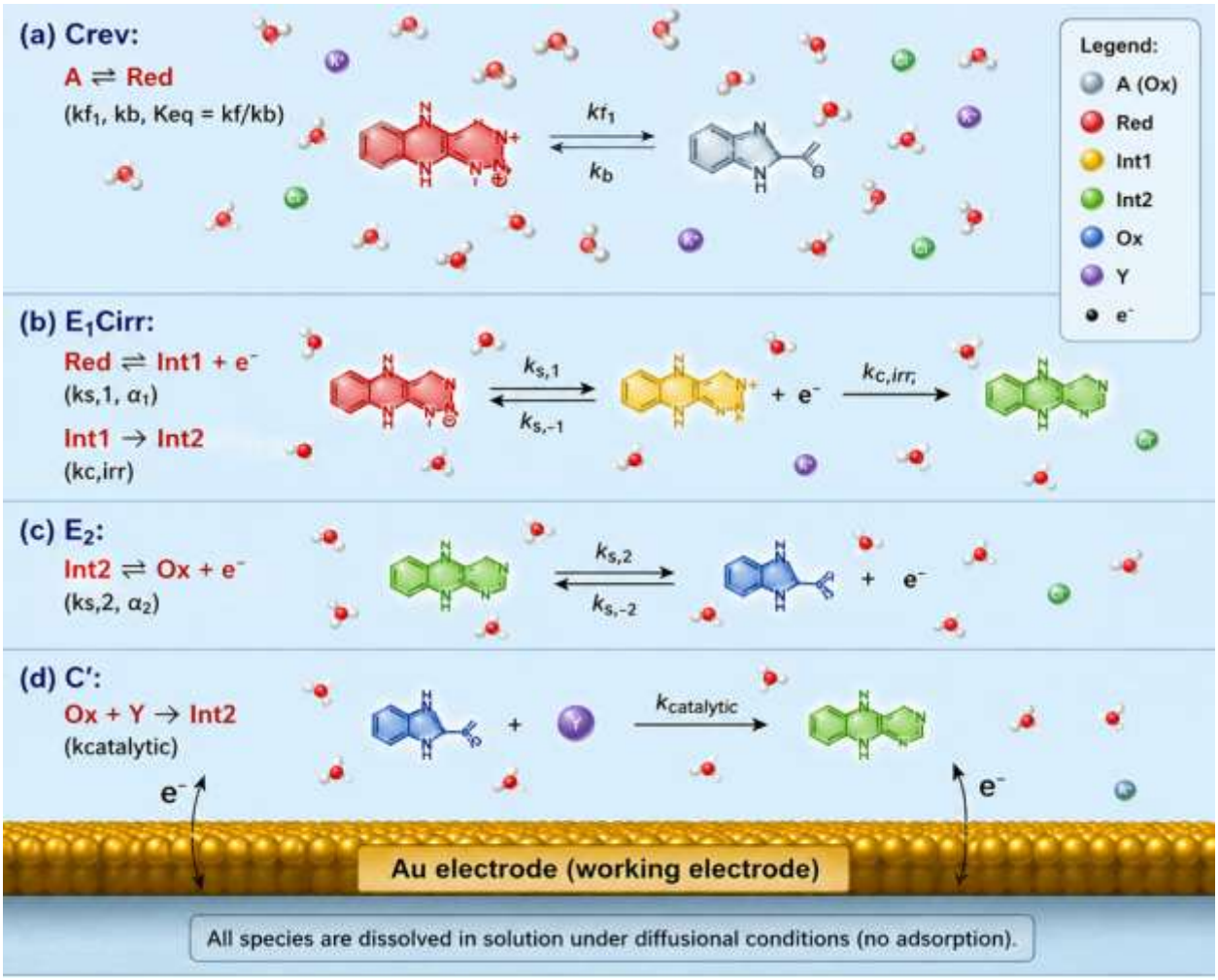
This parameter indicates whether the irreversible conversion of Int1 into Int2 is slow, intermediate, or fast within the experimental time window.

$$K_{cat} = \frac{k_{cat} c_Y^*}{f}$$

This parameter describes the relative importance of catalytic regeneration compared with the square-wave frequency under pseudo-first-order conditions.




Unified diffusional mechanism integrating reversible chemistry, electron transfer, irreversible conversion, and c


(a) Crev:
A ⇌ Red
(kf1, kb, Keq = kf/kb)
kf1
kb
Legend:
A (Ox)
Red
Int1
Int2
Ox
Y
e⁻
(b) E1Cirr:
Red ⇌ Int1 + e⁻
(ks,1, α1)
Int1 → Int2
(kc,irr)
ks,1
ks,-1
+ e⁻
kc,irr
(c) E2:
Int2 ⇌ Ox + e⁻
(ks,2, α2)
ks,2
ks,-2
+ e⁻
(d) C':
Ox + Y → Int2
(kcatalytic)
kcatalytic
e⁻
e⁻
Au electrode (working electrode)
All species are dissolved in solution under diffusional conditions (no adsorption).

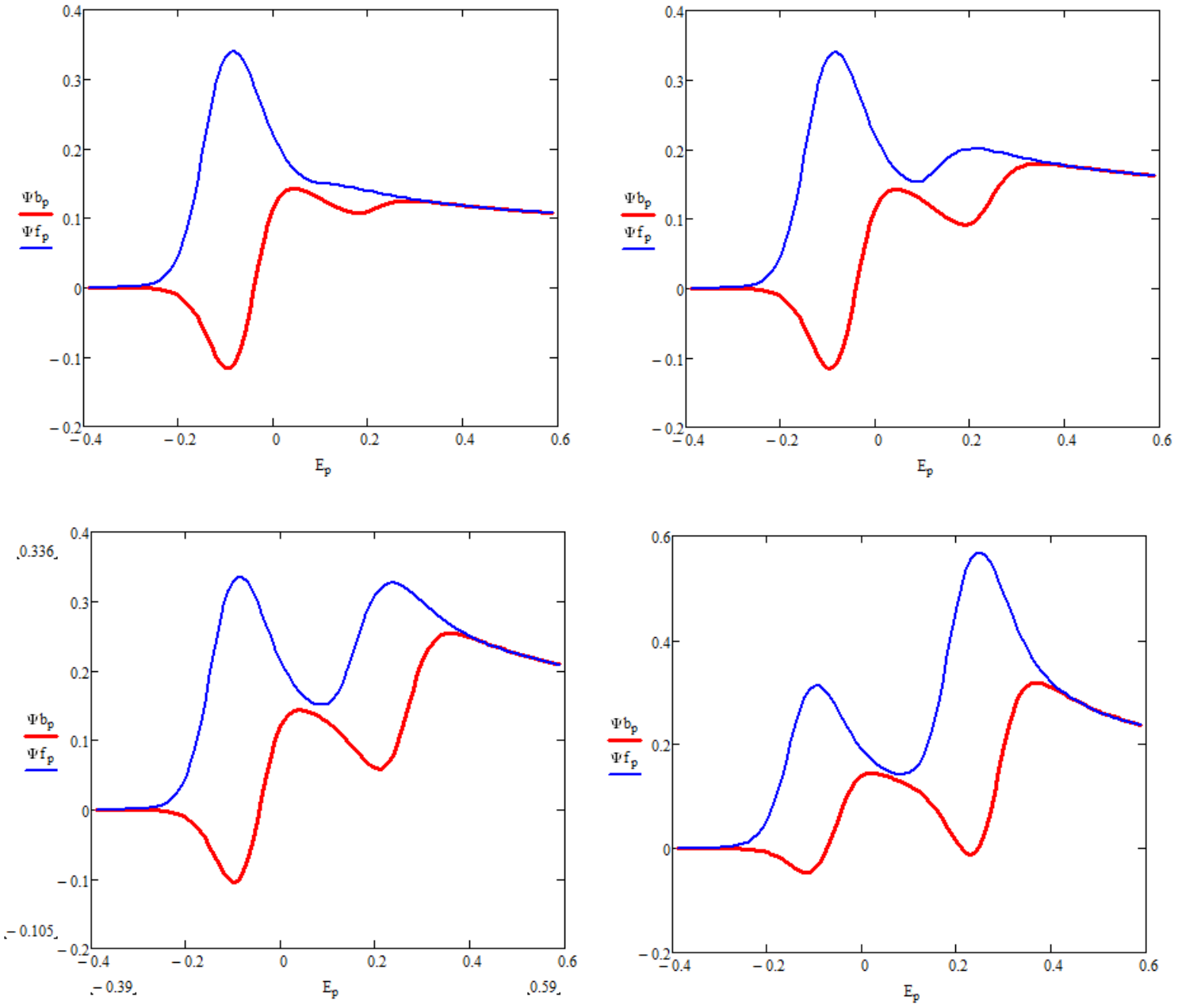
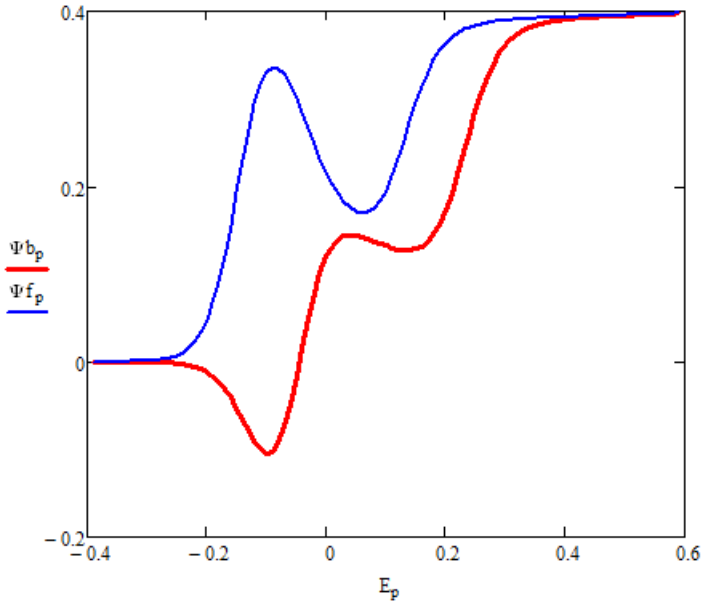
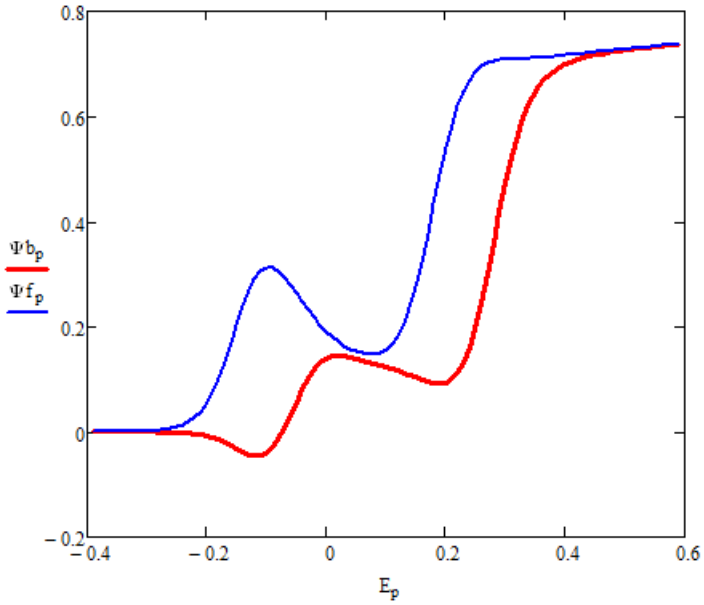



**Figure 1**: Forward and backward voltammograms showing the effect of Kchem,2 i.e. effect of rate of irreversible chemical step


0.4
0.2
0
−0.2
−0.4
−0.2
0
0.2
0.4
0.6
Ep
Ψbp
Ψfp


0.8
0.6
0.4
0.2
0
−0.2
−0.4
−0.2
0
0.2
0.4
0.6
Ep
Ψbp
Ψfp

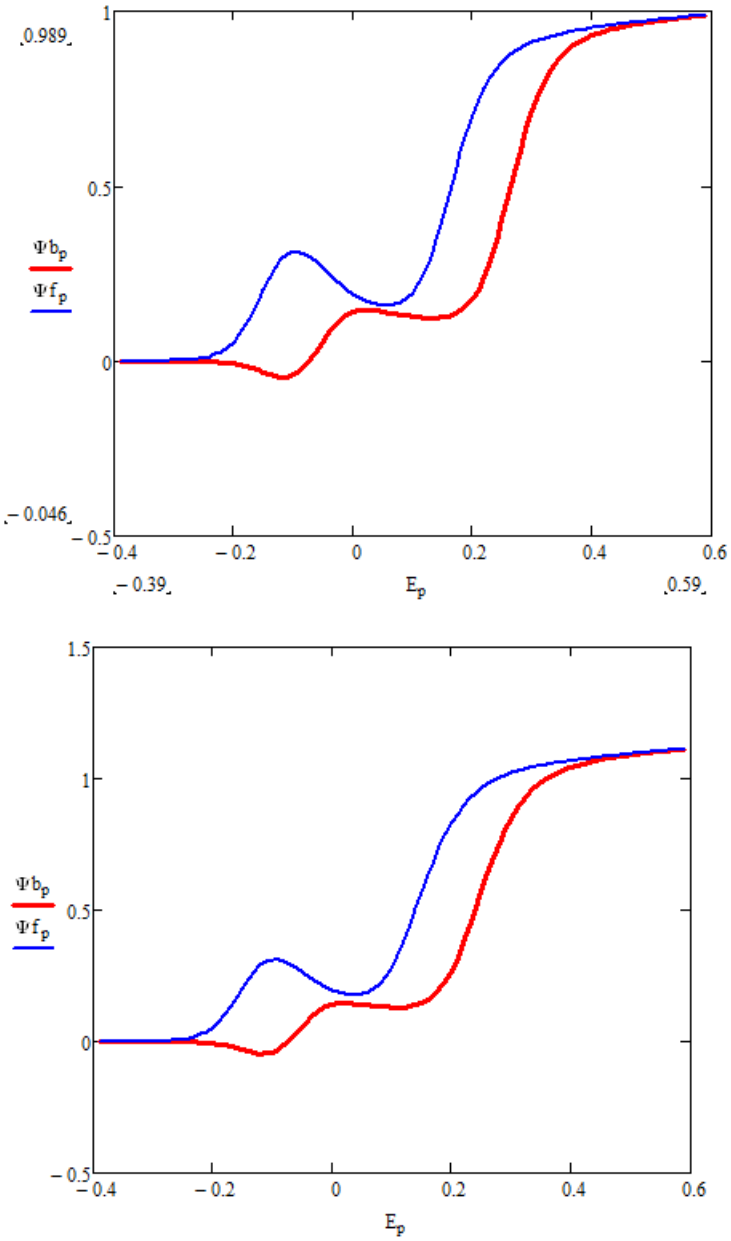



**Figure 2**: Forward and backward square-wave voltammograms showing the effect of Kcat i.e. effect of rate of irreversible regenerative step of CrevE1CirrE2C' mechanism

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