

Generalized Theory for Nanoscale Voltammetric Measurements of Heterogeneous Electron-Transfer Kinetics at Macroscopic Substrates by Scanning Electrochemical Microscopy

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Model. A SECM diffusion problem was defined using the Marcus–Hush–Chidsey (MHC) model. The cyclic sweep of substrate potential at a constant rate, v , is initiated at $t = 0$ from $E_S \gg E^{0'}$ toward the cathodic direction to drive a one-electron process at a macroscopic substrate as



where $k_{\text{f,S}}$ and $k_{\text{b,S}}$ are first-order heterogeneous rate constants. The cathodic rate constant is defined by the MHC formalism as¹

$$k_{\text{s,f}} = k^0 \exp\left(-\frac{E^*}{2}\right) \int_{-\infty}^{\infty} \frac{\exp\left[-\frac{(\varepsilon^* - E^*)^2}{4\lambda^*}\right]}{2 \cosh\left[\frac{\varepsilon^*}{2}\right]} d\varepsilon^* / \int_{-\infty}^{\infty} \frac{\exp\left[-\frac{(\varepsilon^*)^2}{4\lambda^*}\right]}{2 \cosh\left[\frac{\varepsilon^*}{2}\right]} d\varepsilon^* \quad (2)$$

with

$$E^* = \frac{F(E_S - E^{0'})}{RT} \quad (3)$$

$$\lambda^* = \frac{\lambda}{k_{\text{B}}T} \quad (4)$$

$$\varepsilon^* = \frac{\varepsilon}{k_{\text{B}}T} \quad (5)$$

where λ (eV) is the reorganization energy of the redox couple and ε is an integration variable. The potential-independence of k^0 in this model implies that the density of states in the electrode is constant and independent of the potential and that the electronic interaction between a redox molecule and each energy level in the electrode is independent of the energy level and of the neighboring levels.² The Nernst equation requires³

$$k_{\text{s,b}} = k_{\text{s,f}} \exp(E^*) \quad (6)$$

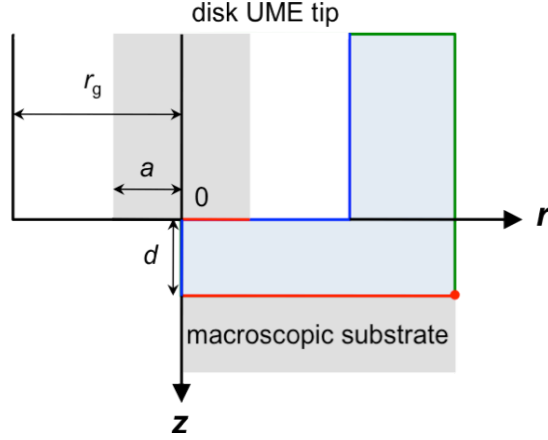


Figure 1. Geometry of a SECM diffusion problem in the cylindrical coordinate. The simulation space (light blue) is surrounded by seven boundaries (red, blue, and green lines). Boundary conditions at the tip and the substrate (red lines) are given in the text. There is no normal flux at symmetry axis and insulating surfaces (blue lines). Simulation space limits are represented by green lines. The flux of species O at the red dot represents a substrate current.

Diffusion Problem. A cylindrical coordinate was employed (Figure 1) to define time-dependent axisymmetric diffusion equations for oxidized and reduced forms of a redox couple, O and R, respectively, as

$$\frac{\partial c_O(r, z, t)}{\partial t} = D_O \left[\frac{\partial^2 c_O(r, z, t)}{\partial r^2} + \frac{1}{r} \frac{\partial c_O(r, z, t)}{\partial r} + \frac{\partial^2 c_O(r, z, t)}{\partial z^2} \right] \quad (7a)$$

$$\frac{\partial c_R(r, z, t)}{\partial t} = D_R \left[\frac{\partial^2 c_R(r, z, t)}{\partial r^2} + \frac{1}{r} \frac{\partial c_R(r, z, t)}{\partial r} + \frac{\partial^2 c_R(r, z, t)}{\partial z^2} \right] \quad (7b)$$

where $c_O(r, z, t)$ and $c_R(r, z, t)$ are concentrations of the respective redox mediators in the solution. Initially, only species O is present in the bulk solution, i.e., $c_O(r, z, 0) = c_O^*$ (the bulk concentration of O) and $c_R(r, z, 0) = 0$. Boundary conditions at insulating walls surrounding a tip and simulation space limits are given in Figure 1.

Simulation in the Dimensionless Form. A SECM diffusion problem based on the Marcus–Hush–Chidsey (MHC) formalism was solved in a dimensionless form using COMSOL Multiphysics (version 4.1[®], COMSOL, Inc., Burlington, MA) linked to Matlab (version 2010b, MathWorks, Natick, MA). Potential-dependent parts of rate constants thus calculated using Matlab were called externally from COMSOL Multiphysics through Livelink Matlab to define the boundary condition at the substrate surface and solve two-dimensional, time-dependent diffusion problems for SECM using the following dimensionless parameters as reported elsewhere⁴

$$L = d / a \quad (\text{dimensionless tip–substrate distance}) \quad (8)$$

$$\sigma = a^2 Fv / 4D_O RT \quad (\text{dimensionless sweep rate for substrate potential}) \quad (9)$$

$$\xi = \sqrt{D_O / D_R} \quad (\text{dimensionless diffusion coefficient ratio}) \quad (10)$$

$$R = r/a \quad (11)$$

$$Z = z/a \quad (12)$$

$$\tau = 4D_O t/a^2 \quad (13)$$

$$C_O(R, Z, \tau) = c_O(r, z, t)/c_O^* \quad (14a)$$

$$C_R(R, Z, \tau) = c_R(r, z, t)/c_O^* \quad (14b)$$

where d is the tip–substrate distance, a is the tip radius, v is the sweep rate for substrate potential, and D_O and D_R are diffusion coefficients of species O and R, respectively, in the bulk solution. Diffusion equations for species O and R in the solution phase (eqs 5a and 5b, respectively) were also expressed in dimensionless forms as

$$\frac{\partial C_O(R, Z, \tau)}{\partial \tau} = 0.25 \left[\frac{\partial^2 C_O(R, Z, \tau)}{\partial R^2} + \frac{1}{R} \frac{\partial C_O(R, Z, \tau)}{\partial R} + \frac{\partial^2 C_O(R, Z, \tau)}{\partial Z^2} \right] \quad (15a)$$

$$\frac{\partial C_R(R, Z, \tau)}{\partial \tau} = \frac{0.25}{\xi^2} \left[\frac{\partial^2 C_R(R, Z, \tau)}{\partial R^2} + \frac{1}{R} \frac{\partial C_R(R, Z, \tau)}{\partial R} + \frac{\partial^2 C_R(R, Z, \tau)}{\partial Z^2} \right] \quad (15b)$$

where values of 0.25 and $0.25/\xi^2$ were used as dimensionless diffusion coefficients. Substrate boundary conditions were given by

$$0.25 \left[\frac{\partial C_O(R, Z, \tau)}{\partial Z} \right]_{Z=L} = \frac{0.25K}{\theta_s^\alpha} [\theta_s C_R(R, Z, \tau) - C_O(R, Z, \tau)] \quad (16a)$$

$$\frac{0.25}{\xi^2} \left[\frac{\partial C_R(R, Z, \tau)}{\partial Z} \right]_{Z=L} = \frac{0.25K}{\theta_s^{\alpha-1}} \left[\frac{C_O(R, Z, \tau)}{\theta_s} - C_R(R, Z, \tau) \right] \quad (16b)$$

with

$$K = k^0 a / D_O \quad (17)$$

$$\lambda'_O = k^0 d / D_O \quad (\text{dimensionless standard ET rate constant}) \quad (18)$$

A tip current, i_T , was normalized with respect to a limiting current at an inlaid disk tip in the bulk solution, $i_{T,\infty}$, to obtain a dimensionless tip current, I_T , as

$$I_T = \frac{i_T}{i_{T,\infty}} = \frac{2\pi}{x} \int_0^1 R \left[\frac{\partial C_O(R, L, \tau)}{\partial Z} \right] dR \quad (19)$$

The x values simulated for different RG values at $L = 50$ agree with theoretical values as given by⁵

$$x = 1 + 0.639 \left[1 - \frac{2}{\pi} \arctan \left(\frac{1}{RG} \right) \right] - 0.186 \left\{ 1 - \left[\frac{2}{\pi} \arctan \left(\frac{1}{RG} \right) \right]^2 \right\} \quad (20)$$

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