

# From Single to Double Catalysis: Diffusional EC'EC'' Framework in Cyclic Voltammetry-MATHCAD Simulation Platform

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## Abstract

Multistep redox transformations in solution frequently proceed through sequential electron-transfer events coupled to regenerative chemical reactions, yielding stable intermediates that can re-enter catalytic cycles. Such behavior is characteristic of numerous molecular systems, including organic mediators, quinone/hydroquinone couples, and cofactor-driven processes (e.g., flavins and NAD(P)H analogues), where all redox forms may participate in feedback loops that shape the observed electrochemical response. Here we present, for the first time, a comprehensive theoretical treatment of a **two-step double catalytic EC'EC'' mechanism** under conditions of mass transfer occurring exclusively via diffusion in **cyclic voltammetry**. The model describes a sequence of two electron transfers separated by consecutive regenerative chemical steps, with both catalytic loops explicitly incorporated into the mass-transport-kinetic framework. Numerical solutions of the governing equations reveal distinct voltammetric signatures arising from the interplay between diffusion, electron-transfer kinetics, and the rates of the two catalytic steps. Systematic variation of the kinetic parameters for each regenerative pathway demonstrates how peak currents, peak separations, and waveform distortions encode the relative contributions of the two catalytic cycles, enabling their discrimination and quantification.

Importantly, under well-defined limiting conditions, the general EC'EC'' scheme **can converge to several classical mechanisms**, including EE, EC'E, EEC', EC', and simple E mechanism. This convergence establishes the present formulation as a **unified theoretical platform** for interpreting a wide range of electrochemical behaviors within a single framework. The results provide new mechanistic insight into complex catalytic redox systems and offer practical guidance for extracting kinetic information from cyclic voltammetric data in systems exhibiting tandem catalytic processes. Original MATHCAD platform is available for free on the Repository of Goce Delcev University, Stip.

$$E_{fI} = 0.7 \quad E_{fII} = 0.35 \quad \tau = 0.05$$

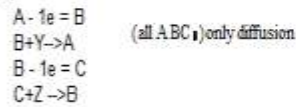
$$E_{sI} = -0.3 \quad \Delta E = 1 \quad dE = 0.005 \quad E_{sII} = -0.65 \quad r = 1.1$$

$$n = 1 \quad F_{\text{av}} = 96500 \quad R_{\text{av}} = 0.314 \quad T_{\text{av}} = 298.15 \quad \Delta E_I = E_{fI} - E_{sI} \quad K_I = 10^5$$

$$M = 25 \quad \Delta E_{II} = E_{fII} - E_{sII} \quad K_{II} = 10^{0.5}$$

$$j = 1.2 \frac{\Delta E}{dE} \cdot 25 \quad d = \frac{\tau}{M} \quad \alpha_2 = 0.5 \quad \alpha_1 = 0.5$$

TWO STEP DIFFUSIONAL Double Regenerative  
 EC'EC'cat Mechanism in CYCLIC  
 VOLTAMMETRY--towards Oxidation Version date: 03  
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$$k_{c1} = 100$$

$$k_{c2} = 200$$

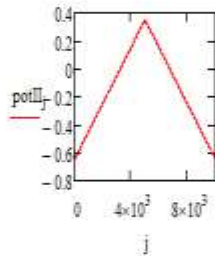
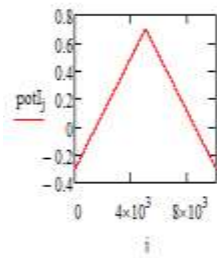
$\lambda$  i  $z$  se definirani kako odnos  
 na  $Kc_1x$  i  $kc_2x\tau$

$$potI_j = if \left[ j \leq \frac{\Delta E}{dE} \cdot 25, E_{sI} + \left( \frac{j}{25} \right) dE - dE \right], E_{fI} - \left[ \frac{j - \left( \frac{\Delta E}{dE} \cdot 25 \right)}{25} \right] dE - dE \right]$$

$$potII_j = if \left[ j \leq \frac{\Delta E}{dE} \cdot 25, E_{sII} + \left( \frac{j}{25} \right) dE - dE \right], E_{fII} - \left[ \frac{j - \left( \frac{\Delta E}{dE} \cdot 25 \right)}{25} \right] dE - dE \right]$$

$\lambda$  e kinetički parametar na ireverzibilna hemiska  
 reakcija na regeneracija  
 povzana so prv elektroden cekor

$$K_{II} = 3.162$$



$$\lambda = .00581001000985$$

$$z = .0581001049035$$

$z$  e katalitički parametar vo ovoj  
 model povznan so stvor cekor

$$A_j = \left( 1 - \operatorname{erfc} \left( \sqrt{\frac{\lambda}{25}} j \right) \right) - \left[ 1 - \operatorname{erfc} \left( \sqrt{\frac{\lambda}{25}} (j-1) \right) \right]$$

$$B_j = \left( 1 - \operatorname{erfc} \left( \sqrt{\frac{z}{25}} j \right) \right) - \left[ 1 - \operatorname{erfc} \left( \sqrt{\frac{z}{25}} (j-1) \right) \right]$$

$$\Phi I_j = n \frac{F}{R \cdot T} \cdot potI_j \quad \Phi II_j = n \frac{F}{R \cdot T} \cdot potII_j$$

$$x = 0.001$$

$$\Psi I_1 = \frac{K_I e^{\alpha_1 \Phi I_1}}{1 + K_I \lambda^{-0.5} A_1 e^{\alpha_1 \Phi I_1} (1 + e^{-\Phi I_1})}$$

$$\Psi II_1 = \frac{\lambda^{-0.5} K_{II} e^{\alpha_2 \Phi II_1}}{1 + \frac{K_{II} A_1}{z^{0.5}} e^{\alpha_2 \Phi II_1} (1 + e^{-\Phi II_1})} \cdot \Psi I_1 \cdot A_1$$

$$\phi_j^I = \frac{K_I e^{-\alpha_1 \phi_j^I} \left[ 1 - \frac{1 + e^{-\phi_j^I}}{\lambda^{0.5}} \sum_{i=1}^{j-1} (\phi_i^I A_{j-i+1}) \right]}{1 + K_I \frac{1}{\lambda^{0.5}} A_1 e^{-\alpha_1 \phi_j^I} (1 + e^{-\phi_j^I})}$$

$$\phi_j^{II} = \frac{K_{II} \frac{1}{\lambda^{0.5}} e^{-\alpha_2 \phi_j^{II}} \sum_{i=1}^j (\phi_i^I A_{j-i+1}) - \frac{1}{(\lambda^{0.5})} K_{II} e^{-\phi_j^{II} \alpha_2} \sum_{i=1}^{j-1} (\phi_i^{II} B_{j-i+1}) - \frac{1}{(\lambda^{0.5})} K_{II} e^{-\phi_j^{II} (1-\alpha_2)} \sum_{i=1}^{j-1} (\phi_i^{II} B_{j-i+1})}{1 + \frac{1}{(\lambda^{0.5})} K_{II} e^{-\phi_j^{II} \alpha_2} + \frac{1}{(\lambda^{0.5})} K_{II} e^{-\phi_j^{II} (1-\alpha_2)}}$$

$$p = 1, 2 \frac{\Delta E_I}{\Delta E} - 1$$

serial number of potential step

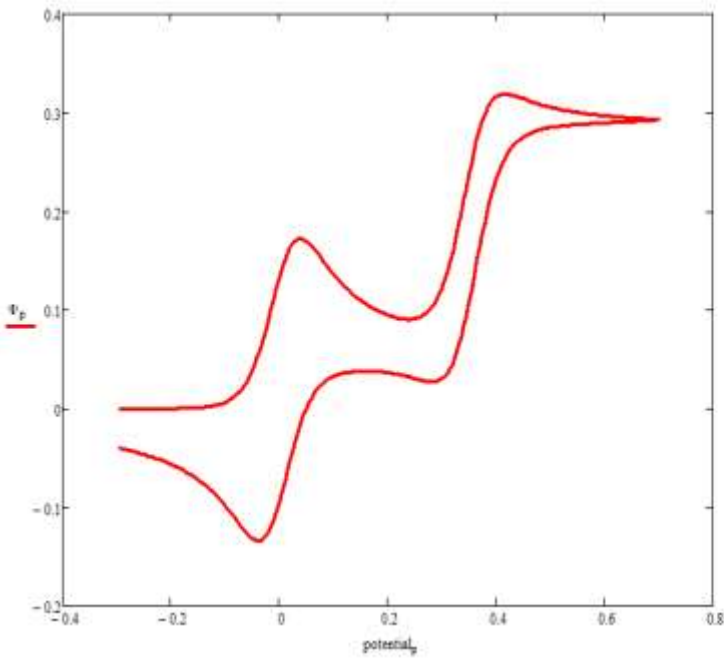
$$\psi_p^I = \psi_1^I \left( \frac{\tau}{4.25 + p} \right)^{2.5}$$

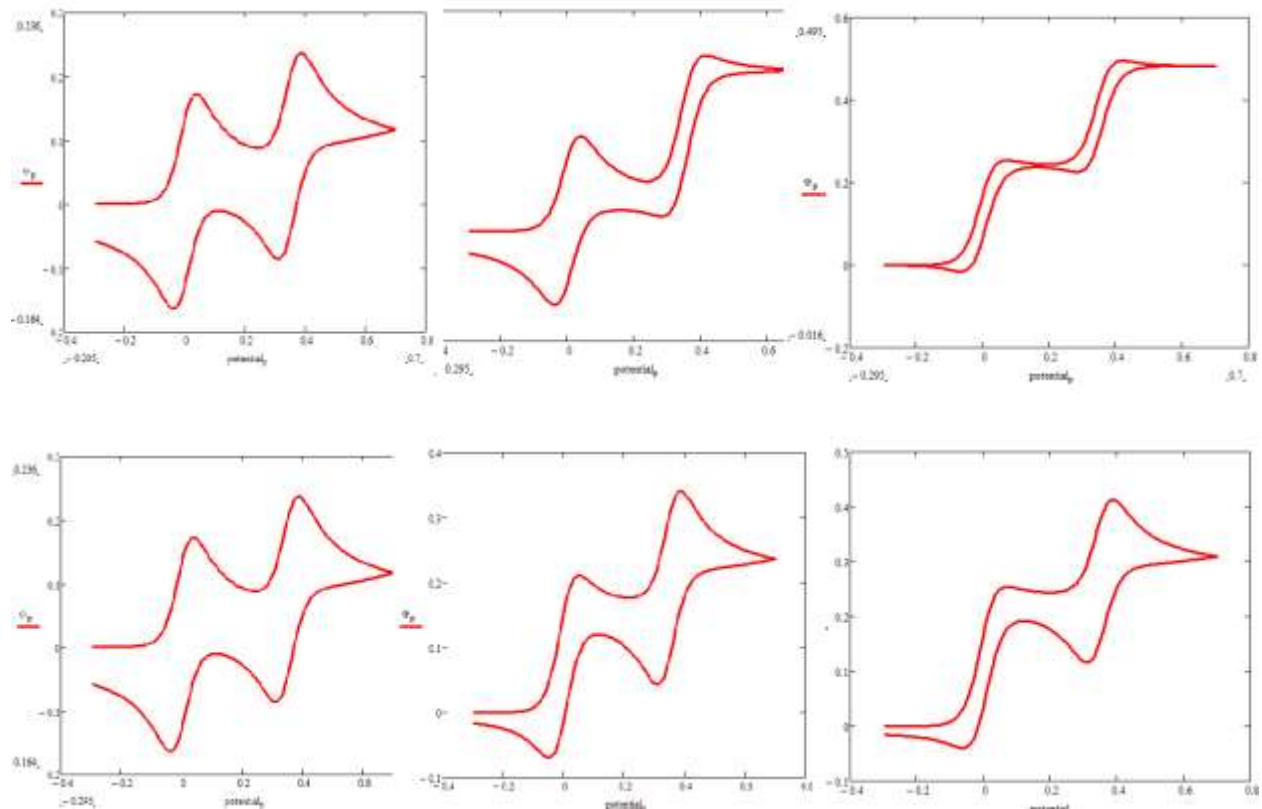
dimensionless current at the end of each potential step of first electrode reaction  $\psi^I$  and of second electrode reaction  $\psi^{II}$   
 $\psi_p$  is symbol the cumulative current measured as final output

$$\psi_p^{II} = \psi_1^{II} \left( \frac{\tau}{4.25 + p} \right)^{2.5}$$

$$\psi_p = \psi_p^I + \psi_p^{II}$$

$$\text{potential}_p = E \left[ p \leq \frac{\Delta E_I}{\Delta E} E_{s1} + p \Delta E, E_{s1} - \left( p - \frac{\Delta E_I}{\Delta E} \right) \Delta E \right] \quad \text{potential value of each potential step in V}$$





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