Supporting Information

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

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Abstract

The Supporting Information includes the model and results of finite element simulation, the model and derivations of analytical equations, experimental details for tip fabrication and characterization, and an $i_t-E_s$ voltammogram with current spikes.
Finite Element Simulation. The SECM diffusion problem defined in this section 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, $i_{T,\infty}$, to obtain a dimensionless tip current, $I_T$, as

$$I_T = \frac{i_T}{i_{T,\infty}} = \frac{2\pi}{x} \int_0^\infty R \left[ \frac{\partial C_0(R,L,\tau)}{\partial Z} \right] dR$$  \hspace{1cm} (S-1)

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

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

The reliability of our simulation results was further confirmed by the good agreement of positive feedback current under diffusion limits, $I_{T,d}(L)$, with theoretical values as given by

$$I_{T,d}(L) = \alpha(RG) + \frac{\pi}{4x \arctan(L)} \left[ 1 - \alpha(RG) - \frac{1}{2x} \right] \frac{2}{\pi} \arctan(L)$$  \hspace{1cm} (S-3)

with

$$\alpha(RG) = \ln 2 + \ln \left[ 1 - \frac{2}{\pi} \arctan \left( \frac{1}{RG} \right) \right] - \ln \left[ 1 - \left( \frac{2}{\pi} \arctan \left( \frac{1}{RG} \right) \right)^2 \right]$$  \hspace{1cm} (S-4)
**Model.** A cylindrical coordinate was employed (Figure S-1) to define time-dependent axisymmetric diffusion equations for oxidized and reduced forms of a redox couple, O and R, respectively, as

\[
\frac{\partial c_o(r,z,t)}{\partial t} = D_o \left[ \frac{\partial^2 c_o(r,z,t)}{\partial r^2} + \frac{1}{r} \frac{\partial c_o(r,z,t)}{\partial r} + \frac{\partial^2 c_o(r,z,t)}{\partial z^2} \right] \tag{S-5a}
\]

\[
\frac{\partial c_r(r,z,t)}{\partial t} = D_r \left[ \frac{\partial^2 c_r(r,z,t)}{\partial r^2} + \frac{1}{r} \frac{\partial c_r(r,z,t)}{\partial r} + \frac{\partial^2 c_r(r,z,t)}{\partial z^2} \right] \tag{S-5b}
\]

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 \(c_r(r,z,0) = 0\).

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

\[
O + e \rightleftharpoons R \quad \tag{S-6}
\]

\[
k_{f,S}
\]

\[
k_{b,S}
\]

where \(k_{f,S}\) and \(k_{b,S}\) are first-order heterogeneous rate constants. The rate constants are given by the Butler–Volmer relation as\(^{S-2}\)
\[ k_{t,s} = k^0 \exp[-\alpha F(E_s - E_0^\circ)/RT] \] (S-7a)

\[ k_{b,s} = k^0 \exp[(1 - \alpha)F(E_s - E_0^\circ)/RT] \] (S-7b)

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 \( \alpha \) value of 0.5 and reach a diffusion limitation at substrate potentials where the Marcus model may be more appropriate, e.g., \( |E_s - E_0^\circ| \geq 0.15 \) \( \text{V} \) for a redox couple with a reorganization energy of 1 eV.\(^3\) Boundary conditions at insulating walls surrounding a tip and simulation space limits are given in Figure S-1.

**Figure S-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.
Simulation Result. Attached is the simulation result of a quasi-steady-state $i_{1-E_S}$ voltammogram in the SG/TC mode for a nearly reversible substrate reaction under the tip ($\lambda'_{0} = 2$) as obtained using the following dimensionless parameters.

$$R = r/a$$  \hspace{1cm} (S-8)

$$Z = z/a$$  \hspace{1cm} (S-9)

$$\tau = 4D_0 t/a^2$$  \hspace{1cm} (S-10)

$${C_O}(R, Z, \tau) = {c_0}(r, z, t)/c_o^*$$  \hspace{1cm} (S-11a)

$${C_R}(R, Z, \tau) = {c_R}(r, z, t)/c_o^*$$  \hspace{1cm} (S-11b)

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

$$\frac{\partial {C_O}(R, Z, \tau)}{\partial \tau} = 0.25 \left[ \frac{\partial^2 {C_O}(R, Z, \tau)}{\partial R^2} + \frac{1}{R} \frac{\partial {C_O}(R, Z, \tau)}{\partial R} + \frac{\partial^2 {C_O}(R, Z, \tau)}{\partial Z^2} \right]$$  \hspace{1cm} (S-12a)

$$\frac{\partial {C_R}(R, Z, \tau)}{\partial \tau} = 0.25 \left[ \frac{\partial^2 {C_R}(R, Z, \tau)}{\partial R^2} + \frac{1}{R} \frac{\partial {C_R}(R, Z, \tau)}{\partial R} + \frac{\partial^2 {C_R}(R, Z, \tau)}{\partial Z^2} \right]$$  \hspace{1cm} (S-12b)
where values of 0.25 and 0.25/$\xi^2$ were used as dimensionless diffusion coefficients. Substrate boundary conditions were given by

\[
0.25 \left[ \frac{\partial C_o(R, Z, \tau)}{\partial Z} \right]_{Z=L} = \frac{0.25 K}{\theta^a_s} [\theta^a_s C_{o,r}(R, Z, \tau) - C_o(R, Z, \tau)]
\]  \hspace{1cm} (S-13a)

\[
\frac{0.25}{\xi^2} \left[ \frac{\partial C_r(R, Z, \tau)}{\partial Z} \right]_{Z=L} = \frac{0.25 K}{\theta^{a-1}_s} \left[ \frac{C_{o,r}(R, Z, \tau)}{\theta_s} - C_r(R, Z, \tau) \right]
\]  \hspace{1cm} (S-13b)

with

\[
K = k^0 a/D_0
\]  \hspace{1cm} (S-14)

In the attached simulation result, $K = 8$ at $L = 0.25$ is equivalent to $\lambda'_o = 2$. Other boundary conditions and initial conditions were also defined in dimensionless forms. The overall simulation space is large enough and does not control simulation results.
**Mediator Concentrations under Quasi-Steady-State Conditions.** Figure S-2 shows the simulated concentration profile of a substrate-generated species, R, detected at the tip at a diffusion-limited rate in the SG/TC mode.

**Figure S-2.** Simulated concentration profile of species R in the SG–TC mode for a reversible substrate reaction at $E_S = E^o$ and $L = 0.25$. See Figure 2 for other parameters.
**Effect of Unequal Diffusion Coefficients on $i_T{-}E_S$ Voltammograms.** Various $D_R$ values were employed to examine their effect on $\sigma$ values required for obtaining quasi-steady-state $i_T{-}E_S$ voltammograms at a tip with $RG = 1.5$ or 10 (Figure S-3) under the identical condition as employed for the simulation of voltammograms in Figure 3. With $D_R \neq D_O$, a voltammogram at a tip with $RG = 1.5$ is slightly unretraceable at $\sigma = 0.1$ to give a little larger limiting current in the SG/TC mode than expected from eq 8 (Figure S-3a). With $D_R \neq D_O$, a much smaller $\sigma$ value of 0.001 is required for obtaining nearly retraceable voltammograms at a conventional tip with $RG = 10$ to fit well with eqs 6 and 8 (Figure S-3b).

![Figure S-3](image-url)

**Figure S-3.** Effect of $D_R/D_O$ on $i_T{-}E_S$ voltammograms (solid lines) for a reversible substrate reaction as obtained at a tip with $RG = (a)$ 1.5 or (b) 10 at $L = 0.25$ in feedback (top) and SG/TC (bottom) modes. Closed circles represent eqs 6 and 8.
Reversibility of Substrate Voltammograms. Figure S-4 shows substrate voltammograms with various $\lambda'_o$ values as obtained simultaneously with $i_{T-E_S}$ voltammograms in Figure 4. At $\sigma = 0.01$, substrate voltammograms are reversible or nearly reversible with $\lambda'_o \geq 0.3$ while a smaller $\lambda'_o$ value results in a less reversible substrate voltammogram.

Figure S-4. Effect of normalized standard ET rate constant, $\lambda'_o$, on substrate voltammograms at $\sigma = 0.01$ as simultaneously obtained with $i_{T-E_S}$ voltammograms in Figure 4.
Equilibrium Mediator Concentrations at the Surface of a Macroscopic Substrate. When a heterogeneous ET reaction is reversible at the surface of a macroscopic substrate except under the tip, mediator concentrations at the exterior surface, $c^e_{O,S}$ and $c^e_{R,S}$, for species O and R, respectively, are equilibrated with and uniquely correspond to substrate potentials as give by

$$c^e_{O,S} = c^e_0 \xi \theta_0 / (\xi \theta_0 + 1) \quad (S-15a)$$

$$c^e_{R,S} = c^e_0 \xi / (\xi \theta_0 + 1) \quad (S-15b)$$

These equations were derived as follows using the convolution principle. When a solution initially contains only species O, mediator concentrations at the exterior surface are given by

$$c^e_{O,S} = c^e_0 - \frac{I_S(t)}{FA\sqrt{D_0}} \quad (S-16a)$$

$$c^e_{R,S} = \frac{I_S(t)}{FA\sqrt{D_R}} \quad (S-16a)$$

where $I_S(t)$ represents the semi-integral of substrate current. In addition, the Nernst equation is given by

$$E_S = E_0^c - \frac{RT}{nF} \ln \frac{c^e_{R,S}}{c^e_{O,S}} \quad (S-17)$$

The combination of eq S-17 with eqs S-16a and S-16b gives eqs S-15a and S-15b.
Kinetically Limited $i_T-E_s$ Voltammograms with Partially Retraceable Regions. In Figure 4, $i_T-E_s$ voltammograms for non-reversible substrate reactions with $\lambda_{O_{\text{f}}} \leq 0.1$ at $\sigma = 0.01$ are retraceable at $E_s >> E_{pa}$ and $E_s << E_{pc}$, where $E_{pa}$ and $E_{pc}$ are anodic and cathodic peak potentials of the corresponding substrate voltammograms. Under these diffusion-limited conditions at the exterior substrate surface, the corresponding concentrations of redox mediators are constant and identical on both forward and reverse potential sweeps. Conspicuously, $i_T-E_s$ voltammograms in the feedback mode are retraceable at $E_s >> E_{pa}$, where substrate surface concentrations are unchanging from the corresponding bulk concentrations, i.e., $c_{O,S}^{ex} = c_{O}^*$ and $c_{R,S}^{ex} = 0$, on both forward and reverse potential sweeps to give the identical tip current under steady-state and quasi-steady-state conditions, respectively. The different conditions are associated with zero and finite substrate currents at $E_s >> E_{pa}$ on the respective potential sweeps. Moreover, constant surface concentrations of $c_{O,S}^{ex} = 0$ and $c_{R,S}^{ex} = \xi c_{O}^*$ are maintained at $E_s << E_{pc}$. Therefore, the identical quasi-steady-state tip current is obtained in the SG/TC mode at $E_s << E_{pc}$ on forward and reverse potential sweeps although the corresponding substrate currents are different.
Analytical Equations for Quasi-Steady-State $i_T-E_S$ Voltammograms. In this section, eqs 6 and 8 are derived as analytical equations for quasi-steady-state $i_T-E_S$ voltammograms in feedback and SG/TC modes, respectively, by extending the theory of quasi-steady-state tip voltammetry.\textsuperscript{S-5}

Model and Assumptions. Analytical equations for quasi-steady-state tip currents at different substrate potentials were obtained by extending a model for an SECM-based thin layer cell (TLC).\textsuperscript{S-5} In the extended model (Figure S-5), the surface of a macroscopic substrate was divided into the TLC region under the tip and its exterior region. Different surface concentrations of redox mediators in the respective regions are given by $c_{O,S}^{\text{TLC}}$ and $c_{O,S}^{\text{ex}}$ for species O and by $c_{R,S}^{\text{TLC}}$ and $c_{R,S}^{\text{ex}}$ for species R. These distinct surface concentrations are due to a higher mass-transport condition at the region under the TLC than at the exterior region. Accordingly, a quasireversible reaction was assumed at the TLC region of the substrate surface. At the same time, a reversible substrate reaction at the exterior surface was assumed as a requirement for obtaining the whole $i_T-E_s$ voltammogram under quasi-steady-state conditions (see eqs S-15a and S-15b). In contrast, surface concentrations of redox mediators at the disk tip, $c_{O,T}$ and $c_{R,T}$ for species O and R, respectively, were assumed to be uniform.\textsuperscript{S-6}

![Figure S-5. Model for an SECM-based thin layer cell.](image)

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The tip current in this leaky thin layer cell, \( i_T \), is approximated as the sum of the feedback (or SG/TC) current from the substrate under the TLC, \( i_{\text{TLC}} \), and the direct current from the bulk solution, \( i_{\text{bulk}} \), thereby yielding:

\[
i_T(E_s, L) = i_{\text{TLC}}(E_s, L) + i_{\text{bulk}}(E_s, L)
\]  
(S-18)

The feedback (or SG/TC) current depends on the kinetics of a quasireversible ET reaction at the substrate surface under the tip and is included in the flux balance across the TLC between the tip and the substrate as

\[
\frac{i_{\text{TLC}}(E_s, L)}{\pi a^2 nF} = -\left(k_{t,s} c_{o,s}^{\text{TLC}} - k_{b,s} c_{r,s}^{\text{TLC}} \right) = -\frac{D_o (c_{o,T} - c_{o,s}^{\text{TLC}})}{d} = -\frac{D_R (c_{r,s}^{\text{TLC}} - c_{r,T})}{d}
\]  
(S-19)

Mass balance in the TLC is also approximated to

\[
c_{o,T} + c_{r,T} + c_{o,s}^{\text{TLC}} + c_{r,s}^{\text{TLC}} = 2 c_{o}^*
\]  
(S-20)

where the equality is satisfied only with \( D_o = D_R \). The direct current from the bulk solution at quasisteady state is determined by the tip–substrate distance and the concentration of a tip-detected species at the exterior surface of a macroscopic substrate (eq S-15a or S-15b for the feedback or SG/TC mode, respectively). This surface concentration is seen by a tip as a bulk concentration at short tip–substrate distances (Figure S-2).
**Feedback Mode.** Eq 6 was obtained for quasi-steady-state $i_{T-E_S}$ voltammograms in the feedback mode as follows. The diffusion-limited reduction of species $O$ at the tip corresponds to $c_{O,T} = 0$ in eqs S-19 and S-20, which gives

$$i_{\text{t.c.}}(E_S, L) = \frac{2 \pi n F D_o c_0 a}{L(2 / \theta_s + 2 \theta_s^{\prime -1} / \lambda_0 + \xi^2 + 1)}$$  \hspace{1cm} (S-21)

The direct tip current from the bulk solution at quasi-steady state is related to the concentration of the original species $O$ at the exterior surface of the substrate (eq S-15a) as

$$i_{\text{bulk}}(E_S, L) = \frac{4 x n F D_o c_0 a \xi \theta_s}{\xi \theta_s + 1} f(L)$$  \hspace{1cm} (S-22)

where $f(L)$ represents the dependence of $i_{\text{bulk}}$ on the tip–substrate distance. The combination of eq S-18 with eqs S-21 and S-22 gives the tip current in the feedback mode, $i_{T,O}^{\text{fb}}(E_S, L)$, as

$$i_{T,O}^{\text{fb}}(E_S, L) = 4 x n F D_o c_0 a \left[ \frac{\pi}{2 x L(2 / \theta_s + 2 \theta_s^{\prime -1} / \lambda_0 + \xi^2 + 1)} + \frac{\xi \theta_s}{\xi \theta_s + 1} f(L) \right]$$  \hspace{1cm} (S-23)

Moreover, $f(L)$ is obtained from the diffusion-limited positive-feedback current at a tip, $I_{T,d}(L)$, using eq S-1 with $E_S \gg E^{\circ}$ as
\[ I_{\tau,d}(L) = \frac{i_{\tau,0}^{PB}(E_s \gg E^0', L)}{4xnFD_0c_0a} \]  \hspace{1cm} (S-24)

where eq S-23 gives

\[ i_{\tau,0}^{PB}(E_s \gg E^0', L) = 4xnFD_0c_0a \left[ \frac{\pi}{2xL(\xi^2 + 1)} + f(L) \right] \]  \hspace{1cm} (S-25)

The combination of eq S-24 with eq S-25 results in

\[ f(L) = I_{\tau,d}(L) - \frac{\pi}{2xL(\xi^2 + 1)} \]  \hspace{1cm} (S-26)

Therefore, eq S-23 is equivalent to

\[ i_{\tau,0}^{PB}(E_s, L) = 4xnFD_0c_0a \left\{ \frac{\pi}{2xL(2 / \theta_s + 2\theta_s^{\text{eq}} / \lambda_0' + \xi^2 + 1)} + \frac{\xi \theta_s}{\xi \theta_s + 1} \left[ I_{\tau,d}(L) - \frac{\pi}{2xL(\xi^2 + 1)} \right] \right\} \]  \hspace{1cm} (S-27)

The normalization of eq S-27 with respect to \( i_{\tau,m} \) (eq 1) gives eq 6.
SG/TC Mode. Eq 8 was derived for the SG/TC mode. When the substrate-generated species, R, is oxidized at the tip at a diffusion-limited rate, i.e., \( c_{R,T} = 0 \), the combination of eq S-19 with eq S-20 yields

\[
i_{NL,C}(E_s, L) = -\frac{2\pi a n F D_R \xi^2 c_o^*}{L(2\xi^2 \theta_s^2 + 2\theta_s^\alpha / \lambda_0 + \xi^2 + 1)} \tag{S-28}
\]

Also, the direct current from the bulk solution is given by the concentration of species R at the exterior substrate surface (eq S-15b) as

\[
i_{\text{bulk}}(E_s, L) = -\frac{4n F D_R \xi c_o^* a}{\xi \theta_s + 1} f(L) \tag{S-29}
\]

The combination of eq S-18 with eqs S-28 and S-29 gives the tip current in the SG/TC mode, \( i_{T,R}^{ST}(E_s, L) \), as

\[
i_{T,R}^{ST}(E_s, L) = -4n F D_R c_o^* a \left[ \frac{\pi \xi}{2xL(2\xi^2 \theta_s^2 + 2\theta_s^\alpha / \lambda_0 + \xi^2 + 1)} + \frac{f(L)}{\xi \theta_s + 1} \right] \tag{S-30}
\]

Now, \( f(L) \) is obtained as follows. When substrate potential is negative enough at \( E_s \ll E^a_0 \), eq S-30 is equivalent to the diffusion-limited tip current as
This diffusion-limited tip current is also obtained from eq S-1 as

\[ i_{T,R}^{ST}(E_s << E^o', L) = -4xnFD_r c_o^* a \xi \left[ \frac{\pi \xi}{2xL(\xi^2 + 1)} + f(L) \right] \]  
(S-31)

where eq S-15b with \( E_s << E^o' \) gives

\[ c_{R,S}^{ex} = \xi c_o^* \]  
(S-33)

The comparison of eq S-31 with eq S-32 yields

\[ f(L) = I_{T,d}(L) - \frac{\pi \xi}{2xL(\xi^2 + 1)} \]  
(S-34)

Overall, eq S-30 is equivalent to

\[ i_{T,R}^{ST}(E_s, L) = -4xnFD_o c_o^* a \left\{ \frac{\pi}{2xL(2z^2 \theta_s + 2\theta_o^o/\lambda_o^o + \xi^2 + 1)} + \frac{1}{\xi \theta_s + 1} \left[ I_{T,d}(L) - \frac{\pi}{2xL(\xi^2 + 1)} \right] \right\} \]  
(S-35)

Eq 8 is obtained by the normalization of eq S-35 with respect to \( i_{T,\infty} \) (eq 1).
Analytical Equations for Quasi-Steady-State $i_{T-E_S}$ Voltammograms for Species R (FcMeOH). Quasi-steady-state $i_{T-E_S}$ voltammograms for FcMeOH were analyzed using analytical equations as obtained when only species R is initially present in the solution. The corresponding tip current based on the oxidation of species R in the feedback mode is given as

$$I_{T,R}^{FB}(E_S, L) = \xi^2 \left\{ \frac{\pi}{2xL(2\xi^2 \theta_s + 2\theta_s^a / \lambda_0 + \xi^2 + 1)} + \frac{1}{\xi \theta_s + 1} \left[ \frac{I_{T,d}(L)}{\xi^2} - \frac{\pi}{2xL(\xi^2 + 1)} \right] \right\}$$

(S-36)

which is normalized with respect to

$$i_{T,w} = 4xnFD_R c^*_R a$$

(S-37)

where $c^*_R$ is the bulk concentration of species R. In the SG/TC mode, the normalized tip current based on the reduction of species O is equivalent to

$$I_{T,O}^{ST}(E_S, L) = -\xi^2 \left\{ \frac{\pi}{2xL(2/\theta_s + 2\theta_s^{-a^{-1}} / \lambda_0 + \xi^2 + 1)} + \frac{\xi \theta_s}{\xi \theta_s + 1} \left[ \frac{I_{T,d}(L)}{\xi} - \frac{\pi}{2xL(\xi^2 + 1)} \right] \right\}$$

(S-38)

Derivations of eqs S-36 and S-38 are very similar to those of eqs 6 and 8 (see above) except for the following points. In the former case, a positive current is based on the oxidation of the original mediator R. Accordingly, the signs in the flux balance in the TLC are chosen to yield
The bulk concentration of species R is used for mass balance in the TLC as

\[ i_{\text{TLC}}(E_s, L) \frac{(S-39)}{\pi a^2 nF} = k_L c_{O,S}^{\text{TLC}} - k_{O,S} c_{R,S}^{\text{TLC}} = \frac{D_O (c_{O,T} - c_{O,S}^{\text{TLC}})}{d} = \frac{D_R (c_{R,S}^{\text{TLC}} - c_{R,T})}{d} \]

where the equality is satisfied only with \( D_O = D_{\text{R,S}} \). Concentrations of redox mediators at the exterior surface of a substrate are given by the convolution principle as

\[ c_{O,T} + c_{R,T} + c_{O,S}^{\text{TLC}} + c_{R,S}^{\text{TLC}} = 2c^*_R \]  \hspace{1cm} (S-40)

\[ c_{O,S}^{\text{ex}} = \frac{\theta_S c^*_R}{\zeta \theta_S + 1} \] \hspace{1cm} (S-41a)

\[ c_{R,S}^{\text{ex}} = \frac{c^*_R}{\zeta \theta_S + 1} \] \hspace{1cm} (S-41b)
**Effects of Thermodynamic and Kinetic Parameters.** Figure S-6 show that a pair of quasi-steady-state $i_T$–$E_S$ voltammograms for a nearly reversible substrate reaction with $(\alpha, \lambda_0', E^0 \text{ mV}) = (0.5, 2, 0)$ is uniquely defined. Voltammograms with different combinations of the kinetic and thermodynamic parameters can be superimposed with each other either for the feedback or SG/TC mode. Voltammograms in the other operation mode, however, are very different.

![Figure S-6](image)

**Figure S-6.** Effect of kinetic ($\alpha$ and $\lambda_0'$) and thermodynamic ($E^0$) parameters on simulated quasi-steady-state $i_T$–$E_S$ voltammograms. A red curve with $(\alpha, \lambda_0', E^0 \text{ mV}) = (0.5, 2, 0)$ is superimposed with black and blue curves (a) for the feedback mode using $(0.2, 0.25, -30)$ and $(0.8, 10, 8)$, respectively, or (b) for the SG/TC mode using $(0.2, 12.5, -10)$ and $(0.8, 0.25, 30)$, respectively. Dotted lines represent reversible curves for $E^0 = 0 \text{ mV}$. 
**Tip Fabrication.** Approximately 0.5-μm-radius Pt tips with small \( RG \) of 1.5–2.5 were fabricated as reported elsewhere.\(^{5-10}\) A Pb-doped glass tube (o.d./i.d. = 1.5 mm/1.1 mm, 10 cm in length, Corning 8161, Warner Instruments, Hamden, CT) was used for tip insulation because of its high resistivity and slightly higher thermal expansion coefficient than that of Pt.\(^{5-11}\) The laser-based mechanical pulling of a glass-insulated Pt tip\(^{5-12,5-13}\) typically gave \( a \approx 0.1 \) μm and \( RG = 5 \) (Figure S-7a). The glass layer surrounding the pulled tip was heated over the Pt-coil heater of a microforge (MF-900, Narishige, Tokyo, Japan) to melt and retract from the tip (Figure S-7b). The exposition of the Pt tip from the thin glass layer was monitored in real time by using the high-magnification optical microscope of the microforge (×35 objective lens and ×15 eyepiece). The focused ion-beam (FIB) milling\(^{5-14}\) of the heat-annealed tip across the meniscus region of the glass layer gave a sharp tip with desirable inner and outer radii (Figure S-7c).

**Figure S-7.** SEM images of pulled, heat-annealed, and FIB-milled Pt tips (from left to right). Scale bars are 2 μm.
**Tip Characterization.** The inner and outer radii of each FIB-milled tip were estimated from its scanning electron microscopic and focused ion beam images.\textsuperscript{S-14} Due to slightly imperfect disk geometries of the metal and surrounding glass (Figure S-7c), apparent radii of a tip vary within ±10 % from average radii. The average values are consistent with values determined from approach curves to an insulating substrate,\textsuperscript{S-15} which agree very well with the corresponding theoretical curve\textsuperscript{S-16} (Figure S-8). Noticeably, a contact between the tip and the smooth glass substrate occurs at a very short distance of $L < 0.1$ ($L = 0.075$ and $d = 31$ nm for $RG = 2.3$ in Figure S-8). This result confirms that a FIB-milled tip is smooth and perpendicularly aligned with respect to the tip length.\textsuperscript{S-14}

![Graph](image_url)

**Figure S-8.** An SECM approach curve to a glass substrate (open circles) as obtained for 0.1 mM TCNQ in acetonitrile/0.1 M TBAClO\textsubscript{4} using a 0.42-μm-radius Pt tip with $RG = 2.3$ held at –0.1 V vs Ag. Probe scan rate, 22.5 nm/s. The solid line represents a theoretical approach curve to an insulator ($RG = 2.3$ in ref. S-16).
Interestingly, a positive approach curve with a sharp FIB-milled tip to a Pt substrate shows a dramatic and quick increase in the tip current due to their direct contact at a short tip–substrate distance ($L = 0.18$ and $d = 86$ nm in Figure S-9). This result indicates a direct contact between the flat Pt tip and the highest protrusion from the macroscopic Pt surface under the tip (the inset of Figure S-9), indicating the significant roughness of the substrate surface. Nevertheless, the excellent fit between experimental and theoretical approach curves for the Pt substrate demonstrates that the most region of the substrate surface under the tip is flat enough to give well defined tip–substrate distances.

Figure S-9. An SECM approach curve to a 2.5-mm-radius disk Pt electrode (open circles) as obtained for 0.5 mM FcMeOH in 0.2 M NaCl using a 0.48-µm-radius Pt tip with $RG = 1.5$. The tip and the substrate were held at 0.35 and 0 V vs Ag/AgCl, respectively. Probe scan rate, 15.0 nm/s. The solid line represents a theoretical approach curve to a conductor (eq S-3 from ref. S-1). The inset shows a scheme for a contact between the flat tip and the highest protrusion at the polished Pt substrate.
Observation of Current Spikes in $i_T$–$E_S$ Voltammograms. Numerous current spikes were observed for FcMeOH and TCNQ in feedback and SG/TC modes when a tip was positioned very close to a contact distance. For instance, $d = \sim 80$ nm is obtained from the limiting current in the $i_T$–$E_S$ voltammogram for TCNQ in the SG/TC mode as shown in Figure S-10. In this example, current spikes were observed on the reverse sweep of substrate potential. Some of the spikes at $-0.1 \, V < E_S < 0.0 \, V$ exceeded a measurable limit of $-1.2 \, nA$. We ascribe these current spikes to high tunneling current between the flat Pt tip and the protrusions at the rough Pt substrate (the inset of Figure S-9). Similar current spikes were observed in a tip voltammogram at a roughly polished Pt nanotip positioned above a smooth Au substrate.$^{12}$

Figure S-10. An $i_T$–$E_S$ voltammogram for 0.1 mM TCNQ in acetonitrile/0.1 M TBAClO$_4$ with a 2.5-mm-radius disk Pt electrode (red line) as obtained using a 0.51-µm-radius Pt tip with $RG = 2.0$ in the SG/TC mode. The tip was held at 0.2 V vs Ag. Substrate potential was cycled at 50 mV/s.
REFERENCES


(S-4) Ref S-2, pp 247.


