This model was developed in the following paper.

Chen, R.; Najarian, A. M.; Kurapati, N.; Balla, R. J.; Oleinick, A.; Svir, I.; Amatore, C.; McCreery, R. L.; Amemiya, S. "Self-inhibitory electron transfer of the Co(III)/Co(II)-complex redox couple at pristine carbon electrode." *Anal. Chem.* **2018**, *90*, 11115.

This model is also applicable to the system discussed in the following paper.

Chen, R.; Balla, R. J.; Li, Z. T.; Liu, H. T.; Amemiya, S. "Origin of asymmetry of paired nanogap voltammograms based on scanning electrochemical microscopy: Contamination not adsorption." *Anal. Chem.* **2016**, *88*, 8323.

SECM Model. Here we define a theoretical model to quantitatively describe SECM-based nanogap voltammograms of adsorption-coupled electron transfer (ET) in feedback and SG/TC modes. We consider an SECM configuration in the cylindrical coordinates (Figure 1) to define the following diffusion problem.

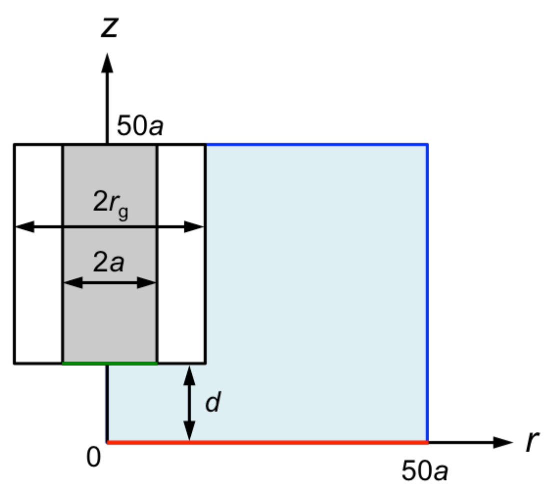

Figure 1. Scheme of the SECM configuration with a glass-insulated Pt tip ($RG = r_g/a$) positioned over a macroscopic substrate substrate. The red boundary represents the substrate surface. The green boundary represents the tip surface. Black boundaries are insulating or a symmetry axis. Blue boundaries represent the bulk solution.

A model for SECM-based nanogap voltammetry is based on the adsorption of A, that proceeds its oxidation to B, as given by

$$\mathrm{A} \rightleftharpoons \mathrm{A_{ads}} \tag{1}$$

$$\mathrm{A} \rightleftharpoons \mathrm{B} + \mathrm{e}^{-} \tag{2}$$

Diffusion equations for species, i (= A or B), is given in the cylindrical coordinates (Figure 1) to yield

$$\frac{\partial c_{\mathrm{i}}}{\partial t} = D_{\mathrm{i}}\left[\frac{\partial^2 c_{\mathrm{i}}}{\partial r^2} + \frac{1}{r}\frac{\partial c_{\mathrm{i}}}{\partial r} + \frac{\partial^2 c_{\mathrm{i}}}{\partial z^2}\right] \tag{3}$$

where D_{i} is the diffusion coefficient of species i (= A or B). The rate of the electron-transfer (ET) reaction, v_{et}, is given by the Butler–Volmer model as

$$v_{\mathrm{et}} = k_{\mathrm{red}} c_{\mathrm{B}} - k_{\mathrm{ox}} c_{\mathrm{A}} \tag{4}$$

with

$$k_{\mathrm{red}} = k_0 \exp\left[-\alpha_{\mathrm{ET}} F\left(E - E^{0'}\right)/RT\right] \tag{5}$$

$$k_{\mathrm{ox}} = k_0 \exp\left[\left(1-\alpha_{\mathrm{ET}}\right) F\left(E - E^{0'}\right)/RT\right] \tag{6}$$

where k_{red} and k_{ox} are oxidation and reduction rate constants, k_0 is the heterogeneous standard ET rate constant, c_{A} and c_{B} represents the concentrations of non-adsorbed species A and B near the electrode surface, respectively, α_{ET} is transfer coefficient, E is the substrate potential, and $E^{0'}$ is the formal potential. In addition, we considered adsorption and desorption kinetics of species A on the substrate surface by using a Frumkin isotherm based on the Bragg–Williams approximation as given by

$$c_{\mathrm{A}} = \frac{\theta_{\mathrm{A}}}{\beta\left(1-\theta_{\mathrm{A}}\right)}\exp\left[-g'\theta_{\mathrm{A}}\right] \tag{7}$$

where θ_{A} is the coverage of the substrate surface with species A and is given by the ratio of the surface concentration of A, Γ_{A}, with respect to its saturated concentration, Γ_s, β is an equilibrium parameter in the isotherm, and g' is a parameter characterizing the magnitude of interactions among adsorbed molecules. With the Frumkin isotherm, the adsorption rate of A, v_{ads}, is given by

$$v_{\mathrm{ads}} = k_{\mathrm{ads}} c_{\mathrm{A}} \left(\Gamma_{\mathrm{s}} - \Gamma_{\mathrm{A}} \right) - k_{\mathrm{des}} \Gamma_{\mathrm{A}} \tag{8}$$

with

$$k_{\mathrm{ads}} = k_{\mathrm{ads}}^{0} \exp\left(\alpha_{\mathrm{ads}} g' \theta_{\mathrm{A}} \right) \tag{9}$$

$$k_{\mathrm{des}} = k_{\mathrm{des}}^{0} \exp\left[-\left(1 - \alpha_{\mathrm{ads}} \right) g' \theta_{\mathrm{A}} \right] \tag{10}$$

where k_{ads}^{0} and k_{des}^{0} are standard adsorption and desorption rate constant, and α_{ads} is a symmetry coefficient ($0 < \alpha_{ads} < 1$) regulating the effect of g' on the adsorption activation barrier. Adsorption equilibrium is achieved at $t = 0$ to yield eq 7 with $\beta = k_{\mathrm{ads}}^{0} / k_{\mathrm{des}}^{0}$. Accordingly, boundary conditions at the substrate surface are given by

$$-D_{\mathrm{A}} \left[\frac{\partial c_{\mathrm{A}}}{\partial z} \right]_{z=0} = v_{\mathrm{et}} - v_{\mathrm{ads}} \tag{11}$$

$$-D_{\mathrm{B}} \left[\frac{\partial c_{\mathrm{B}}}{\partial z} \right]_{z=0} = -v_{\mathrm{et}} \tag{12}$$

$$\left[\frac{\partial \Gamma_{\mathrm{A}}}{\partial t} \right] = v_{\mathrm{ads}} \tag{13}$$

Boundary conditions at the tip depend on the operation mode, i.e., $c_A = 0$ in the feedback mode and $c_B = 0$ in the SG/TC mode. In either operation mode, a current response at the tip, i_T, is given by

$$i_{\mathrm{T}} = 2\pi F \int_{0}^{a} r v_{\mathrm{et}} \, dr \tag{14}$$

The tip potential is given by E_{tip}.

Dimensionless SECM Model. Diffusion equations for species i (= A or B) are defined by using the following dimensionless parameters and solved by using a commercial finite element simulation package, Multiphysics 5.4a (COMSOL, Burlington, MA). Specifically, diffusion equations in dimensionless forms are defined from eq S-3 for species i (= A or B) as

$$\frac{\partial C_{\mathrm{i}}}{\partial \tau} = \gamma_{\mathrm{i}} \left[\frac{\partial^2 C_{\mathrm{i}}}{\partial R^2} + \frac{1}{R} \frac{\partial C_{\mathrm{i}}}{\partial R} + \frac{\partial^2 C_{\mathrm{i}}}{\partial Z^2} \right] \tag{15}$$

with

$$C_{\mathrm{i}} = c_{\mathrm{i}} / c_0 \tag{16}$$

$$R = r / a \tag{17}$$

$$Z = z / a \tag{18}$$

$$\tau = D_{\mathrm{A}} t / a^2 \tag{19}$$

$$\gamma_{\mathrm{i}} = D_{\mathrm{i}} / D_{\mathrm{A}} \tag{20}$$

In addition, the potential sweep rate, v, is converted to the dimensionless form, σ, as

$$\sigma = a^2 v F / D_{\mathrm{A}} R T \tag{21}$$

Importantly, mass transport across the tip–substrate gap maintains a quasi-steady state when $\sigma < 1$. Boundary conditions at the substrate surface (eqs 11–13) are given by using dimensionless rates, $V_{\mathrm{et}}^{\mathrm{SECM}}$ and $V_{\mathrm{ads}}^{\mathrm{SECM}}$, as

$$\left[\frac{\partial C_{\mathrm{A}}}{\partial Z} \right]_{Z=0} = V_{\mathrm{et}}^{\mathrm{SECM}} - V_{\mathrm{ads}}^{\mathrm{SECM}} \tag{22}$$

$$\left[\frac{\partial C_{\mathrm{B}}}{\partial Z} \right]_{Z=0} = -\frac{V_{\mathrm{et}}^{\mathrm{SECM}}}{\gamma_{\mathrm{i}}} \tag{23}$$

$$\left[\frac{\partial \theta_{\mathrm{A}}}{\partial \tau} \right] = \frac{V_{\mathrm{ads}}^{\mathrm{SECM}}}{K_{\mathrm{SECM}}} \tag{24}$$

with

$$\theta_A = \Gamma_A / \Gamma_s \tag{25}$$

$$K_{SECM} = \Gamma_s / ac_0 \tag{26}$$

$$L = d / a \tag{27}$$

Each dimensionless rate is given as follows. The dimensionless ET rate, V_{et}^{SECM}, is given by

$$V_{et}^{SECM} = \Lambda_{het}^{SECM}\left[\left(\theta_{ET}\right)^{-\alpha_{ET}} C_B - \left(\theta_{ET}\right)^{1-\alpha_{ET}} C_A\right] \tag{28}$$

with

$$\Lambda_{het}^{SECM} = k^0 a / D_A \tag{29}$$

$$\theta_{ET} = \exp\left[\frac{F(E - E_{initial})}{RT}\right] / \exp\left[\frac{F(E^0 - E_{initial})}{RT}\right] \tag{30}$$

where $F(E^0 - E_{initial})/RT$ serves as a scaling factor and the substrate potential is cycled between $E_{initial}$ and E_{λ} as the switching potential. The adsorption rate is defined in the dimensionless form, V_{ads}^{SECM}, as

$$V_{ads}^{SECM} = \Lambda_{ads}^{SECM}\left(\theta_{ads}\right)^{\alpha_{ads}} C_A\left(1-\theta_A\right) - \Lambda_{des}^{SECM}\left(\theta_{ads}\right)^{\alpha_{ads}-1}\theta_A \tag{31}$$

with

$$\Lambda_{ads}^{SECM} = k_{ads}^0 \Gamma_s a / D_A \tag{32}$$

$$\Lambda_{des}^{SECM} = k_{des}^0 \Gamma_s a / c_0 D_A \tag{33}$$

$$\theta_{ads} = \exp\left(g'\theta_A\right) \tag{34}$$

The corresponding initial condition is given by

$$\frac{\Lambda_{ads}^{SECM}}{\Lambda_{des}^{SECM}} = \frac{\theta_A}{1-\theta_A}\exp\left(-g'\theta_A\right) \tag{35}$$

Finally, a normalized tip current response, I_T, is given by

$$I_{\mathrm{T}} = \frac{i_{\mathrm{T}}}{FD_{\mathrm{A}}c_0 a} = \int_0^1 \left(2\pi R V_{\mathrm{et}}\right) dR \tag{36}$$

where the integral is calculated by COMSOL.

Table 1. Parameters Used in COMSOL and Dimensionless Models.

Parameters		Equation
COMSOL	Dimensionless Model	
rg	RG	
Esw	$E_{\lambda} - E^0$	
Erange	$E \ \ - E_{\mathrm{initial}}$	
sigma	$\sigma = a^2 vF / D_{\mathrm{A}} RT$	21
lamda	$\Lambda_{\mathrm{het}}^{\mathrm{SECM}} = k^0 a / D_{\mathrm{A}}$	29
theta0	$K_{\mathrm{SECM}} = \Gamma_s / ac_0$	26
Lamda	$\Lambda_{\mathrm{ads}}^{\mathrm{SECM}} / \Lambda_{\mathrm{des}}^{\mathrm{SECM}}$	32 and 33
gprime	g'	7
kappa	$\Lambda_{\mathrm{ads}}^{\mathrm{SECM}} = k_{\mathrm{ads}}^0 \Gamma_s a / D_{\mathrm{A}}$	32
alpha	α_{ET}	5 and 6
beta	α_{ads}	9 and 10
gamma	$\gamma_{\mathrm{B}} = D_{\mathrm{B}} / D_{\mathrm{A}}$	20
Etip	$E_{\mathrm{tip}} - E^0$	