This model was developed in the following paper.

Kurapati, N.; Pathirathna, P.; Chen, R.; Amemiya, S. "Voltammetric measurement of adsorption isotherm for ferrocene derivatives on highly oriented pyrolytic graphite." *Anal. Chem.* **2018**, *90*, 13632.

This model is also applicable to the system discussed 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.

CV Model. A model for CV is based on the adsorption of a ferrocene derivative, FcXY, on HOPG, which proceeds its oxidation to Fc^+XY as given by

$$FcXY(aq) \rightleftharpoons FcXY(HOPG) \quad (1)$$

$$Fc^{\cdot}XY(aq) + e \rightleftharpoons FcXY(aq) \quad (2)$$

Diffusion equations for FcXY and Fc^+XY are given by

$$\frac{\partial c_i}{\partial t} = D\left(\frac{\partial^2 c_i}{\partial x^2}\right) \quad (3)$$

where the diffusion coefficient of FcXY, D, is equivalent to that of Fc^+XY, D_{Fc^+XY}. The rate of heterogeneous electron transfer, v_{et}, is given by the Butler-Volmer model as

$$v_{et} = k_{red} c_{Fc^+XY} - k_{ox} c_{FcXY} \quad (4)$$

with

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

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

where k_{red} and k_{ox} are oxidation and reduction rate constants, k_0 is the heterogeneous standard electron-transfer rate constant, α_{ET} is transfer coefficient, E is the HOPG potential, and $E^{0'}$ is the formal potential

of the redox couple. The substrate potential is cycled between E_{initial} and E_{λ} as the switching potential. The adsorption rate of FcXY, v_{ads}, is given phenomenologically by

$$v_{\text{ads}} = k_{\text{ads}} c_{\text{FcXY}} \left(\Gamma_s - \Gamma_{\text{FcXY}} \right) - k_{\text{des}} \Gamma_{\text{FcXY}} \tag{7}$$

with

$$k_{\text{ads}} = k_{\text{ads}}^0 \exp\left(2\alpha_{\text{ads}} g \Gamma_{\text{FcXY}} / RT \right) \tag{8}$$

$$k_{\text{ads}} = k_{\text{ads}}^0 \exp\left[-2\left(1 - \alpha_{\text{ads}} \right) g \Gamma_{\text{FcXY}} / RT \right] \tag{9}$$

$$g = g' RT / 2\Gamma_s \tag{10}$$

where k_{ads}^0 and k_{des}^0 are standard adsorption and desorption rate constant, Γ_{FcXY} is the surface concentration of FcXY, g is the energy of interaction between adsorbed molecules, and α_{ads} is a symmetry coefficient ($0 < \alpha_{\text{ads}} < 1$) regulating the effect of g on the adsorption activation barrier. Adsorption equilibrium is achieved at $t = 0$ to yield the Frumkin isotherm based on the Bragg–Williams approximation as given by

$$c_{\text{FcXY}} = \frac{\Gamma_{\text{FcXY}} / \Gamma_s}{\beta\left(1 - \Gamma_{\text{FcXY}} / \Gamma_s \right)} \exp\left(-g' \Gamma_{\text{FcXY}} / \Gamma_s \right) \tag{11}$$

where c_{FcXY} is the concentration of ferrocene derivatives near the HOPG surface, Γ_s is the saturated surface concentration of FcXY, and $\beta (= k_{\text{ads}}^0 / k_{\text{des}}^0)$ and g' are parameters characterizing the magnitude of ferrocene–HOPG and ferrocene–ferrocene interactions, respectively. Accordingly, boundary conditions at the substrate surface are given by

$$D\left[\frac{\partial c_{\text{FcXY}}}{\partial x} \right]_{x=0} = v_{\text{et}} - v_{\text{ads}} \tag{12}$$

$$D\left[\frac{\partial c_{\mathrm{Fc^+XY}}}{\partial x}\right]_{x=0} = -v_{\mathrm{et}} \tag{13}$$

$$\left[\frac{\partial \Gamma_{\mathrm{FcXY}}}{\partial t}\right] = v_{\mathrm{ads}} \tag{14}$$

Finally, a current response for CV, i, is given by

$$i = FS_{\mathrm{el}}v_{\mathrm{et}} \tag{15}$$

Dimensionless CV Model. The aforementioned diffusion problem was redefined by using dimensionless parameters and solved by using a commercial finite element simulation package, COMSOL Multiphysics 5.4 (COMSOL, Burlington, MA). Specifically, eq 3 yielded

$$\frac{\partial C_{\mathrm{i}}}{\partial \tau} = \left[\frac{\partial^2 C_{\mathrm{i}}}{\partial X^2}\right] \tag{16}$$

where

$$C_{\mathrm{i}} = c_{\mathrm{i}} / c_0 \tag{17}$$

$$\tau = Fvt / RT \tag{18}$$

$$X = x\sqrt{\frac{Fv}{RTD}} \tag{19}$$

Dimensionless parameters were also introduced for boundary conditions (eqs S-8–S-10) to obtain

$$\left[\frac{\partial C_{\mathrm{FcXY}}}{\partial X}\right]_{X=0} = V_{\mathrm{et}} - V_{\mathrm{ads}} \tag{12}$$

$$\left[\frac{\partial C_{\mathrm{Fc^+XY}}}{\partial Z}\right]_{X=0} = -V_{\mathrm{et}} \tag{13}$$

$$\left[\frac{\partial\theta_{\mathrm{FcXY}}}{\partial\tau}\right]=\frac{V_{\mathrm{ads}}}{K} \tag{14}$$

where

$$K=\frac{\Gamma_s}{c_0}\sqrt{\frac{Fv}{DRT}} \tag{15}$$

In these boundary conditions, the electron-transfer rate was normalized to yield

$$V_{\mathrm{et}}=\Lambda_{\mathrm{het}}\left[\left(\theta_{\mathrm{ET}}\right)^{-\alpha_{\mathrm{ET}}}C_{\mathrm{Fc^{+}XY}}-\left(\theta_{\mathrm{ET}}\right)^{1-\alpha_{\mathrm{ET}}}C_{\mathrm{FcXY}}\right] \tag{16}$$

with

$$\Lambda_{\mathrm{het}}=k_0\sqrt{\frac{RT}{DFv}} \tag{17}$$

The adsorption rate was given in the dimensionless form as

$$V_{\mathrm{ads}}=\Lambda_{\mathrm{ads}}\left(\theta_{\mathrm{ads}}\right)^{\alpha_{\mathrm{ads}}}C_{\mathrm{FcXY}}\left(1-\theta_{\mathrm{FcXY}}\right)-\Lambda_{\mathrm{dse}}\left(\theta_{\mathrm{ads}}\right)^{\alpha_{\mathrm{ads}}-1}\theta_{\mathrm{FcXY}} \tag{18}$$

with

$$\Lambda_{\mathrm{ads}}=k_{\mathrm{ads}}^{0}\Gamma_s\sqrt{\frac{RT}{DFv}} \tag{19}$$

$$\Lambda_{\mathrm{des}}=k_{\mathrm{des}}^{0}\frac{\Gamma_s}{c_0}\sqrt{\frac{RT}{DFv}} \tag{20}$$

Adsorption equilibrium was achieved at $t = 0$ to yield

$$\frac{\Lambda_{\mathrm{ads}}}{\Lambda_{\mathrm{des}}}=\frac{\theta_{\mathrm{FcXY}}}{1-\theta_{\mathrm{FcXY}}}\exp\left(-g'\theta_{\mathrm{FcXY}}\right) \tag{21}$$

Overall, V_{et} is equivalent to a normalized current response, I, to yield

$$I = V_{\text{et}} = \frac{i}{FS_{\text{el}}c_0}\sqrt{\frac{RT}{DFv}} \tag{22}$$

where $FS_{\text{el}}c_0\sqrt{DFv/RT}$ is a scaling factor and V_{et} = 0.4463 for a reversible CV without adsorption.

Table 1. Parameters Used in COMSOL and Dimensionless Models.

Parameters		Equation
COMSOL	Dimensionless Model	
Esw	$E_\lambda - E^0$	
Erange	$E_\lambda - E_{\text{initial}}$	
k0	$\Lambda_{\text{het}} = k_0\sqrt{\frac{RT}{DFv}}$	17
theta0	$K = \frac{\Gamma_s}{c_0}\sqrt{\frac{Fv}{DRT}}$	15
Lamda	$\frac{\Lambda_{\text{ads}}}{\Lambda_{\text{des}}}$	19 and 20
g	$g' = 2g\Gamma_s / RT$	10
kappa	$\Lambda_{\text{ads}} = k^0_{\text{ads}}\Gamma_s\sqrt{\frac{RT}{DFv}}$	19
alpha	α_{ET}	5 and 6
beta	α_{ads}	8 and 9
gamma	$D_{\text{Fc}^+\text{XY}} / D$	