Square-wave Theory of Two-Step Surface Electrode Mechanism Associated with Intermediate Irreversible Regenerative Chemical Reaction-Surface ECatE mechanism

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SURCACE ECatE in SWV

Model for two-step surface electrode mechanism associated with intermediate regenerative step

$EsI := 0.15 \quad \Delta E := 0.8 \quad dE := 0.004 \quad Esw := 0.05 \quad EsII := 0.45$

$n := 2 \quad F := 96500 \quad R := 8.314 \quad T := 298.15 \quad \alpha := 0.5$

$k := 1..1 \quad ks1 := 1 \quad ks2 := 10.1000001$

$f := 10$

$KI := \frac{ks1}{f}$

$K := .4315097954321100000011$

K e konstanta na brzina na regenerativna reakcija

$KII := \frac{ks2}{f}$

$\lambda := \frac{K}{f}$

ks [s-1]
K [s-1]

λ e hemiski parametar

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

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

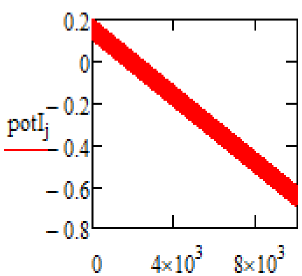
$$potII_j := EsII + Esw - \left[\left(ceil\left(\frac{j}{25} - \frac{1}{2}\right) \cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25} - \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw\right) - dE\right]$$

Mechanism

Ox(ads) + 1e- = Red1(ads) + Y = Ox(ads)

+1e-

Red2(ads)



$$M_j := e^{-\lambda \cdot \frac{j}{50}} - e^{-\lambda \cdot \frac{j+1}{50}}$$

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

$x := 0.001$

$$M_1 = 8.619 \times 10^{-4}$$

$$\Psi I_1 := \frac{KI \cdot e^{-\alpha \cdot \Phi I_1}}{1 + \frac{KI \cdot \lambda^{-1} \cdot M_1}{1} \cdot e^{-\alpha \cdot \Phi I_1} + \frac{KI}{1} \lambda^{-1} \cdot e^{\Phi I_1 \cdot (1-\alpha)} \cdot M_1}$$

$$\Psi I_1 = 7.156 \times 10^{-6}$$

$$M_2 = 8.612 \times 10^{-4}$$

$$\Psi II_1 := \frac{\left(\Psi I_1 \cdot \frac{KII}{1} \cdot e^{-\alpha \cdot \Phi II_1}\right) - KII \cdot \frac{1}{1} \cdot e^{(1-\alpha) \cdot \Phi II_1} \cdot \Psi I_1 \cdot 1}{1 + \frac{KII \cdot e^{-\alpha \cdot \Phi II_1} \cdot 1}{1 \cdot 1} \cdot \left(1 + e^{\Phi II_1}\right)}$$

$$\Psi II_1 = -7.156 \times 10^{-6}$$

$$x := 0.001$$

$$\Psi I_j := \frac{\frac{KI}{1} \cdot e^{-\alpha \cdot \Phi I_j} - \frac{KI \cdot \lambda^{-1}}{1} \cdot e^{-\alpha \cdot \Phi I_j} \cdot \sum_{i=1}^{j-1} \left(\Psi I_i \cdot M_j\right) - \frac{KI}{1} \lambda^{-1} \cdot e^{\Phi I_j \cdot (1-\alpha)} \cdot \sum_{i=1}^{j-1} \left(\Psi I_i \cdot M_j\right)}{1 + \frac{KI \cdot \lambda^{-1} \cdot M_1}{1} \cdot e^{-\alpha \cdot \Phi I_j} + 1\lambda^{-1} \cdot e^{\Phi I_j \cdot (1-\alpha)} \cdot M_1}$$

$$\Psi II_j := \frac{\frac{KII \cdot 1}{1} \cdot e^{-\alpha \cdot \Phi II_j} \cdot \sum_{i=1}^{j} \Psi I_i - KII1 \cdot e^{-\alpha \cdot \Phi II_j} \cdot \sum_{i=1}^{j-1} \left(\Psi II_i \cdot 1\right) - \frac{KII \cdot 1}{1} \cdot e^{(1-\alpha) \cdot \Phi II_j} \cdot (1) \cdot \sum_{i=1}^{j-1} \Psi II_i}{50 + \frac{KII \cdot 1}{1} \cdot e^{-\alpha \cdot \Phi II_j} \cdot \left(1 + e^{\Phi II_j}\right)}$$

$$z := 2$$

$$\phi I_j := z \cdot \frac{F}{R \cdot T} \cdot potI_j$$

$$II_1 := \frac{KI \cdot e^{-\alpha \cdot \phi I_1}}{1 + \frac{KI \cdot e^{-\alpha \cdot \phi I_1} \cdot \left(1 + e^{\phi I_1}\right)}{50}}$$

$$II_j := \frac{KI \cdot e^{-\alpha \cdot \phi I_j} - KI \cdot e^{-\alpha \cdot \phi I_j} \cdot \frac{\left(1 + e^{\phi I_j}\right)}{50} \cdot \sum_{i=1}^{j-1} II_i}{1 + \frac{KI \cdot e^{-\alpha \cdot \phi I_j} \cdot \left(1 + e^{\phi I_j}\right)}{50}}$$

These are formula for
Simple one-step surface
E-mechanism Ox(ads)→Red(ads)

$$\Psi_j := \Psi I_j + \Psi II_j$$

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

$$\Psi If_p := \Psi I_{(p+1) \cdot 50} \qquad \Psi Ib_p := \Psi I_{50 \cdot p + 25} \qquad \Psi Inet_p := \Psi If_p - \Psi Ib_p$$

$$IIf_p := II_{(p+1) \cdot 50}$$

$$IIb_p := II_{50 \cdot p + 25}$$

$$\Psi IIb_p := \Psi II_{50 \cdot p + 25} \qquad \Psi IIf_p := \Psi II_{(p+1) \cdot 50} \qquad \Psi IInet_p := \Psi IIf_p - \Psi IIb_p$$

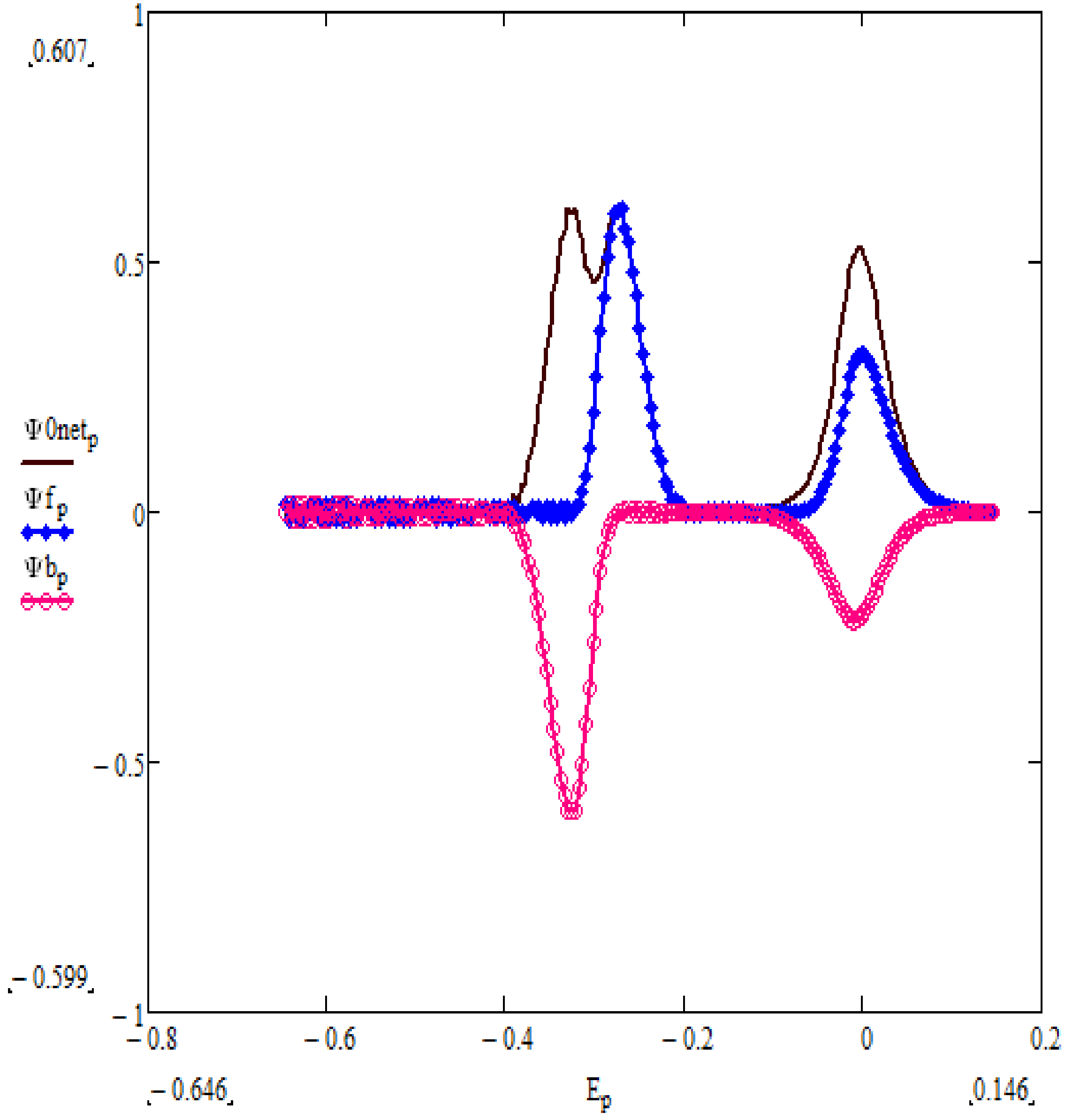
$$IInet_p := IIf_p - IIb_p$$

$$\Psi f_p := \Psi If_p + \Psi IIf_p$$

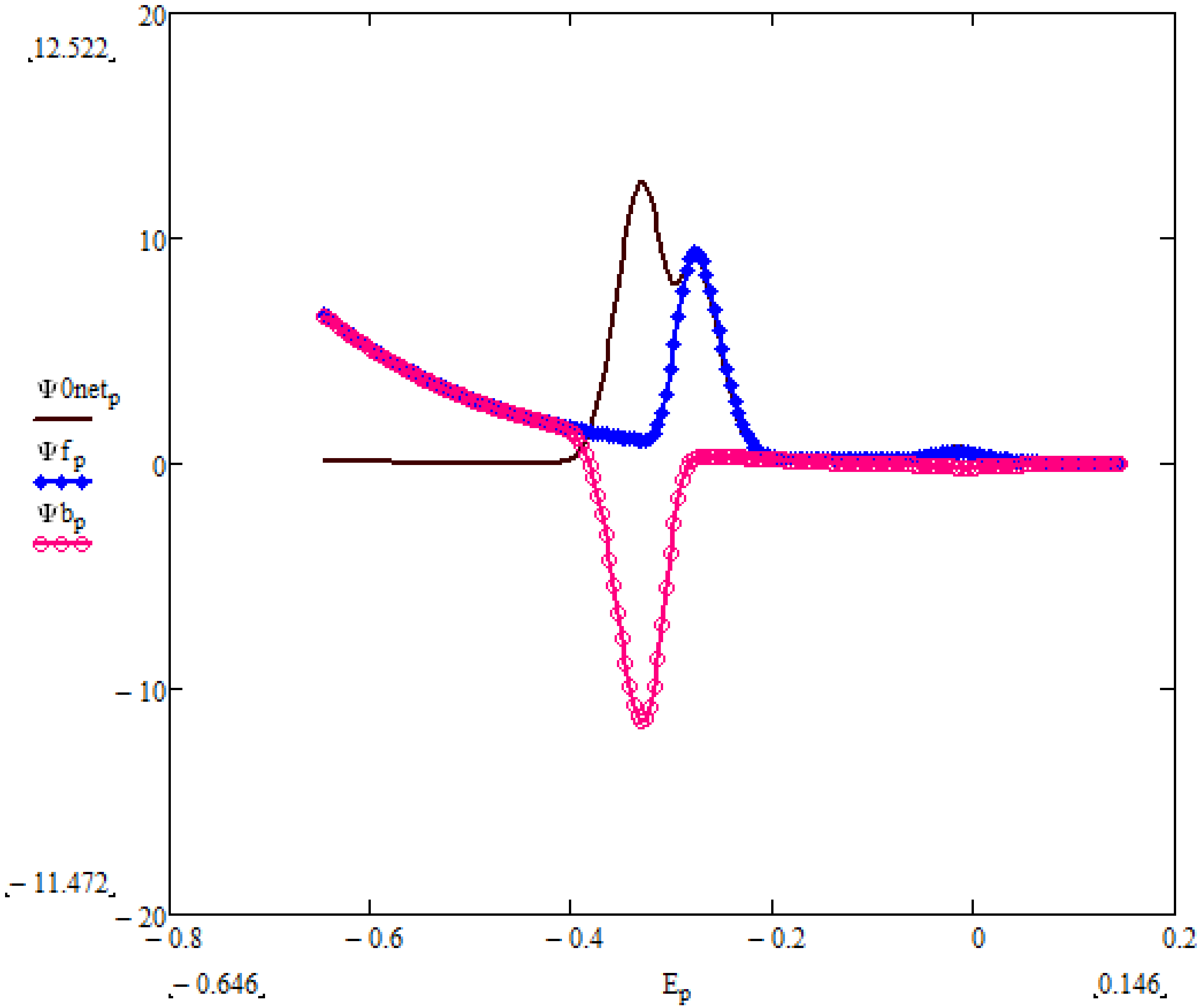
$$E_p := EsI - p \cdot dE \qquad \Psi b_p := \Psi Ib_p + \Psi IIb_p \qquad \Psi net_p := \Psi f_p - \Psi b_p$$

$$\Psi 0net_p := \Psi Inet_p + \Psi IInet_p$$

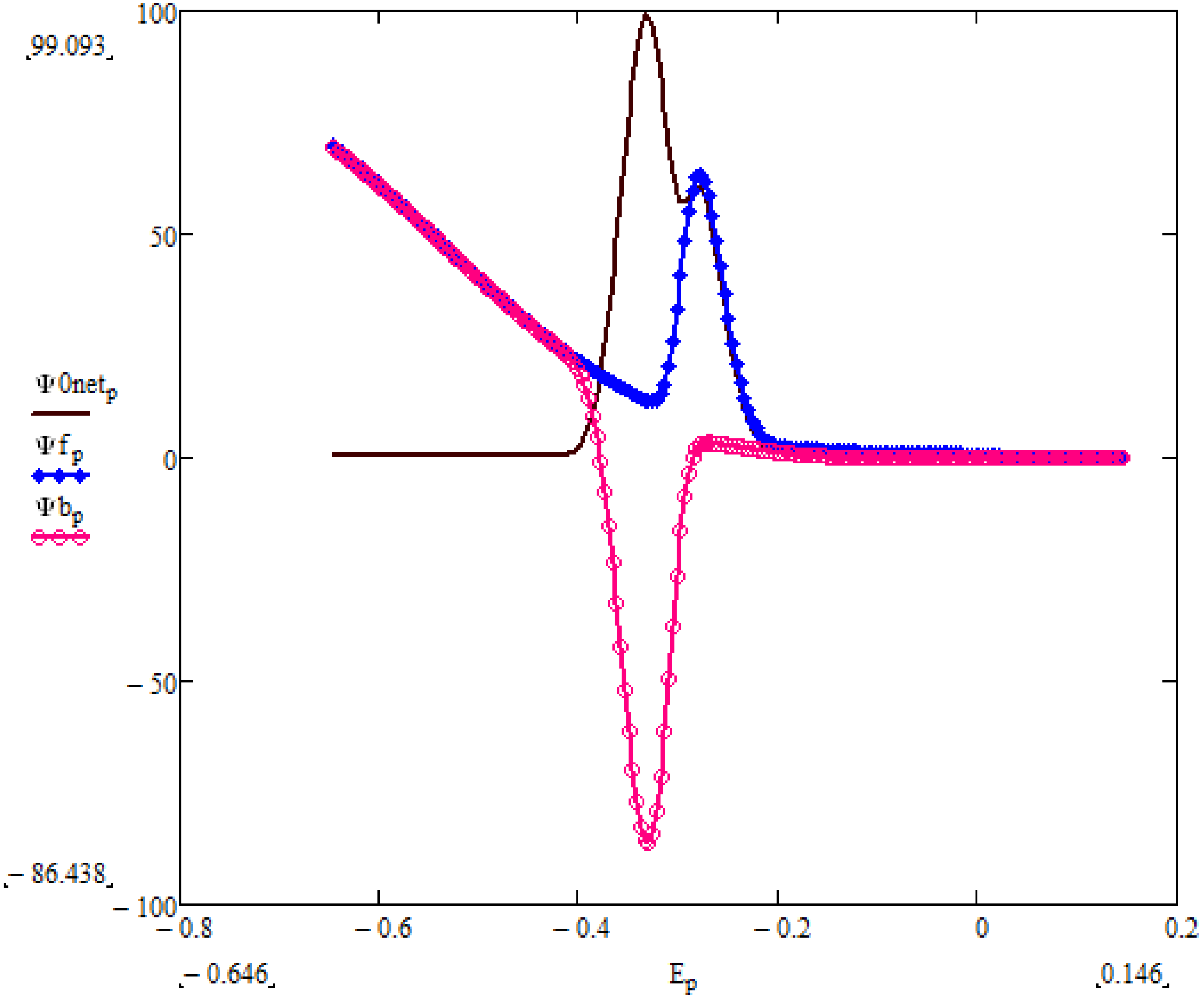
0.6



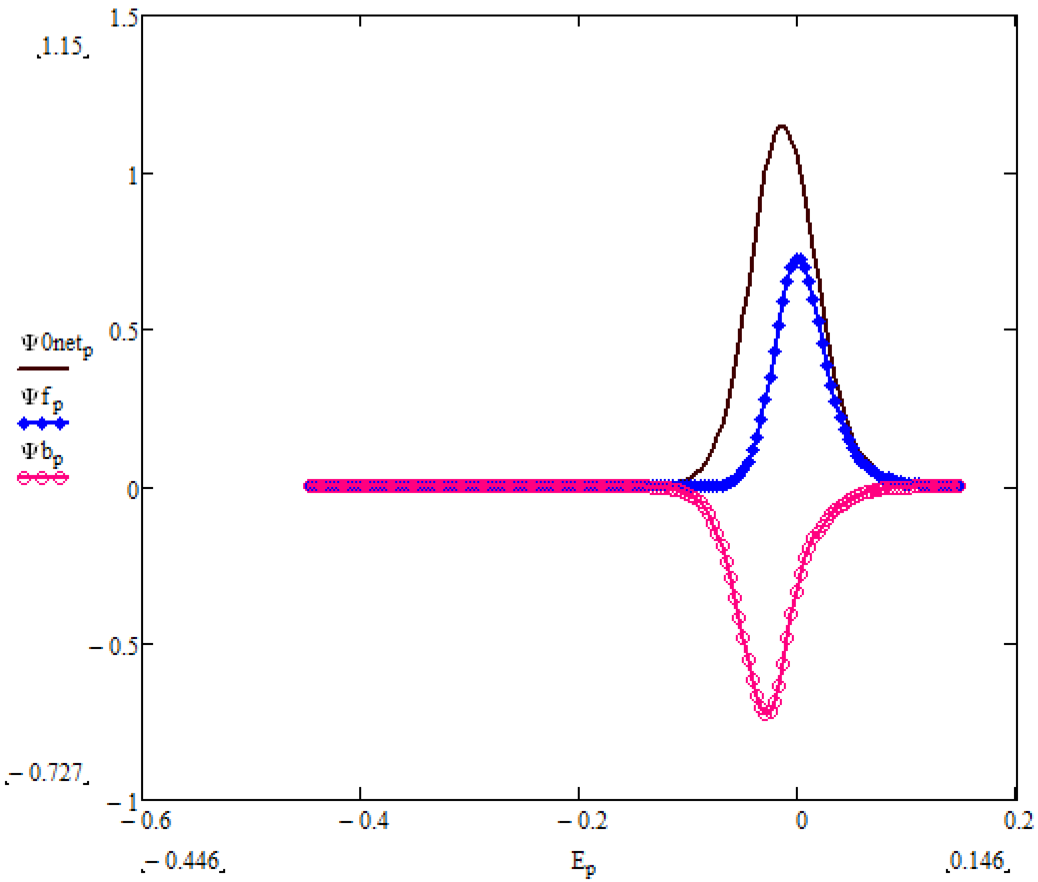
No regenerative reaction
Mechanism
Behaves
As
Surface E-E mechanism



Rate of Regenerative Reaction Increases

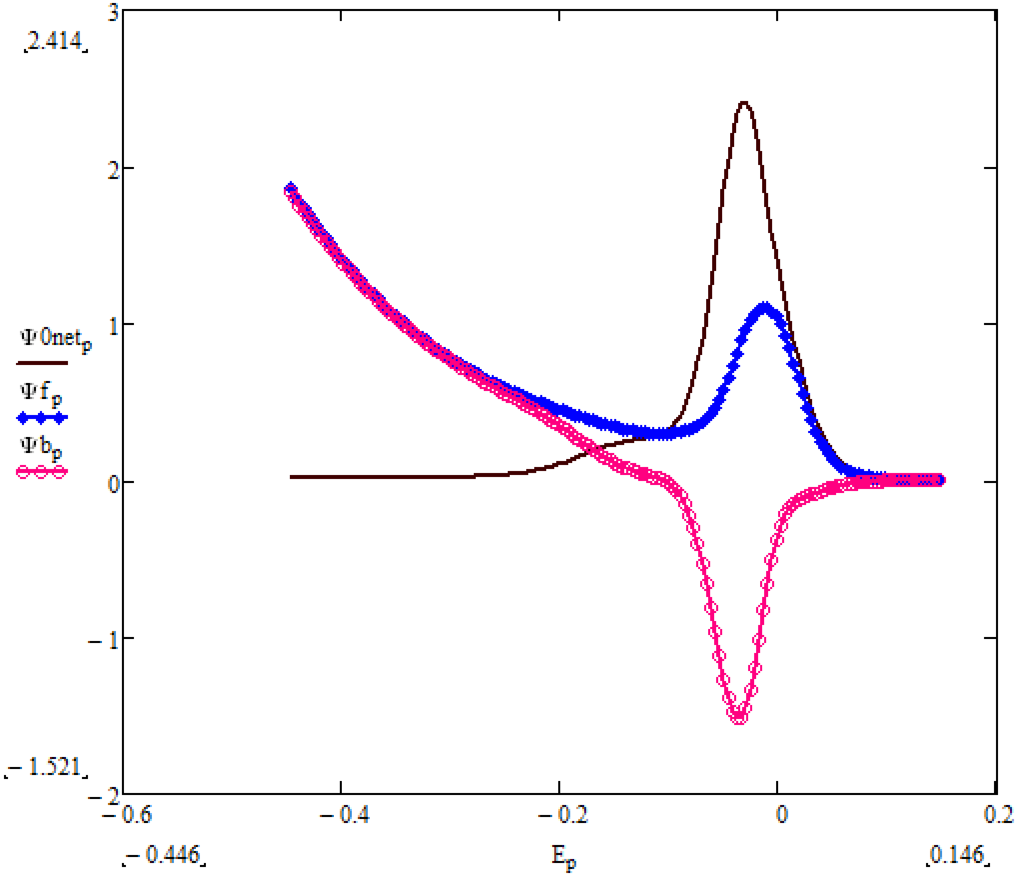


High Rate of Regenerative Reaction

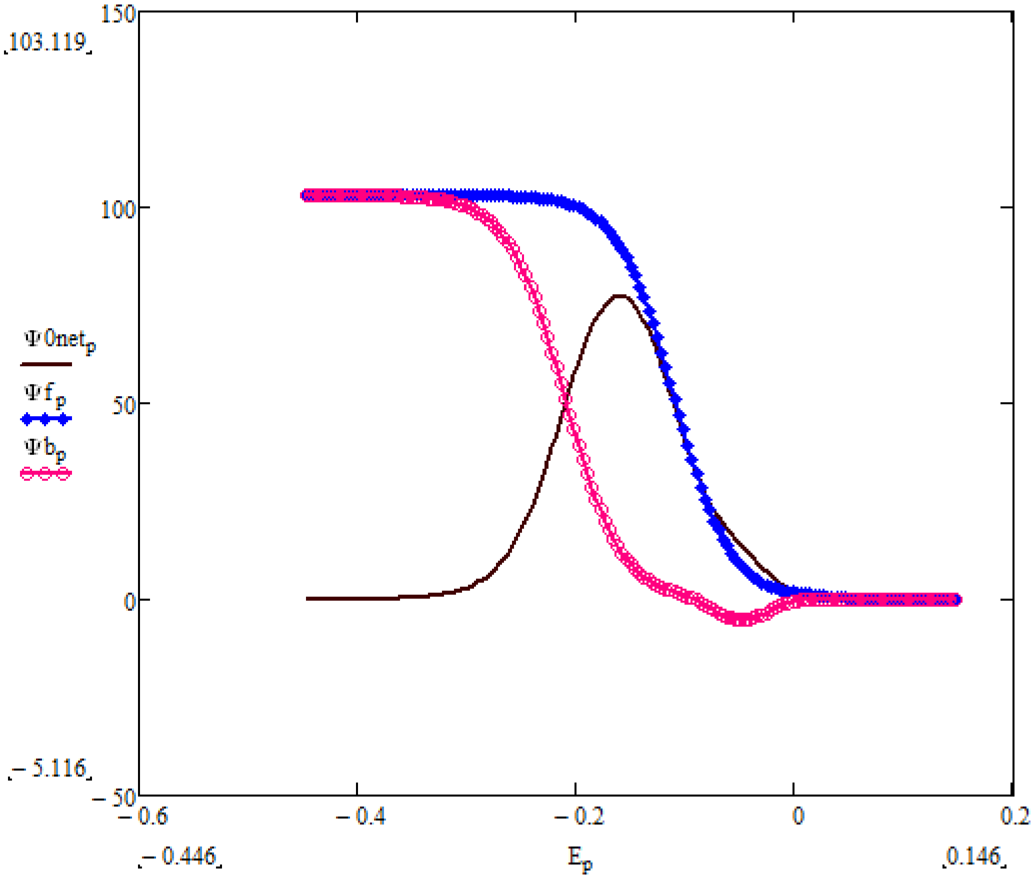


Scenario with both Electrode Steps taking place at Very Same potential (one peak portrays both EE processes)

A. No regenerative reaction



A. Moderate rate of Regenerative Chemical Reaction



C. High rate of Regenerative Chemical Rection

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