

Supporting information for: Electrochemical Nonadiabatic Electron Transfer via Tunneling to Solution Species through Thin Insulating Films

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Mathematical Appendices

Table S1: Definition of Mathematical Symbols

Symbol	Typical Units	Definition
a	$\text{eV}^{-1/2} \text{Å}^{-1}$	Numerical factor $\left(\sqrt{\frac{2m_e}{\hbar^2}}\right)$
A/B		Terms in image charge corrections
α		Butler-Volmer transfer coefficient
β		Tunneling constant
C_{dl}	F	Double layer capacitance
C_I	F	Capacitance of insulating film
χ		Tunneling probability
E	V	Electrode Potential
$E^{0'}$	V	Formal reduction potential
E_{pzc}	V	Potential of zero charge
ϵ	eV	Energy vs. metal conduction band edge

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Table S1 – Continued from previous page.

Symbol	Typical Units	Definition
ϵ_F	eV	Fermi energy of metal
ϵ		Static dielectric constant
ϵ_0	F m ⁻¹	Vacuum permittivity
$f(\epsilon)$		Fermi-Dirac distribution
γ		Electron transfer “efficiency”
Γ	cm	Effective interaction distance
Γ^0	cm	$\Gamma(E = E^0)$
h	eV s	Planck’s constant
\hbar	eV s	Planck’s constant divided by 2π
$H(x)$		Heaviside step function
j	$\text{\AA}^{-2} \text{s}^{-1} \text{eV}^{-1} \text{sr}^{-1}$	Electron flux at electrode surface
k_1	s ⁻¹	Forward adiabatic rate
k_{-1}	s ⁻¹	Reverse adiabatic rate
k_2	s ⁻¹	Tunneling rate
$k_b T$	eV	Boltzmann’s constant times temperature
k_f/k_b	cm s ⁻¹	Forward/back heterogeneous rate constant
k_{OR}	s ⁻¹	Rate of $\text{O} + \text{e}^- \longrightarrow \text{R}$
k^0	cm s ⁻¹	Butler-Volmer heterogeneous rate constant
λ	eV	Reorganization energy
m_e	eV s ² \AA^{-2}	Electron mass
n^2		Optical dielectric constant
Ω	sr	Solid angle
P_{O^\ddagger}	eV ⁻¹	Distribution of O^\ddagger states in solution
ϕ	rad	Azimuthal angle of tunneling electron
$\bar{\varphi}$	eV	Average tunneling barrier height
q	C	Charge of one electron
ρ_F	eV ⁻¹ $\text{\AA}^{-3} \text{sr}^{-1}$	Fermi level density of states
R_k		Ratio of k_2/k_{-1}
r_{O}	\AA	Molecular radius of O/R
s	\AA	Distance from underlying electrode surface
σ	\AA^2	Molecular cross-section
θ	rad	Normal angle of tunneling electron
v_F	cm s ⁻¹	Fermi velocity

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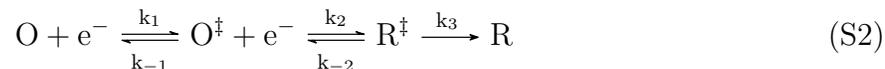
Table S1 – Continued from previous page.

Symbol	Typical Units	Definition
V_S	eV	Solvent conduction band edge
V_I	eV	Insulator conduction band edge
V_{ic}	eV	Image charge potential
V_O	eV	Potential of redox molecule
w	Å	Insulator thickness
z	Å	Distance from insulator surface
$[z : z]$	mol cm ⁻³	Concentration of electrolyte

General Rate Equations. Consider the general, outer sphere, 1 e⁻ transfer reaction:



where O and R are oxidized and reduced species, respectively. We will treat this reaction as being composed of several steps:



Here, O[‡]/R[‡] represent the transition state complex immediately before and after electron transfer. In general, the concentrations of these species are governed by a set of coupled differential equations:^{S1}

$$\frac{d[\text{O}]}{dt} = -k_1[\text{O}] + k_{-1}[\text{O}^\ddagger] \quad (\text{S3})$$

$$\frac{d[\text{O}^\ddagger]}{dt} = k_1[\text{O}] - (k_{-1} + k_2)[\text{O}^\ddagger] + k_{-2}[\text{R}^\ddagger] \quad (\text{S4})$$

$$\frac{d[\text{R}^\ddagger]}{dt} = k_2[\text{O}^\ddagger] - (k_{-2} + k_3)[\text{R}^\ddagger] \quad (\text{S5})$$

$$\frac{d[\text{R}]}{dt} = k_3[\text{R}^\ddagger] \quad (\text{S6})$$

By assuming quasi-steady state conditions ($\frac{d[\text{O}^\ddagger]}{dt} = \frac{d[\text{R}^\ddagger]}{dt} = 0$) these equations can be solved straightforwardly to yield an overall forward rate constant:

$$\frac{d[\text{R}]}{dt} = k_{\text{OR}}[\text{O}] = \left[\frac{k_1}{1 + \frac{k_{-1}}{k_2} \left(1 + \frac{k_{-2}}{k_3}\right)} \right] [\text{O}] \quad (\text{S7})$$

When $k_{-1} \approx k_3$ and $k_2 \approx k_{-2}$,^{S2} this simplifies to:

$$k_{\text{OR}} = \frac{k_1}{2 + \frac{k_{-1}}{k_2}} = k_1 \left(\frac{k_2}{2k_2 + k_{-1}} \right) \quad (\text{S8})$$

or, defining $R_k = \frac{k_2}{k_{-1}}$ and $\gamma = \frac{R_k}{1+2R_k}$:

$$k_{\text{OR}} = k_1 \left(\frac{R_k}{1 + 2R_k} \right) = \gamma k_1 \quad (\text{S9})$$

Here, γ can be regard as an ‘‘efficiency’’ for electron transfer.^{S3}

The overall forward rate, k_f (in cm s^{-1}), will be given by the following expression:

$$k_f(E) = \iint k_{\text{OR}}(\epsilon_{\text{O}}, E, z) d\epsilon_{\text{O}} dz = \iint \gamma(\epsilon_{\text{O}}, E, z) k_1(\epsilon_{\text{O}}) d\epsilon_{\text{O}} dz \quad (\text{S10})$$

Where ϵ_{O} denotes the energy of O in solution and E is the applied electrode potential (which is assumed to correspond to the Fermi energy of the metal electrode, ϵ_F). In order to treat variations in the overall rate with distance from the electrode surface, k_1 will be assumed to follow the typical expression of Marcus theory for a homogeneous reaction:^{S4}

$$k_1(\epsilon_{\text{O}}) = \frac{k_b T}{h} P_{\text{O}^\ddagger}(\epsilon_{\text{O}}) \quad (\text{S11})$$

$$P_{\text{O}^\ddagger}(\epsilon_{\text{O}}) = \frac{1}{\sqrt{4\pi\lambda k_b T}} e^{-\frac{(\epsilon_{\text{O}} - qE^{0'} - \lambda)^2}{4\lambda k_b T}} \quad (\text{S12})$$

Here, P_{O^\ddagger} represents the equilibrium distribution of O^\ddagger states in solution, q is the charge of one electron, $E^{0'}$ is the formal potential of the electrode reaction, and λ is the reorganization

energy of Marcus theory.

The Nonadiabatic Rate, k_2 . The electron transfer rate, k_2 , will be treated by calculating the tunneling rate between a metal electrode and $\text{O}^\ddagger/\text{R}^\ddagger$ with a particular energy ϵ in solution in close analogy with tunneling in Metal-Insulator-Metal (MIM) systems.^{S5,S6} Thus, k_2 will be written as:

$$k_2(\epsilon_O, E, z) = \iint j(\epsilon_M, \theta) \sigma(\epsilon_M) F(\epsilon_M, \epsilon_O) \chi(\epsilon_M, \theta, E, z) d\Omega d\epsilon_M \quad (\text{S13})$$

where F is a distribution function:

$$F(\epsilon_M, \epsilon_O) = \begin{cases} f(\epsilon_M) & \text{if } |\epsilon_M - \epsilon_O| < \Delta\epsilon \\ 0 & \text{otherwise} \end{cases} \quad (\text{S14})$$

$$f(\epsilon_M) = \frac{1}{1 + e^{\frac{\epsilon_M - \epsilon_F}{k_b T}}} \quad (\text{S15})$$

where f is the Fermi-Dirac distribution function and ϵ_F is the Fermi energy of electrons in the metal. The quantity $\Delta\epsilon$ accounts for the broadening of the O^\ddagger state in solution. This form for k_2 can be viewed as the product of (1) the rate at which electrons strike the electrode surface per unit area/time/energy/solid angle (j , in $\text{\AA}^{-2} \text{s}^{-1} \text{eV}^{-1} \text{sr}^{-1}$), (2) a molecular cross-section for electron capture (σ , in \AA^2), (3) energetic overlap between the metal conduction band and $\text{O}^\ddagger/\text{R}^\ddagger$ in solution (F , unitless), and (4) a probability for tunneling across insulator/solvent layers (χ , unitless).

This form for k_2 can be further simplified by assuming (1) electron transfer occurs from states in the metal where $\epsilon_M \approx \epsilon_F$ and (2) that $f(\epsilon_M)$ behaves as a step function.^{S7} Making these assumptions, Eq. (S13) simplifies to:

$$k_2(\epsilon_O, E, z) \approx 2\Delta\epsilon\sigma_F H(\epsilon_F - \epsilon_O) \int j_F(\theta) \chi_F(\theta, E, z) d\Omega \quad (\text{S16})$$

where $H(\epsilon_F - \epsilon_O)$ is the Heaviside step function^{S8} and a subscript F denotes a value taken at the Fermi energy of the metal electrode. $\Delta\epsilon$ will be taken as $\frac{\hbar k-1}{2}$, based on elementary uncertainty considerations.^{S1} σ will be treated simply as:

$$\sigma_F = \pi \left(r_O + \frac{\lambda_F}{2\pi} \right)^2 = \pi r_O^2 \left(1 + \frac{\hbar}{m_e v_F r_O} \right)^2 \quad (\text{S17})$$

where λ_F and v_F are taken to be the De Broglie wavelength and velocity of an electron at the Fermi energy, respectively. j will be treated as:

$$j_F(\theta) = \rho_F v_z(\theta) \quad (\text{S18})$$

where ρ_F is the electronic density of states at the Fermi energy of the metal electrode and v_z is the velocity normal to the electrode surface. Assuming an isotropic velocity distribution, This becomes:

$$j_F(\theta) = \rho_F v_F \cos \theta \quad (\text{S19})$$

The tunneling probability will be treated through the WKB-approximation of electron tunneling. In this picture, χ_F becomes:

$$\chi_F(\theta, E, z) = e^{-2a(w+z)(q\bar{V}(E,z)-\epsilon_z(\theta))^{1/2}} \quad (\text{S20})$$

where $\bar{V}(E, z)$ is the average potential through the insulator/solvent layers, w is the insulator thickness, z is the distance between the insulator surface and the redox molecule in solution, $\epsilon_z = \frac{1}{2}m_e v_F^2 \cos^2 \theta$ is the kinetic energy in the z direction, and a is a numerical constant $(\sqrt{\frac{2m_e}{\hbar^2}})$.

Using these expressions, k_2 can then be written as:

$$k_2(\epsilon_O, E, z) = \hbar k_{-1} \sigma_F \rho_F v_F H(\epsilon_F - \epsilon_O) \iint e^{-2a(w+z)(q\bar{V}(E,z) - \frac{1}{2}m_e v_F^2 \cos^2 \theta)^{1/2}} \sin \theta \cos \theta d\theta d\phi \quad (\text{S21})$$

$$k_2(\epsilon_O, E, z) = 2\pi \hbar k_{-1} \sigma_F \rho_F v_F H(\epsilon_F - \epsilon_O) \int_0^{\pi/2} e^{-2a(w+z)(q\bar{V}(E,z) - \frac{1}{2}m_e v_F^2 \cos^2 \theta)^{1/2}} \sin \theta \cos \theta d\theta \quad (\text{S22})$$

This integral (I) has a simple analytical solution:

$$I = \frac{1}{2a^2 m_e v_F^2 (w+z)^2} \left[\left(1 + 2a(w+z) \left[q\bar{V}(E, z) - \frac{1}{2}m_e v_F^2 \right]^{1/2} \right) e^{-2a(w+z)[q\bar{V}(E,z) - \frac{1}{2}m_e v_F^2]^{1/2}} - (1 + 2a(w+z)q\bar{V}(E, z)^{1/2}) e^{-2a(w+z)q\bar{V}(E,z)^{1/2}} \right] \quad (\text{S23})$$

which, for common values of \bar{V} and v_F (e.g., $\frac{1}{2}m_e v_F^2 \approx 4$ eV and \bar{V} 1-2 eV above this value) will simplify to:

$$I \approx \frac{1}{2a^2 m_e v_F^2 (w+z)^2} [1 + 2a(w+z)\bar{\varphi}(E, z)^{1/2}] e^{-2a(w+z)\bar{\varphi}(E,z)^{1/2}} \quad (\text{S24})$$

where $\bar{\varphi}(E, z) = q\bar{V}(E, z) - \frac{1}{2}m_e v_F^2$. The ratio $R_k = \frac{k_2}{k_{-1}}$ can then be expressed as:

$$R_k(\epsilon_O, E, z) = \frac{S \sigma_F H(\epsilon_F - \epsilon_O)}{(w+z)^2} [1 + \beta(E, z)] e^{-\beta(E,z)} \quad (\text{S25})$$

$$\beta(E, z) = 2a(w+z)\bar{\varphi}^{1/2}(E, z) \quad (\text{S26})$$

$$S = \frac{\pi \hbar \rho_F}{a^2 m_e v_F} \quad (\text{S27})$$

Final Rate Equations. The forward rate constant, k_f , can finally be written as:

$$k_f(E) = \iint \gamma(\epsilon_O, E, z) k_1(\epsilon_O) d\epsilon_O dz \quad (\text{S28})$$

$$\gamma(\epsilon_O, E, z) = \frac{R_k(\epsilon_O, E, z)}{1 + 2R_k(\epsilon_O, E, z)} \quad (\text{S29})$$

$$k_1(\epsilon_O) = \frac{k_b T}{h} P_{O^\ddagger}(\epsilon_O) = \frac{k_b T}{h} \frac{1}{\sqrt{4\pi\lambda k_b T}} e^{-\frac{(\epsilon_O - qE^{0'} - \lambda)^2}{4\lambda k_b T}} \quad (\text{S30})$$

This can be simplified to:

$$k_f(E) = \frac{k_b T}{h} \int_{-\infty}^{\epsilon_F} \frac{1}{\sqrt{4\pi\lambda k_b T}} e^{-\frac{(\epsilon_O - qE^{0'} - \lambda)^2}{4\lambda k_b T}} d\epsilon_O \int_{z_0}^{\infty} \gamma'(E, z) dz \quad (\text{S31})$$

where $\gamma'(E, z)$ refers to the γ of Eq. (S29) where H has been replaced by 1.^{S9} The first integral can be evaluated straightforwardly to yield:

$$k_f(E) = \frac{k_b T}{h} \Gamma(E) \left[\frac{1}{2} \operatorname{erfc} \left(\frac{\lambda + q(E - E^{0'})}{\sqrt{4\lambda k_b T}} \right) \right] \quad (\text{S32})$$

$$\Gamma(E) = \int_{r_O}^{\infty} \gamma'(E, z) dz \quad (\text{S33})$$

Here, it has been assumed that the distance of closest approach, z_0 , is equal to the molecular radius of O, r_O . An equivalent form for k_b naturally follows:

$$k_b(E) = \frac{k_b T}{h} \Gamma(E) \left[\frac{1}{2} \operatorname{erfc} \left(\frac{\lambda - q(E - E^{0'})}{\sqrt{4\lambda k_b T}} \right) \right] \quad (\text{S34})$$

Equivalent Butler-Volmer Expressions. The derived forms for $k_f(E)/k_b(E)$ given in Eqs. (S32) and (S34) can be shown to agree with the classical Butler-Volmer formalism for

electrode kinetics at low overpotentials:

$$k_f = k^0 e^{-\frac{\alpha q(E-E^{0'})}{k_b T}} \quad (\text{S35})$$

$$k_b = k^0 e^{\frac{(1-\alpha)q(E-E^{0'})}{k_b T}} \quad (\text{S36})$$

where k^0 is the standard heterogeneous rate constant and α is the transfer coefficient.

Eq. (S32) can be brought into an equivalent form by noting:

$$\text{erfc}(a+x) \approx \frac{1}{\sqrt{\pi}(a+x)} e^{-(a+x)^2} \quad (\text{S37})$$

for $a+x > 2$ ($q(E-E^{0'}) > 2\sqrt{4\lambda k_b T} - \lambda$). For $x \approx 0$ ($|q(E-E^{0'})| < 0.1\lambda$), this simplifies further to:

$$\text{erfc}(a+x) \approx \frac{1}{\sqrt{\pi}a} e^{-(a+x)^2} \quad (\text{S38})$$

Both of the above conditions are met under typical conditions when $|E-E^{0'}| < 50$ mV.

Applying this to Eq. (S32), one obtains:

$$k_f(E) \approx \frac{(k_b T)^{3/2}}{h(\pi\lambda)^{1/2}} \Gamma(E) e^{-\frac{(\lambda+q(E-E^{0'}))^2}{4\lambda k_b T}} \quad (\text{S39})$$

The Butler-Volmer parameters k^0 and α are then:

$$k^0 = \frac{(k_b T)^{3/2}}{h(\pi\lambda)^{1/2}} \Gamma^0 e^{-\frac{\lambda}{4k_b T}} \quad (\text{S40})$$

$$\alpha(E) = \frac{1}{2} + \frac{q(E-E^{0'})}{2\lambda} - \frac{k_b T}{q\Gamma(E)} \frac{\partial \Gamma(E)}{\partial E} \quad (\text{S41})$$

where $\Gamma^0 = \Gamma(E = E^{0'})$.

Assumed Potential Profile for Tunneling in MIS Systems. The general form for the tunneling profile assumed in the treatment of $\bar{V}(E, z)$, the average potential through the

barrier/solvent layers, is given in Fig. S1. $\bar{V}(E, z)$ is calculated as:

$$\bar{V}(E, z) = \frac{1}{w+z} \int_0^{w+z} V(E, s) ds \quad (\text{S42})$$

$$V(E, s) = \begin{cases} V_I + \frac{(\Delta\Phi + q(E - E^{0'}))s}{w} + V_{ic}^I(s) + V_O^I(s) & s \leq w \\ V_S + \Delta\Phi + q(E - E^{0'}) + V_{ic}^S(s) + V_O^S(s) & s > w \end{cases} \quad (\text{S43})$$

Here, V_I/V_S are the conduction band edges of the insulator/solvent, $\Delta\Phi = \Phi_M - qE^{0'}$, the difference between the metal work function and the standard reduction potential, and V_{ic}/V_O refer to the potentials felt due to the image charge of the electron and the charge on the redox species in solution, respectively. Superscripts denote potentials felt in the insulating film (I) and solvent (S). The inclusion of V_{ic} and V_O significantly affect the potential felt by the tunneling electron, and are responsible for the barrier height going to zero at s equal to ca. 2, 10, (V_{ic}) and 17 Å (V_O) in Fig. S1. Changing the applied potential alters the linear component of the potential profile within the insulating layer. Analytical expressions for V_{ic} can be written as:

$$V_{ic}^I(s) = -\frac{q^2}{4\pi n_I^2 \epsilon_0} \left[\frac{1}{2s} + \sum_{i=1}^{\infty} A^i \left(\frac{iw}{i^2 w^2 - s^2} - \frac{1}{iw} \right) \right] \quad (\text{S44})$$

$$V_{ic}^S(s) = -\frac{q^2}{4\pi n_S^2 \epsilon_0} \left[-\frac{A}{2(s-w)} + \frac{B_+ B_-}{2} \sum_{i=1}^{\infty} \frac{A^{i-1}}{(i-1)w + s} \right] \quad (\text{S45})$$

$$A = \frac{n_S^2 - n_I^2}{n_S^2 + n_I^2} \quad B_+ = \frac{2n_S^2}{n_S^2 + n_I^2} \quad B_- = \frac{2n_I^2}{n_S^2 + n_I^2} \quad (\text{S46})$$

where n_I^2/n_S^2 refer to the optical dielectric constants of the insulator/solvent, respectively. The potential due to the charge on the redox molecule must also be taken into account. For

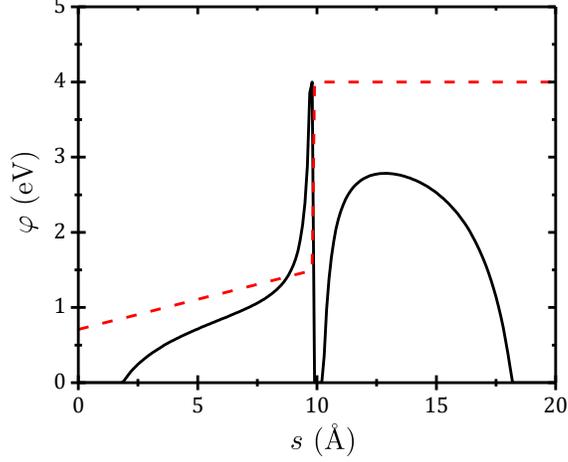


Figure S1: Example barrier height ($\varphi = V(s) - \frac{1}{2}m_e v_F^2$) profile for tunneling in an MIS system. The calculation of φ was made for the Ta_2O_5 -FcMeOH system with $w = z = 10 \text{ \AA}$ and $q(E - E^{0'}) = -100 \text{ mV}$. The black line shows the full calculation according to Eq. (S43), while the red dashed line shows the same calculation omitting V_{ic} and V_O .

the oxidation of a neutral species (i.e., $\text{R} \longrightarrow \text{O}^+ + \text{e}^-$), this potential can be calculated as:

$$V_{\text{O}}^I(s) = \frac{q}{4\pi n_I^2 \varepsilon_0} \sum_{i=1}^{\infty} B_- A^{i-1} \left[\frac{2s}{(z + w^{2i-1})^2 - s^2} \right] \quad (\text{S47})$$

$$V_{\text{O}}^S(s) = \frac{q}{4\pi n_S^2 \varepsilon_0} \left[\frac{1}{z - s + w} + \frac{A}{z + s - w} - B_+ B_- \sum_{i=1}^{\infty} A^{i-1} \left(\frac{1}{z + s + w^{2i-1}} \right) \right] \quad (\text{S48})$$

Calculation of Outer Sphere Reorganization Energy for MIS Systems. In the present treatment, only the outer sphere contribution to the reorganization energy will be considered. For the case of a redox molecule with radius r_{O} positioned at a distance z from a bare electrode surface, this reorganization energy (λ) assumes the well known form:^{S10}

$$\lambda(z) = \frac{q^2}{8\pi \varepsilon_0} \left(\frac{1}{r_{\text{O}}} - \frac{1}{2z} \right) \left(\frac{1}{n_s^2} - \frac{1}{\varepsilon_S} \right) \quad (\text{S49})$$

In the present MIS system, where the electrode surface is modified by an insulating film, this expression must be modified. The modified expression can be found to be:

$$\lambda(z) = \frac{q^2}{8\pi\epsilon_0} \left[\frac{1}{r_0} \left(\frac{1}{n_s^2} - \frac{1}{\epsilon_s} \right) + \frac{1}{2z} \left(\frac{A^{n^2}}{n_s^2} - \frac{A^\epsilon}{\epsilon_s} \right) - \frac{B_+^{n^2} B_-^{n^2}}{2n_s^2} \sum_{i=1}^{\infty} \frac{(A^{n^2})^{i-1}}{z + iw} + \frac{B_+^\epsilon B_-^\epsilon}{2\epsilon_s} \sum_{i=1}^{\infty} \frac{(A^\epsilon)^{i-1}}{z + iw} \right] \quad (\text{S50})$$

Here, the factors A and B_+/B_- refer to the same expressions given in Eq. (S46), where the superscript n^2/ϵ refer to the optical or static dielectric constants being employed in the calculation. It can be seen easily that in the limit of a metal film ($A \rightarrow -1$, $B_+/B_- \rightarrow 0$), this expression agrees with that of Eq. (S49). For simplicity, the reorganization will be taken to be a constant evaluated at $z = r_0$, the assumed distance of closest approach.

Estimation of Film Thicknesses from Differential Capacitance. The measured differential capacitance (C , in $\mu\text{F cm}^{-2}$) of the electrode can be related to the thickness of an insulating film (w) via:

$$\frac{1}{C} = \frac{1}{C_I} + \frac{1}{C_{dl}} \quad (\text{S51})$$

$$C_I = \frac{\epsilon_I \epsilon_0}{w} \quad (\text{S52})$$

$$w = \epsilon_I \epsilon_0 \left(\frac{1}{C} - \frac{1}{C_{dl}} \right) \quad (\text{S53})$$

where C_I is the capacitance of the insulator and C_{dl} is the differential capacitance of the electrical double layer, which can be treated through Guoy-Chapman theory:^{S10}

$$C_{dl} = \sqrt{\frac{2z^2 q^2 \epsilon_s \epsilon_0 [z : z]}{k_b T}} \cosh \left[\frac{zq(E - E_{pzc})}{2k_b T} \right] \quad (\text{S54})$$

which is valid for a symmetric, or “ $z : z$ ” electrolyte. Here, z is the charge on the electrolyte, ϵ_s is the static dielectric constant of the solvent, $[z : z]$ is the electrolyte concentration (in

cm^{-3}), and E_{pzc} is the potential of zero charge for the electrode. The rough approximation will be made here that the value of C_{dl} at $E = E_{pzc}$ will be appropriate. w can then be estimated from the measured capacitance as:

$$w = \varepsilon_I \varepsilon_0 \left(\frac{1}{C} - \sqrt{\frac{k_b T}{2z^2 q^2 \varepsilon_S \varepsilon_0 [z : z]}} \right) \quad (\text{S55})$$

References

- (S1) Marcus, R. *The Journal of Chemical Physics* **1956**, *24*, 966–978.
- (S2) Since the electron transfer is assumed to occur isoenergetically, $\Delta G_2 = -T\Delta S_2 = -k_b T \ln \frac{\Omega_{R^\ddagger}}{\Omega_{O^\ddagger}}$, where Ω denotes the number of configurations of the system before or after electron transfer. From the equilibrium constant, one can then write $K_2 = \frac{k_2}{k_{-2}} = \frac{\Omega_{R^\ddagger}}{\Omega_{O^\ddagger}}$. Typically, $\Omega_{O^\ddagger} \approx \Omega_{R^\ddagger}$ and thus $k_2 \approx k_{-2}$.
- (S3) It is obvious from this expression that γ varies between 0 and 1/2. This can be considered an artifact of treating the reaction scheme as a multi-step process, where a transition complex with a given lifetime is first created followed by electron transfer. In this picture, in the limit of $k_2 \gg k_{-1}$, the reaction complex would rapidly “tautomerize” between the O^\ddagger and R^\ddagger states before the complex was destroyed.
- (S4) Savéant, J. M. *Journal of Physical Chemistry B* **2002**, *106*, 9387–9395.
- (S5) Simmons, J. G. *Journal of Applied Physics* **1963**, *34*, 1793–1803.
- (S6) Chazalviel, J.; Allongue, P. *Journal of the American Chemical Society* **2011**, *133*, 762–764.
- (S7) The former approximation would be formally justified in the limit of an infinitely sharp distribution function P_{O^\ddagger} . Both (1) and (2) would be effectively satisfied at low T . At common experimental temperatures, (1) is a much more drastic approximation.

(S8) $H(x) = 1$ for $x \geq 0$, and 0 otherwise.

(S9) I.e., consider the integral involving $H(a - x)$ and some other function $f(x)$:

$$\int_{-\infty}^{\infty} f(x)H(a - x)dx = \int_{-\infty}^a f(x)dx.$$

(S10) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*, 2nd ed.; Wiley, 2001.