Quasi-Steady-State Voltammetry of Rapid Electron Transfer Reactions at the Macroscopic Substrate of the Scanning Electrochemical Microscope

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Model. We simulated tip current (i_T) –substrate potential (E_S) voltammograms under various geometric and kinetic conditions by solving standard diffusion problems for SECM (Figure 1). The cyclic sweep of substrate potential at a constant rate, v, is initiated at $t = 0$ from $E_S >> E^{0'}$ toward the cathodic direction to drive a one-electron process at a macroscopic substrate as

$$\mathrm{O} + \mathrm{e} \underset{k_{\mathrm{b,S}}}{\overset{k_{\mathrm{f,S}}}{\rightleftharpoons}} \mathrm{R} \tag{1}$$

where $k_{\mathrm{f,S}}$ and $k_{\mathrm{b,S}}$ are first-order heterogeneous rate constants. The rate constants are given by the Butler–Volmer relation as[1]

$$k_{\mathrm{f,s}} = k^0 \exp[-\alpha F(E_\mathrm{S} - E^{0'})/RT] \tag{2}$$

$$k_{\mathrm{b,s}} = k^0 \exp[(1-\alpha) F(E_\mathrm{S} - E^{0'})/RT] \tag{3}$$

The use of the Butler–Volmer model is justified in this work, which is mainly concerned about the simple substrate reactions that give a normal α value of 0.5 and reach a diffusion limitation at substrate potentials where the Marcus model may be more appropriate, e.g., $\left|E_\mathrm{S} - E^{0'}\right| \geq 0.15$ V for a redox couple with a reorganization energy of 1 eV.[2] Boundary conditions at insulating walls surrounding a tip and simulation space limits are given in Figure 1.

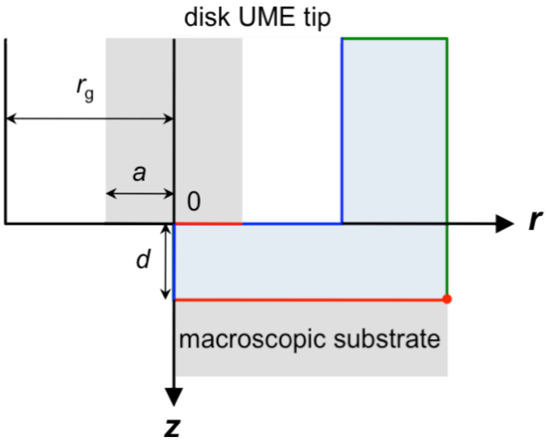

Figure 1. Geometry of a SECM diffusion problem in the cylindrical coordinate. The simulation space (light blue) is surrounded by seven boundaries (red, blue, and green lines). Boundary conditions at the tip and the substrate (red lines) are given in the text. There is no normal flux at symmetry axis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

$$\frac{\partial c_{\mathrm{O}}(r,z,t)}{\partial t} = D_{\mathrm{O}}\left[\frac{\partial^2 c_{\mathrm{O}}(r,z,t)}{\partial r^2} + \frac{1}{r}\frac{\partial c_{\mathrm{O}}(r,z,t)}{\partial r} + \frac{\partial^2 c_{\mathrm{O}}(r,z,t)}{\partial z^2}\right] \tag{4a}$$

$$\frac{\partial c_{\mathrm{R}}(r,z,t)}{\partial t} = D_{\mathrm{R}}\left[\frac{\partial^2 c_{\mathrm{R}}(r,z,t)}{\partial r^2} + \frac{1}{r}\frac{\partial c_{\mathrm{R}}(r,z,t)}{\partial r} + \frac{\partial^2 c_{\mathrm{R}}(r,z,t)}{\partial z^2}\right] \tag{4b}$$

where $c_{\mathrm{O}}(r, z, t)$ and $c_{\mathrm{R}}(r, z, t)$ are concentrations of the respective redox mediators in the solution. Initially, only species O is present in the bulk solution, i.e., $c_{\mathrm{O}}(r, z, 0) = c_{\mathrm{O}}^{*}$ (the bulk concentration of O) and $c_{\mathrm{R}}(r, z, 0) = 0$. Other boundary conditions are defined in Figure 1.

Simulation in the Dimensionless Form. The axisymmetric, time-dependent diffusion problems were solved using the following dimensionless parameters by employing COMSOL Multiphysics finite element package (version 3.5a®, COMSOL, Inc., Burlington, MA).

$$R = r/a \tag{5}$$

$$Z = z/a \tag{6}$$

$$\tau = 4D_{\mathrm{O}}t/a^2 \tag{7}$$

$$C_{\mathrm{O}}(R, Z, \tau) = c_{\mathrm{O}}(r, z, t)/c_{\mathrm{O}}^{*} \tag{8a}$$

$$C_{\mathrm{R}}(R, Z, \tau) = c_{\mathrm{R}}(r, z, t)/c_{\mathrm{O}}^{*} \tag{8b}$$

$L = d / a$ (dimensionless tip–substrate distance) (9)

$\sigma = a^2 F v / 4 D_{\mathrm{O}} R T$ (dimensionless sweep rate for substrate potential) (10)

$\xi = \sqrt{D_{\mathrm{O}} / D_{\mathrm{R}}}$ (dimensionless diffusion coefficient ratio) (11)

$\lambda_{\mathrm{O}}' = k^0 d / D_{\mathrm{O}}$ (dimensionless standard ET rate constant) (12)

Diffusion equations for species O and R in the solution phase (eqs 5a and 5b, respectively) were also expressed in dimensionless forms as

$$\frac{\partial C_{\mathrm{O}}(R,Z,\tau)}{\partial \tau} = 0.25\left[\frac{\partial^2 C_{\mathrm{O}}(R,Z,\tau)}{\partial R^2} + \frac{1}{R}\frac{\partial C_{\mathrm{O}}(R,Z,\tau)}{\partial R} + \frac{\partial^2 C_{\mathrm{O}}(R,Z,\tau)}{\partial Z^2}\right] \tag{13a}$$

$$\frac{\partial C_{\mathrm{R}}(R,Z,\tau)}{\partial \tau} = \frac{0.25}{\xi^2}\left[\frac{\partial^2 C_{\mathrm{R}}(R,Z,\tau)}{\partial R^2} + \frac{1}{R}\frac{\partial C_{\mathrm{R}}(R,Z,\tau)}{\partial R} + \frac{\partial^2 C_{\mathrm{R}}(R,Z,\tau)}{\partial Z^2}\right] \tag{13b}$$

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

$$0.25\left[\frac{\partial C_{\mathrm{O}}(R,Z,\tau)}{\partial Z}\right]_{Z=L} = \frac{0.25K}{\theta_{\mathrm{S}}^{\alpha}}[\theta_{\mathrm{S}} C_{\mathrm{R}}(R,Z,\tau) - C_{\mathrm{O}}(R,Z,\tau)] \tag{14a}$$

$$\frac{0.25}{\xi^2}\left[\frac{\partial C_{\mathrm{R}}(R,Z,\tau)}{\partial Z}\right]_{Z=L}=\frac{0.25K}{\theta_{\mathrm{S}}^{\alpha-1}}\left[\frac{C_{\mathrm{O}}(R,Z,\tau)}{\theta_{\mathrm{S}}}-C_{\mathrm{R}}(R,Z,\tau)\right] \tag{14b}$$

with

$$K=k^0a/D_{\mathrm{O}} \tag{15}$$

A current was calculated for the diffusion-limited detection of the original mediator, O, in the feedback mode or the substrate-generated species, R, in the SG–TC mode to give a pair of i_{T}–E_{S} voltammograms at the same tip–substrate distance. Positive tip (and substrate) currents are based on the reduction of the original mediator so that feedback and SG/TC tip responses appear in the upper and lower panels of the following graphs, respectively. The dimensionless flux of species O at the edge of a macroscopic substrate (red dot in Figure 1) represents a substrate current. A SECM diffusion problem was solved in a dimensionless form by employing the finite element method. A tip current, i_{T}, was normalized with respect to a limiting current at an inlaid disk tip in the bulk solution, $i_{\mathrm{T},\infty}$, to obtain a dimensionless tip current, I_{T}, as

$$I_{\mathrm{T}}=\frac{i_{\mathrm{T}}}{i_{\mathrm{T},\infty}}=\frac{2\pi}{x}\int_0^1 R\left[\frac{\partial C_{\mathrm{O}}\left(R,L,\tau\right)}{\partial Z}\right]dR \tag{16}$$

The x values simulated for different RG values at L = 50 agree with theoretical values as given by[3]

$$x=1+0.639\left[1-\frac{2}{\pi}\arctan\left(\frac{1}{RG}\right)\right]-0.186\left\{1-\left[\frac{2}{\pi}\arctan\left(\frac{1}{RG}\right)\right]^2\right\} \tag{17}$$

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