# Electrochemical-Catalytic Mechanism Can Reveal Two-Step Mechanism of Redox Systems with Inverted Potentials in Square-Wave Voltammetry

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**Abstract**

Many electrochemical processes of important systems (enzymes, redox proteins etc.) under physiological conditions occur in two successive electron transfer steps. If the energy of second electron tansfer is lower than that of the first electron transfer step, then both processes appear in a single voltammetric peak. By modeling two-step diffusional mechanism coupled with regenerative chemical reaction to the product of second electron transfer one gets so-called EEC' (or EECat) mechanism. By making analysis associated with an increase of the kinetics of the regenerative chemical step, one obtains shift of the potential of the net-peak of second electron transfer step towards more negative potentials. At large rates of chemical regenerative reaction, one gets separation of both electron transfer steps that appear in two distinct peaks, separated by more than 100 mV. This is the frist time to explore the features of EEC' mechanism to separate and distinguish between systems with inverted redox potentials in SWV.

TWO STEP DIFFUSIONAL EEC'cat Mechanism in SWV---Dec 2023

$EsI := 0.35$ $\Delta E := 1$ $dE := 0.01$ $Esw := 0.05$ $EsII := 0.65$ $r := 1..1$

$n := 1$ $F := 96500$ $R := 8.314$ $T := 298.15$ $KI_r := 10^{.75\cdot r}$

$KII := 10^{.75}$

$j := 1..\frac{\Delta E}{dE}\cdot 50$

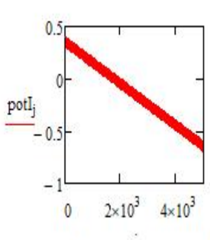
$\alpha 2 := 0.5$

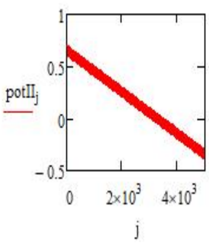
$\alpha 1 := 0.5$ $\log(KI_r) = 0.75$

$KI_1 = 5.623$

$$potI_j := EsI + Esw - \left[\left(\mathrm{ceil}\left(\frac{j}{25}-\frac{1}{2}\right)\cdot dE + \mathrm{if}\left(\frac{\mathrm{ceil}\left(\frac{j}{25}\right)}{2} = \mathrm{ceil}\left(\frac{j}{25}-\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - dE\right]$$

$$potII_j := EsII + Esw - \left[\left(\mathrm{ceil}\left(\frac{j}{25}-\frac{1}{2}\right)\cdot dE + \mathrm{if}\left(\frac{\mathrm{ceil}\left(\frac{j}{25}\right)}{2} = \mathrm{ceil}\left(\frac{j}{25}-\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - dE\right]$$




$$M1_j := \sqrt{\frac{j}{1}} - \sqrt{\frac{j-1}{1}}$$

$z := 1.000000500$

$$B_j := \left(1 - \mathrm{erfc}\left(\sqrt{\frac{z}{50\times 1}}\cdot j\right)\right) - \left[1 - \mathrm{erfc}\left[\sqrt{\frac{z}{50\times 1}}\cdot(j-1)\right]\right]$$

z e kataliticki parametar vo ovoj model povrzan so hemiska regeneracija na reaktant od vtor elektrohemiski cekor

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

$x := 0.001$

$$\Psi I_{1,r} := \frac{KI_r\cdot e^{-\alpha 1\cdot\Phi I_1}}{1 + KI_r\cdot\frac{2}{\sqrt{\pi\cdot 50}}\cdot M1_1\cdot e^{-\alpha 1\cdot\Phi I_1} + KI_r\cdot\frac{2}{\sqrt{\pi\cdot 50}}\cdot e^{\Phi I_1\cdot(1-\alpha 1)}\cdot M1_1}$$

$$\Psi II_{1,r} := \frac{KII\cdot\frac{2}{\sqrt{\pi\cdot 50}}\cdot e^{-\alpha 2\cdot\Phi II_1}\cdot\Psi I_{1,r}\cdot M1_1}{1 + \frac{1\cdot B_1}{(\sqrt{z})}KII\cdot e^{1\cdot\Phi II_1\cdot(-\alpha 2)} + \frac{1\cdot B_1}{(\sqrt{z})}KII\cdot e^{1\cdot\Phi II_1\cdot(1-\alpha 2)}}$$

$$\Psi I_{j,r} := \frac{KI_r \cdot e^{-\alpha 1 \cdot \Phi I_j} - KI_r \cdot \frac{2}{\sqrt{\pi \cdot 50}} \cdot e^{-\alpha 1 \cdot \Phi I_j} \cdot \sum_{i=1}^{j-1} \left(\Psi I_{i,r} \cdot M1_{j-i+1}\right) - KI_r \cdot \frac{2}{\sqrt{\pi \cdot 50}} \cdot e^{\Phi I_j \cdot (1-\alpha 1)} \cdot \sum_{i=1}^{j-1} \left(\Psi I_{i,r} \cdot M1_{j-i+1}\right)}{1 + KI_r \cdot \frac{2}{\sqrt{\pi \cdot 50}} \cdot M1_1 \cdot e^{-\alpha 1 \cdot \Phi I_j} + KI_r \cdot \frac{2}{\sqrt{\pi \cdot 50}} \cdot e^{\Phi I_j \cdot (1-\alpha 1)} \cdot M1_1}$$

$$\Psi II_{j,r} := \frac{KII \frac{2}{\sqrt{\pi \cdot 50}} \cdot e^{-\alpha 2 \cdot \Phi II_j} \cdot \sum_{i=1}^{j} \left(\Psi I_{i,r} \cdot M1_{j-i+1}\right) - \frac{1}{\left(\sqrt{z}\right)} KII \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot B_{j-i+1}\right) - \frac{1}{\left(\sqrt{z}\right)} KII \cdot e^{1 \cdot \Phi II_j \cdot (1-\alpha 2)} \cdot \sum_{i=1}^{j-1} \left(\Psi II_{i,r} \cdot B_{j-i+1}\right)}{1 + \frac{1 \cdot B_1}{\left(\sqrt{z}\right)} KII \cdot e^{1 \cdot \Phi II_j \cdot (-\alpha 2)} + \frac{1 \cdot B_1}{\left(\sqrt{z}\right)} KII \cdot e^{1 \cdot \Phi II_j \cdot (1-\alpha 2)}}$$

$\Psi_{j,r} := \Psi I_{j,r} + \Psi II_{j,r}$

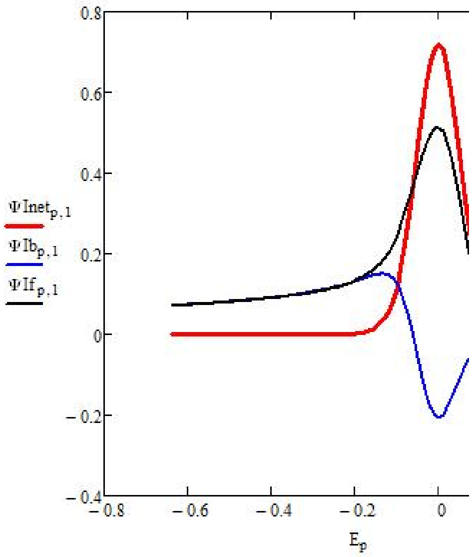
$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$

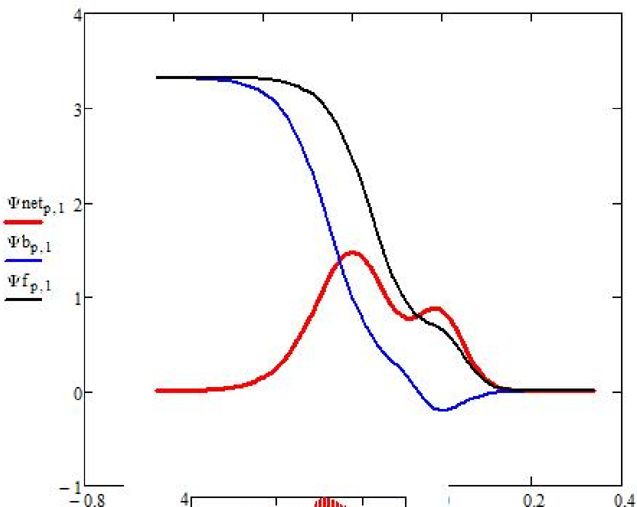
$\Psi If_{p,r} := \Psi I_{(p+1)\cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50\cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

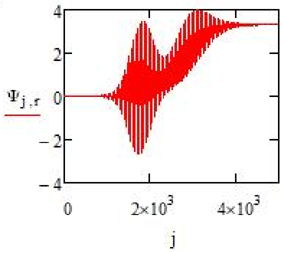
$\Psi IIb_{p,r} := \Psi II_{50\cdot p+25,1}$ $\Psi IIf_{p,r} := \Psi II_{(p+1)}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

$E_p := EsI - p \cdot dE$

$\Psi b_{p,r} := \Psi_{50\cdot p+25,r}$ $\Psi f_{p,r} := \Psi_{(p+1)\cdot 5(}$ $\Psi net_{p,r} := \Psi f_{p,r} - \Psi b_{p,r}$

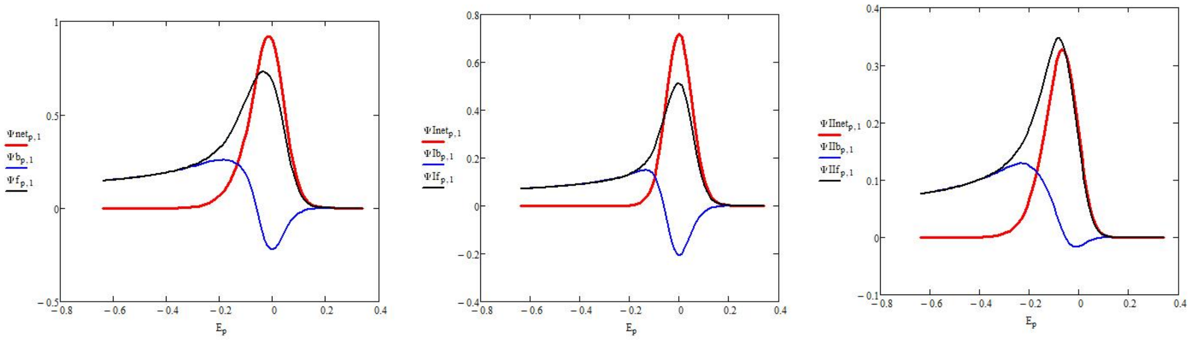


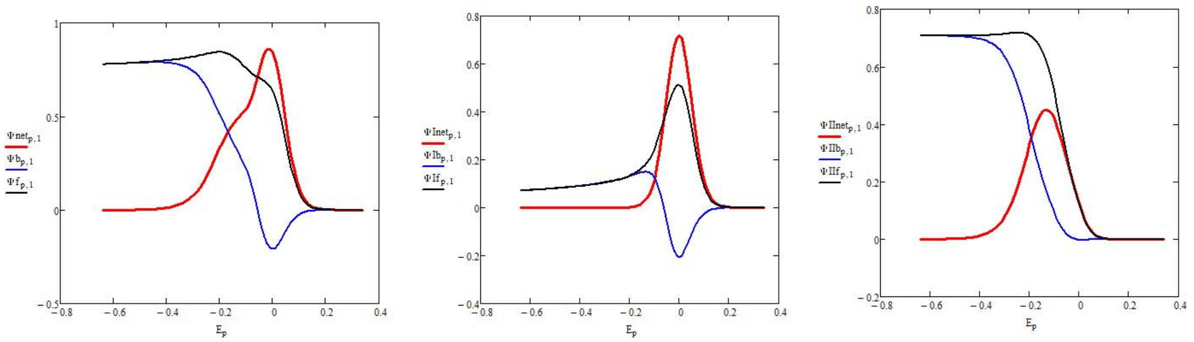




| $\Psi f_{p,1} =$ | $\Psi b_{p,1} =$ |
|---|---|
| $9.208\cdot 10^{-6}$ | $-1.879\cdot 10^{-6}$ |
| $1.322\cdot 10^{-5}$ | $-3.312\cdot 10^{-6}$ |
| $1.931\cdot 10^{-5}$ | $-5.158\cdot 10^{-6}$ |
| $2.836\cdot 10^{-5}$ | $-7.781\cdot 10^{-6}$ |
| $4.176\cdot 10^{-5}$ | $-1.16\cdot 10^{-5}$ |
| $6.156\cdot 10^{-5}$ | $-1.721\cdot 10^{-5}$ |
| $9.081\cdot 10^{-5}$ | $-2.546\cdot 10^{-5}$ |
| | $-3.762\cdot 10^{-5}$ |

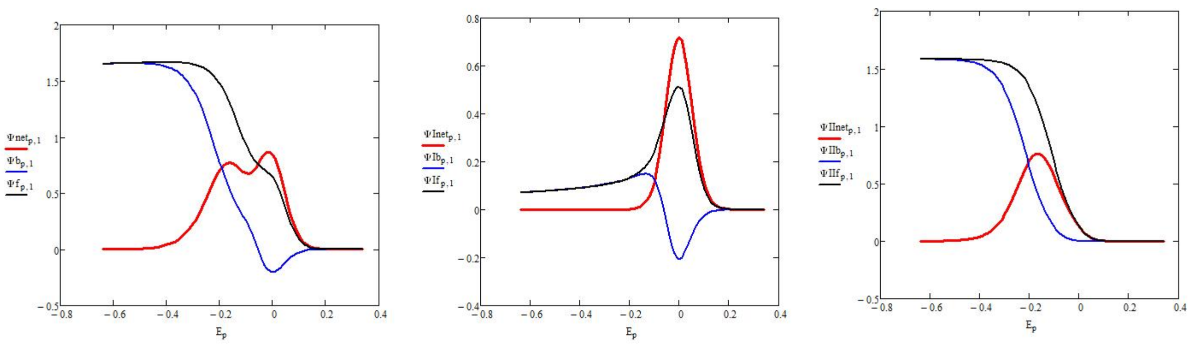
Kcatalytc is very small (0.0001)-both peaks appear at same potential



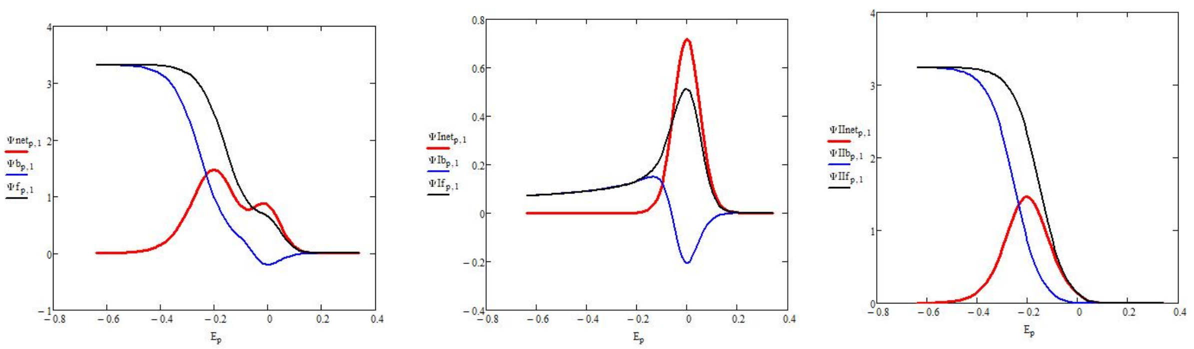

Kcatalytic is 0.5-small differences are observed, 2[nd] peak shifts towards more negative potentials




Kcatalytic is 2.5




Kcatalytic is 10-two distinct NET PEAKS appear



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