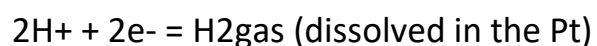


## Square-wave Voltammetry of Surface Electrode Mechanisms with Non-Unity Stoichiometry-Simulation Protocol in MATHCAD

Rubin Gulaboski

### Abstract

Many metal ions and other physiologically active systems undergo electrochemical transformation in a fashion that is different from 1:1 stoichiometry. Cu II ions, and H<sup>+</sup> ions, for example, are typical systems whose reduction happens in non-unity stoichiometry. As we know, reduction of H<sup>+</sup> ions at platinum electrode goes via redox scheme



We present in this simulation model for the first time simulation procedure of 2:1 stoichiometry under conditions of square-wave voltammetry. As expected, the peak potential of SWV voltammetric patterns of such systems is sensitive to analyte concentration, shifting for -59 mV in negative direction per decadic increase of  $c(\text{H}^+)$ . In addition, other SW voltammetric parameters are also affected by the analyte concentrations of 2:1 stoichiometric systems. This model is suitable for studying metal-ligand complexes of many transient metal ions, but also of many drugs that undergo direct 2 electron transformation, as the quinones in aqueous media, for example. A general explicit solution of all non-stoichiometry mechanisms for diffusional systems is published in recent work in *Journal of Electroanalytical Chemistry*. Here we present model only for 2:1 specific surface stoichiometry.

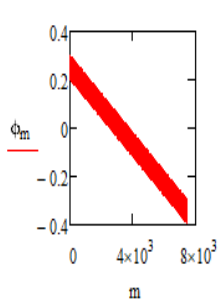
$$E_s := 0.25$$

$$\Delta E := 0.004 \quad E_{sw} := 0.05$$

$$m := 1 \cdot \frac{0.6}{\Delta E} \cdot 50$$

$$\text{relativenpot}_m := \left[ \left[ \text{ceil} \left( \frac{m}{25} \cdot \frac{1}{2} \right) \cdot \Delta E + \text{if} \left( \frac{\text{ceil} \left( \frac{m}{25} \right)}{2} = \text{ceil} \left( \frac{m}{25} \cdot \frac{1}{2} \right), 1, -1 \right) \cdot E_{sw} + E_{sw} \right] - \Delta E \right]$$

$$\phi_m := E_s + E_{sw} - \text{relativenpot}_m$$



$$\alpha := 0.5$$

$$F := 96500 \quad n := 2 \quad R := 8.314 \quad T := 273.15 \quad i := 1 \dots 1$$

$$\gamma_i := 10^{-5.0003+i \cdot 0} \quad \lambda_i := 10^{-0.25 \cdot i}$$

$$k := 1 \cdot \frac{0.6}{\Delta E} \cdot 50 \quad M_{k,i} := e^{-\frac{\gamma_i}{50} \cdot (k-1)} - e^{-\frac{\gamma_i}{50} \cdot (k)}$$

$$\log(\gamma_i) =$$

$$-5.0003$$

$$\log(\lambda_i) =$$

$$-0.25$$

$$\Phi_m := \frac{n \cdot F}{R \cdot T} \cdot \phi_m$$

$$I_{1,i} := \lambda_i \cdot e^{-\alpha \cdot \Phi_1} \left[ 1 + \lambda_i \cdot e^{-\alpha \cdot \Phi_1} \cdot (1 + e^{\Phi_1}) \cdot R^{-1} \right]^{-1}$$

$$I_{m,i} := \lambda_i \cdot e^{-\alpha \cdot \Phi_m} \left[ 1 - (1 + e^{\Phi_m}) \cdot R^{-1} \cdot \sum_{j=1}^{m-1} I_{j,i} \right] \cdot \left[ 1 + \lambda_i \cdot e^{-\alpha \cdot \Phi_m} \cdot (1 + e^{\Phi_m}) \cdot R^{-1} \right]^{-1}$$

Povrsinska reakcija  
SURFACE Mechanism  
OX(ads) + ne = Red(ads)

$$\cdot (1 - \alpha \cdot \Phi_1)^2$$

$$I_{m,i} := \lambda_i \cdot e^{-\alpha \cdot \Phi_m} \left[ 1 - (1 + e^{\Phi_m}) \cdot R^{-1} \cdot \sum_{j=1}^{m-1} I_{j,i} \right] \cdot \left[ 1 + \lambda_i \cdot e^{-\alpha \cdot \Phi_m} \cdot (1 + e^{\Phi_m}) \cdot R^{-1} \right]^{-1}$$

$$I_{m,i} := \lambda_i \cdot e^{-\alpha \cdot \Phi_m} \left[ 1 - (1 + e^{\Phi_m}) \cdot R^{-1} \cdot \sum_{j=1}^{m-1} I_{j,i} \right] \cdot \left[ 1 + \lambda_i \cdot e^{-\alpha \cdot \Phi_m} \cdot (1 + e^{\Phi_m}) \cdot R^{-1} \right]^{-1}$$

Povrsinska reakcija  
SURFACE Mechanism  
OX(ads) + ne = Red(ads)

$$\Psi_{1,i} := \frac{1 \cdot (\lambda_i \cdot e^{-\alpha \cdot \Phi_1})^2}{1 + (\lambda_i \cdot e^{-\alpha \cdot \Phi_1})^2 \cdot (1 + e^{\Phi_1}) \cdot \frac{M_{1,i}}{\gamma_i}}$$

$$\Psi_{m,i} := \frac{1 \cdot (\lambda_i \cdot e^{-\alpha \cdot \Phi_m})^2 - \left[ \frac{1 + e^{\Phi_m}}{\gamma_i \cdot 2} \cdot \sum_{j=1}^{m-1} [\Psi_{j,i} \cdot M_{(m-j)+1,i}] \right]^2}{1 + (\lambda_i \cdot e^{-\alpha \cdot \Phi_m})^2 + e^{\Phi_m} \cdot \frac{M_{1,i}}{2 \cdot \gamma_i} \cdot (\lambda_i \cdot e^{-\alpha \cdot \Phi_m})^2}$$

$$p := 0 \cdot \frac{0.6}{\Delta E} - 1 E_p := E_s - p \cdot \Delta E$$

$$I_{a,p,i} := I_{50-p+25,i} \quad I_{c,p,i} := I_{(p+1) \cdot 50,i} \quad I_{net,p,i} := I_{c,p,i} - I_{a,p,i}$$

$$\Psi_{a,p,i} := \Psi_{50-p+25,i} \quad \Psi_{c,p,i} := \Psi_{(p+1) \cdot 50,i} \quad \Psi_{net,p,i} := \Psi_{c,p,i} - \Psi_{a,p,i}$$

## SIMPLE SURFACE MECHANISM

with Non-Unity Stoichiometry

$2Ox(ads) + ne = Red(ads)$

with both Ox and Red adsorbed

$Ox(ads) + ne = Red(ads)$

$\lambda$  is dimensionless kinetic parameter related to electron transfer step defined as  $\lambda = ks/f$

$\Delta E$  is step potential

$E_{sw}$  is square-wave amplitude

$\Phi$  is dimensionless potential

$k$  is counter

$I$  is symbol of dimensionless current

SURFACE  $2Ox(adsorbed) + 2e = Red(adsorbed)$

if  $\gamma$  parameter is smaller than 0.00001, then this mechanism

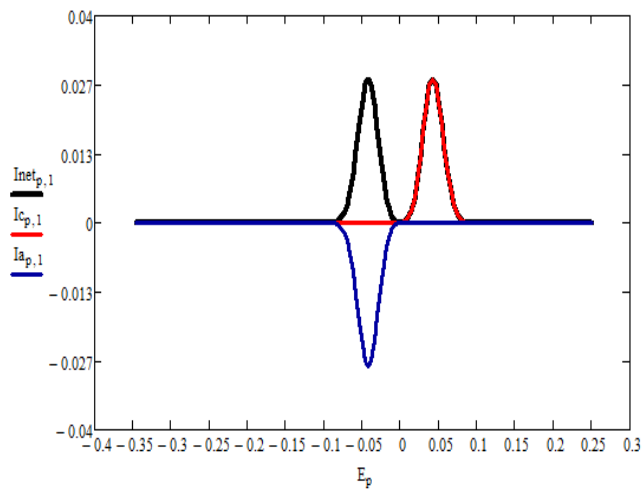
describes the non-unity stoichiometry surface  $2A + ne = B$  mechanism

met by many metal ions and hydrogen ions reduction at Pt electrode

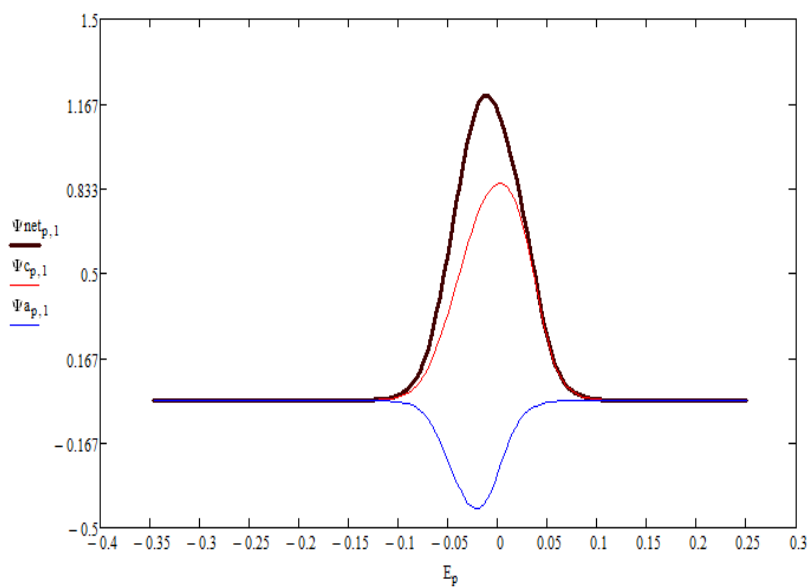
$$p := 0.5 \frac{\Delta E}{E_s} - 1 \quad E_p := E_s - p \cdot \Delta E$$

$$I_{a,p,i} := I_{50-p+25,i} \quad I_{c,p,i} := I_{(p+1) \cdot 50,i} \quad I_{net,p,i} := I_{c,p,i} - I_{a,p,i}$$

$$\Psi_{a,p,i} := \Psi_{50-p+25,i} \quad \Psi_{c,p,i} := \Psi_{(p+1) \cdot 50,i} \quad \Psi_{net,p,i} := \Psi_{c,p,i} - \Psi_{a,p,i}$$



SW Voltammogram of a SIMPLE Surface Mechanism



SW Voltammogram of a  $2Ox(ads) + ne^- = B(ads)$  mechanism with 2:1 stoichiometry

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