Supplementary Material:

MATHCAD FILE for a SURFACE CEC' MECHANISM in Square-Wave Voltammetry

Related to Work: **Theoretical Aspects of a Surface Electrode Reaction Coupled with Preceding and Regenerative Chemical Steps: Square-wave Voltammetry of a Surface CEC' Mechanism**

Electroanalysis 2019, **doi.org/10.1002/elan.201900491**

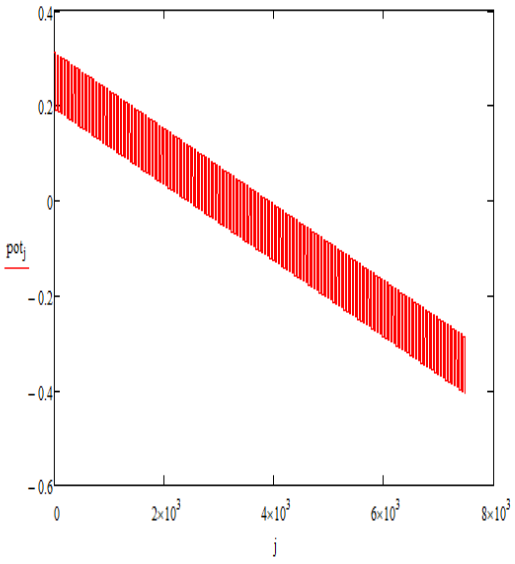
$Es := 0.25 \quad \Delta E := 0.6 \quad dE := 0.004 \quad Esw := 0.06$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15$

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

$\alpha := 0.5$

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



$r := 1..1 \quad f := 10 \quad Kcatalytic := 1.0$

$ks := 50$

$kf := 50$

$kb := 50 \quad z := kf + kb$

$K := \frac{ks}{f} \quad Keq := 10^{-2}$

$K = 5$

$z := 10^2$

$\varepsilon := \frac{z}{f}$

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

k_s is a standard rate constant of electron transfer
K is the dimensionless electrode kinetic parameter
kf is rate constant of forward step of preceding chemical reaction
kb is rate constant of backward step of preceding chemical reaction
z is chemical rate parameter of preceding chemical reaction
ε is dimensionless chemical rate parameter of preceding chemical reaction
Keq is equilibrium constant of preceding chemical reaction
Kcatalytic is dimensionless catalytic parameter
k is integration parameter
S_k and **M_k** are numerical integration factor
Φ is dimensionless potential
Ψ is dimensionless current
Es is starting potential

$S_k := e^{\frac{\varepsilon}{50} \cdot (-k)} - e^{\frac{\varepsilon}{50} \cdot (-k+1)}$

$M_k := e^{-\frac{Kcatalytic}{50} \cdot (k-1)} - e^{-\frac{Kcatalytic}{50} \cdot (k)}$

$\Phi_j := n \cdot \frac{F}{R \cdot T} \cdot pot_j$

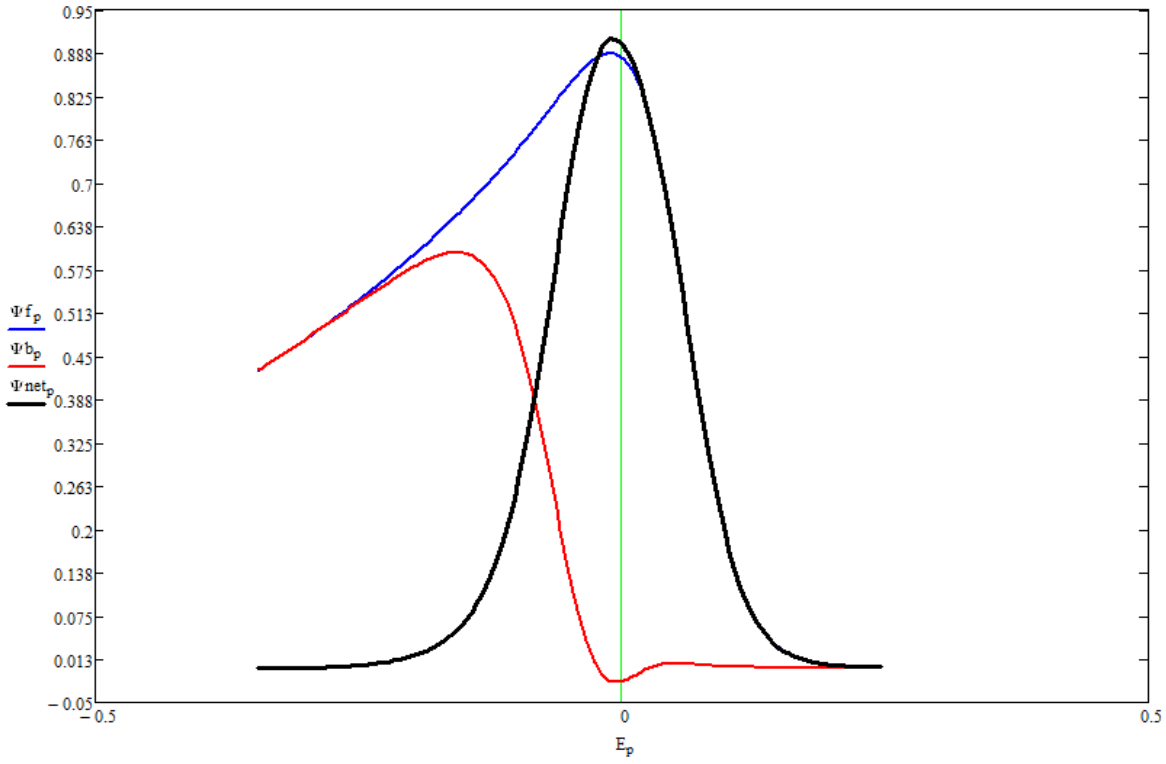
$$\Psi_1 := \frac{\frac{K \cdot e^{-\alpha \cdot \Phi_1}}{1+Keq} \cdot Keq \cdot \left(1 - \frac{1}{50} \cdot 0\right) - (\varepsilon)^{-1} \cdot Keq \cdot \left(\frac{1}{1+Keq}\right) \cdot (-1) \cdot e^{-\alpha \cdot \Phi_1} \cdot 0 + K \cdot e^{-\alpha \cdot \Phi_1} \cdot \left(1 - \frac{1+e^{\Phi_1}}{Kcatalytic} \cdot 0\right)}{\frac{K \cdot e^{-\alpha \cdot \Phi_1}}{(1+Keq)} \cdot Keq \cdot \frac{1}{50} + 1 + (\varepsilon)^{-1} \cdot K \cdot (-1) \cdot \left(\frac{1}{1+Keq}\right) \cdot S_1 \cdot e^{-\alpha \cdot \Phi_1} + \frac{K}{50} \cdot e^{\Phi_1 \cdot (1-\alpha)} + K \cdot e^{-\alpha \cdot \Phi_1} \cdot \left(1 + e^{\Phi_1}\right) \cdot \frac{M_1}{Kcatalytic} + 1}$$

$$\Psi_k := \frac{\frac{K \cdot e^{-\alpha \cdot \Phi_k}}{1+Keq} \cdot Keq \cdot \left(1 - \frac{1}{50} \cdot \sum_{j=1}^{k-1} \Psi_j\right) - (\varepsilon)^{-1} \cdot \frac{K}{Kcatalytic} \cdot \left(\frac{1}{1+Keq}\right) \cdot (-1) \cdot e^{-\alpha \cdot \Phi_k} \cdot \sum_{j=1}^{k-1} \left(\Psi_j \cdot S_{k-j+1}\right) + K \cdot e^{-\alpha \cdot \Phi_k} \cdot \left[1 - \frac{1+e^{\Phi_k}}{Kcatalytic} \cdot \sum_{j=1}^{k-1} \left(\Psi_j \cdot M_{k-j+1}\right)\right]}{\frac{K \cdot e^{-\alpha \cdot \Phi_k}}{(1+Keq)} \cdot Keq \cdot \frac{1}{50} + 1 + (\varepsilon)^{-1} \cdot \frac{K}{Kcatalytic} \cdot (-1) \cdot \left(\frac{1}{1+Keq}\right) \cdot S_1 \cdot e^{-\alpha \cdot \Phi_k} + \frac{K}{50} \cdot e^{\Phi_k \cdot (1-\alpha)} + K \cdot e^{-\alpha \cdot \Phi_k} \cdot \left(1 + e^{\Phi_k}\right) \cdot \frac{M_1}{Kcatalytic} + 1}$$

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

$\Psi f_p := \Psi_{(p+1)\cdot 50}$ $\Psi b_p := \Psi_{50\cdot p+25}$ $\Psi net_p := \Psi f_p - \Psi b_p$

$E_p := Es - p \cdot dE$



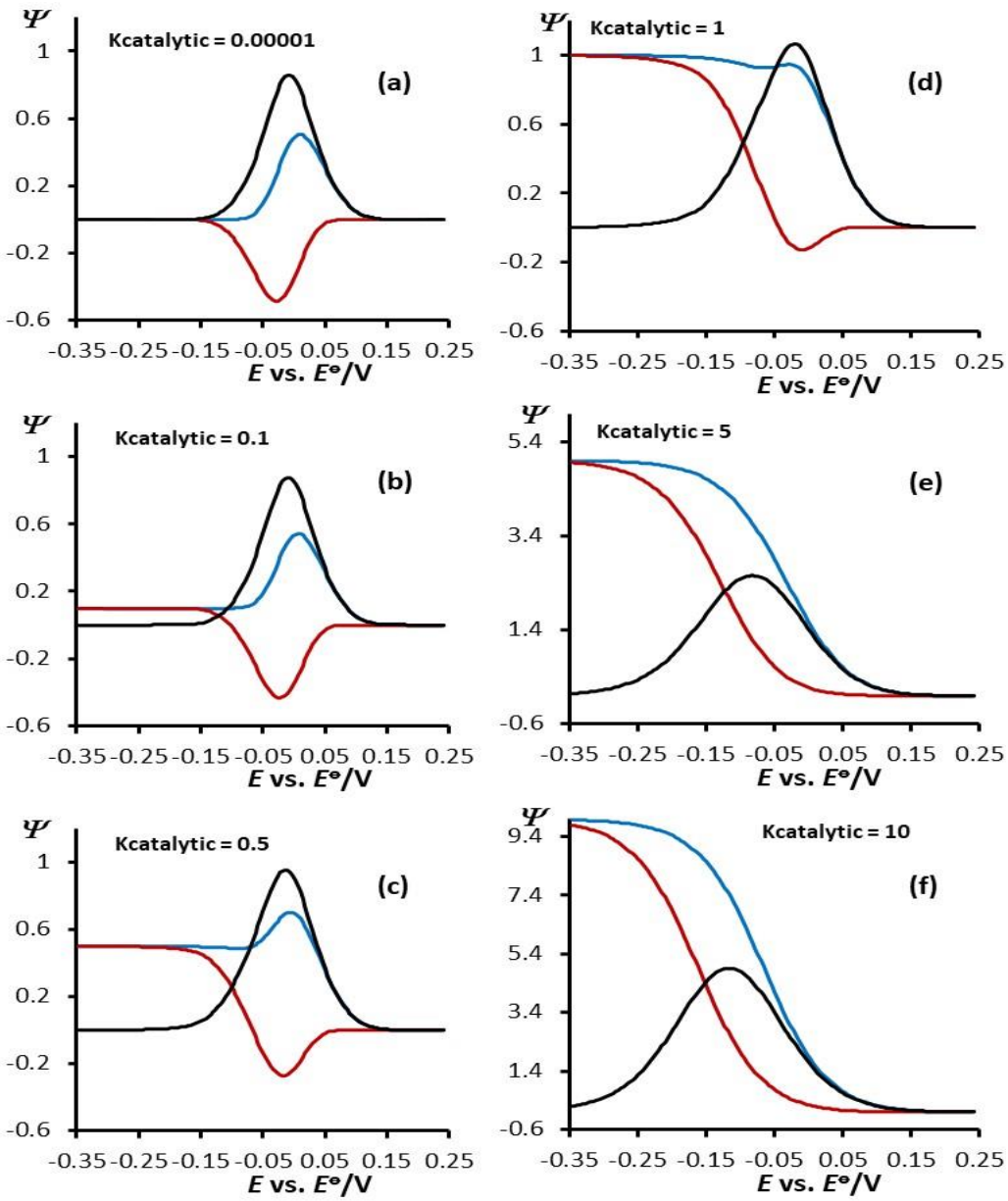


Figure S1: Surface CEC' mechanism: s*cenario with large value of equilibrium constant of preceding chemical reaction*: Square-wave voltammograms of a surface CEC' mechanism showing the effect of rate of catalytic reaction to the features of calculated voltammetric patterns. The simulations are performed under following conditions: dimensionless electrode kinetic parameter $K = 1$ ($k_s = 10\ s^{-1}$; $f = 10$ Hz), equilibrium constant of preceding chemical reaction $K\mathrm{eq} = 1000$, dimensionless rate parameter of preceding chemical reaction $\varepsilon = 1000$, electron transfer coefficient $\alpha = 0.5$, number of electrons exchanged $n = 1$. The potential modulation parameters were set to: potential increment $dE = 4$ mV, and square-wave amplitude $E_{sw} = 60$ mV. The values of the dimensionless catalytic parameter $K_{catalytic}$ are given in the charts.

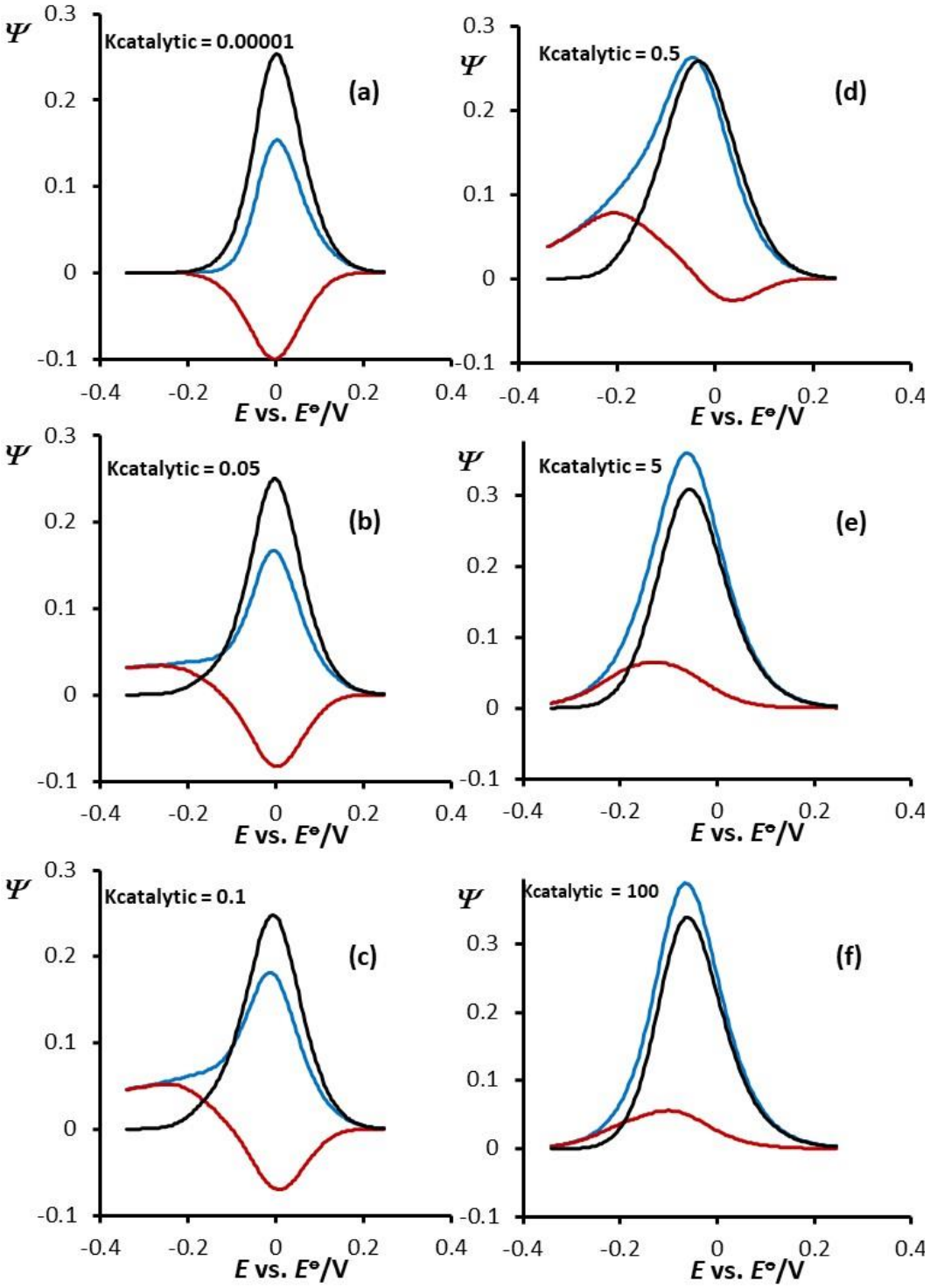


Figure S2. Surface CEC' mechanism: s*cenario with moderate value of equilibrium constant of preceding chemical reaction and moderate kinetics of preceding chemical reaction*: Square-wave voltammograms of a surface CEC' mechanism showing the effect of rate of catalytic reaction to the features of calculated voltammetric patterns. Voltammograms are calculated for $\boldsymbol{\varepsilon = 1}$. The values of the dimensionless catalytic parameter $K_{\text{catalytic}}$ are given in the charts. Other simulation parameters are same as in figure 1.

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