Supporting Information

Electrochemistry at a Metal Nanoparticle on a Tunneling Film: A Steady-State Model of Current Densities at a Tunneling Ultramicroelectrode

Caleb M. Hill, Jiyeon Kim, and Allen J. Bard*

Center for Electrochemistry, Department of Chemistry, The University of Texas at Austin, Austin, Texas, 78712

Koutecký-Levich Approach to Relating Steady State Current Densities

The classic Koutecký-Levich approach, almost always reserved for rotating disk electrode (RDE) studies,[1] can be derived for a UME and a one electron reduction (O + e^- → R) with irreversible kinetics by assuming the system in question satisfies both relations:

$$j = Fm_O\left[C_O^* - C_{O,x=0}\right]$$
$$j = Fk^0 C_{O,x=0} e^{-\alpha f(E-E^{0'})} \qquad \text{S1}$$

where F is the Faraday, m_O the mass transfer coefficient of O, C_O^* the bulk concentration of O, $C_{O,x=0}$ the concentration of O at the electrode surface, k^0 the standard rate constant of the reaction, α the transfer coefficient, E the applied potential, $E^{0'}$ the formal potential of the reaction, and $f = \frac{F}{RT} = \frac{q}{k_b T}$. By defining a mass transfer limited current density, j_{mt}, one can write:

$$j_{mt} = Fm_O C_O^*$$
$$\frac{j}{j_{mt}} = \frac{C_O^* - C_{O,x=0}}{C_O^*} = 1 - \frac{C_{O,x=0}}{C_O^*} \qquad \text{S2}$$
$$C_{O,x=0} = C_O^*\left(1 - \frac{j}{j_{mt}}\right)$$

Plugging this expression for $C_{O,x=0}$ into the second expression in S1 yields:

$$j = Fk^0 C_O^* \left(1 - \frac{j}{j_{mt}}\right) e^{-\alpha f(E - E^{0'})} \qquad \text{S3}$$

Defining a kinetic limiting current density, $j_{et} = Fk^0 C_O^* e^{-\alpha f(E - E^{0'})}$, and rearranging yields Equation S4 (Equation 2 in the main text):

$$\frac{1}{j} = \frac{1}{j_{et}} + \frac{1}{j_{mt}} \qquad \text{S4}$$

Simmons Model for Tunneling in Planar Metal-Insulator-Metal (MIM) Structures

Following Simmons, a general form for the tunneling current from metal 1 to metal 2 in a planar MIM structure can be written as:[2,3]

$$j_f = q \iiint v_x \rho_1 f_1(E)[1 - f_2(E - q\eta)] P_t(E_x) d^3\boldsymbol{k} \qquad \text{S5}$$

where q is the elementary charge, $v_x\rho_1$ is a velocity-weighted density of states (DOS) in metal 1, η is the applied overpotential (bias), f_1/f_2 represent the probability of a state with momentum $\boldsymbol{k}$ being occupied in metal 1/2 according to Fermi-Dirac statistics, and P_t is the probability of tunneling through the barrier. According to free electron theory, the DOS of metal 1, ρ_1, can be expressed as:

$$\rho_1 = \frac{1}{4\pi^3} \qquad \text{S6}$$

which is unitless in k-space (cm^{-3} wavevector^{-3}). The velocity weighted DOS, $v_x\rho_1$, is then:

$$v_x = \frac{1}{\hbar}\frac{dE_x}{dk_x}$$

$$v_x\rho_1 = \frac{1}{2\pi^2 h}\frac{dE_x}{dk_x} \qquad \text{S7}$$

The form of j_f given in Equation S5 can then be expressed in terms of energy by decomposing **k** into parallel ($\mathbf{k_x}$) and "transverse" ($\mathbf{k_t}$) components:

$$E = E_x + E_t = \frac{\hbar^2}{2m}(k_x^2 + k_t^2)$$

$$k_t^2 = k_y^2 + k_z^2 \qquad \text{S8}$$

$$d^3\boldsymbol{k} = k_t dk_x dk_t d\theta_t = \frac{m}{\hbar^2} dk_x dE_t d\theta_t$$

Combining terms, j_f is then:

$$j_f = \frac{2qm}{h^3} \iiint f_1(E)[1 - f_2(E - q\eta)]P_t(E_x)dE_x dE_t d\theta_t \qquad \text{S9}$$

When the geometry is symmetric with respect to θ_t, j_f can be integrated to yield:

$$j_f = \frac{4\pi qm}{h^3} \iint f_1(E)[1 - f_2(E - q\eta)]P_t(E_x)dE_x dE_t \qquad \text{S10}$$

The measured current density (J) is then the difference between the forward and reverse current densities:

$$J = j_f - j_b = \frac{4\pi qm}{h^3} \iint [f_1(E) - f_2(E - q\eta)]P_t(E_x)dE_x dE_t \qquad \text{S11}$$

According to Fermi-Dirac statistics, the probability of occupation for an electronic state in a metal with energy E is:

$$f(E) = \frac{1}{1 + e^{\frac{E - E_F}{k_b T}}} \qquad \text{S12}$$

At 0 K, $f(E)$ effectively becomes a step function:

$$f(E) = \begin{cases} 1, & E \le E_F \\ 0, & E > E_F \end{cases} \qquad \text{S13}$$

Equation S11 can then be simplified to:[4]

$$J = \frac{4\pi qm}{h^3}\left[\int_0^{E_F+q\eta} P_t dE_x \int_{E_F+q\eta-E_x}^{E_F-E_x} dE_t + \int_{E_F+q\eta}^{E_F} P_t dE_x \int_0^{E_F-E_x} dE_t\right]$$

$$J = \frac{4\pi qm}{h^3}\left[-q\eta \int_0^{E_F+q\eta} P_t dE_x + \int_{E_F+q\eta}^{E_F} (E_F - E_x) P_t dE_x\right] \quad \text{S14}$$

The tunneling probability, P_t, is taken to be:

$$P_t = e^{-2\beta_t w}$$

$$\beta_t = \left[\frac{2m(\bar{E}_b - E_x)}{\hbar^2}\right]^{1/2} \quad \text{S15}$$

$$\bar{E}_b = E_b + \frac{q\eta}{2}$$

where E_b is the energy level of the tunneling barrier (the conduction band edge in the case of electron tunneling through a semiconductor layer such as TiO_2). The Simmons model treats the trapezoidal tunneling barrier as a rectangular barrier with an average potential, $\bar{E}_b$. It should also be noted that the absence of any prefactor before the exponential in Equation S15 implies the WKB approximation is being invoked, which is formally valid only when the tunneling barrier potential varies slowly with x.[5] Taking this form of P_t and making the substitution $A = 2w\left(\frac{2m}{\hbar^2}\right)^{1/2}$, J then becomes:

$$J = \frac{4\pi qm}{h^3}[I_1 + I_2 + I_3]$$

$$I_1 = -q\eta \int_0^{E_F+q\eta} e^{-A(\bar{E}_b - E_x)^{1/2}} dE_x \quad \text{S16}$$

$$I_2 = E_F \int_{E_F+q\eta}^{E_F} e^{-A(\bar{E}_b - E_x)^{1/2}} dE_x$$

$$I_3 = -\int_{E_F+q\eta}^{E_F} E_x e^{-A(\bar{E}_b - E_x)^{1/2}}\, dE_x$$

Each of these integrals can be evaluated in a straightforward manner through integration by parts to yield:

$$I_1 = -\frac{2q\eta}{A^2}\left\{\left[1 + A(\bar{E}_b - E_F - q\eta)^{1/2}\right]e^{-A(\bar{E}_b - E_F - q\eta)^{1/2}} - \left[1 + A\bar{E}_b^{1/2}\right]e^{-A\bar{E}_b^{1/2}}\right\}$$

$$I_2 = \frac{2E_F}{A^2}\left\{\left[1 + A(\bar{E}_b - E_F)^{1/2}\right]e^{-A(\bar{E}_b - E_F)^{1/2}} - \left[1 + A(\bar{E}_b - E_F - q\eta)^{1/2}\right]e^{-A(\bar{E}_b - E_F - q\eta)^{1/2}}\right\}$$

$$I_3 = \left\{\frac{2e^{-A(\bar{E}_b - E_x)^{1/2}}}{A^4}\left[A^3 E_x(\bar{E}_b - E_x)^{1/2} + A^2(3E_x - 2\bar{E}_b) - 6A(\bar{E}_b - E_x)^{1/2} - 6\right]\right\}\Bigg|_{E_F}^{E_F+q\eta} \quad \text{S17}$$

I_1 can be simplified by noting that $e^{-A(\bar{E}_b - E_F - q\eta)^{1/2}} \gg e^{-A\bar{E}_b^{1/2}}$ for typical parameter values (i.e., $\bar{E}_b - E_F \approx 1$ eV and $A \approx 10$ eV$^{-1/2}$):

$$I_1 = -\frac{2q\eta}{A^2}\left[1 + A(\bar{E}_b - E_F - q\eta)^{1/2}\right]e^{-A(\bar{E}_b - E_F - q\eta)^{1/2}} \quad \text{S18}$$

I_3 can be simplified by truncating the expression inside the brackets to include the A^3 and A^2 terms only. I_3 can then be evaluated to yield:

$$I_3 = \frac{2}{A^2}\left\{\left[3E_F + 3q\eta - 2\bar{E}_b + A(E_F + q\eta)(\bar{E}_b - E_F - q\eta)^{1/2}\right]e^{-A(\bar{E}_b - E_F - q\eta)^{1/2}} - \left[3E_F - 2\bar{E}_b + AE_F(\bar{E}_b - E_F)^{1/2}\right]e^{-A(\bar{E}_b - E_F)^{1/2}}\right\} \quad \text{S19}$$

J can then be evaluated:

$$J = \frac{16\pi qm}{A^2h^3}\left[(\bar{E}_b - E_F)e^{-A(\bar{E}_b-E_F)^{1/2}} - (\bar{E}_b - E_F - q\eta)e^{-A(\bar{E}_b-E_F-q\eta)^{1/2}}\right] \qquad \text{S20}$$

Making the substitutions $\varphi = \bar{E}_b - E_F - \frac{q\eta}{2}$ and $A = 2aw$, one arrives at the famous result of Simmons:

$$J = \frac{q}{2\pi hw^2}\left[\left(\varphi + \frac{q\eta}{2}\right)e^{-2a\left(\varphi+\frac{q\eta}{2}\right)^{1/2}w} - \left(\varphi - \frac{q\eta}{2}\right)e^{-2a\left(\varphi-\frac{q\eta}{2}\right)^{1/2}w}\right]$$

$$a = \left(\frac{2m}{\hbar^2}\right)^{1/2} \approx 0.512\ \text{eV}^{-1/2}\ \text{Å}^{-1} \qquad \text{S21}$$

A linear J-η relation can be found for small overpotentials. This can be done by assuming η is small and finding $\left(\varphi + \frac{q\eta}{2}\right)^{1/2} \approx \varphi^{1/2}\left(1 + \frac{q\eta}{4\varphi}\right)$ through series expansion. Substitution into the above expression for J and simplification yields:

$$J_{lin} = \frac{q}{2\pi hw^2}e^{-2a\varphi^{1/2}w}\left[\left(\varphi + \frac{q\eta}{2}\right)e^{-\frac{awq\eta}{2\varphi^{1/2}}} - \left(\varphi - \frac{q\eta}{2}\right)e^{\frac{awq\eta}{2\varphi^{1/2}}}\right] \qquad \text{S22}$$

Expanding the exponentials ($e^{c\eta} \approx 1 + c\eta$) and simplifying results in:

$$J_{lin} = \frac{q^2\eta}{2\pi hw^2}e^{-2a\varphi^{1/2}w}\left[1 - a\varphi^{1/2}w\right] \qquad \text{S23}$$

When $a\varphi^{1/2}w \gg 1$, this simplifies to:

$$J_{lin} = -\eta\left(\frac{aq^2}{2\pi h}\right)\frac{\varphi^{1/2}}{w}e^{-2a\varphi^{1/2}w} \qquad \text{S24}$$

Geometric Correction to the TUME System

The tunneling current between a portion of the UME surface, *dA*, and the NP will be assumed to follow Equation S24. The tunneling current in the TUME system is then:

$$i_{tun} = \iint J_{lin} r dr d\theta = 2\pi \int_0^{r_0} J_{lin} r dr \qquad \text{S25}$$

where the variation in tunneling distance with *r*, $w(r) = w_0 + r_0 - (r_0^2 - r^2)^{1/2}$, has been incorporated into J_{lin}. Substituting for J_{lin} and simplifying results in:

$$i_{tun} = -\eta \left(\frac{aq^2 \varphi^{1/2}}{h} \right) e^{-2a\varphi^{1/2}(w_0 + r_0)} \int_0^{r_0} \frac{r e^{2a\varphi^{1/2}(r_0^2 - r^2)^{1/2}}}{w_0 + r_0 - (r_0^2 - r^2)^{1/2}} dr \qquad \text{S26}$$

Making the substitution $u = (r_0^2 - r^2)^{1/2}$:

$$i_{tun} = -\eta \left(\frac{aq^2 \varphi^{1/2}}{h} \right) e^{-2a\varphi^{1/2}(w_0 + r_0)} \int_0^{r_0} \frac{u e^{2a\varphi^{1/2} u}}{w_0 + r_0 - u} du \qquad \text{S27}$$

The integral (χ) in Equation 27 can be separated further:

$$\chi = \int_0^{r_0} \frac{u e^{2a\varphi^{1/2} u}}{w_0 + r_0 - u} du = -\int_0^{r_0} \left[1 + \frac{w_0 + r_0}{u - w_0 - r_0} \right] e^{2a\varphi^{1/2} u} du$$

$$\chi = -\int_0^{r_0} e^{2a\varphi^{1/2} u} du - (w_0 + r_0) \int_0^{r_0} \frac{e^{2a\varphi^{1/2} u}}{u - w_0 - r_0} du \qquad \text{S28}$$

Letting $v = u - w_0 - r_0$:

$$\chi = -\int_0^{r_0} e^{2a\varphi^{1/2} u} du - (w_0 + r_0) \int_{-(w_0 + r_0)}^{r_0 - (w_0 + r_0)} \frac{e^{2a\varphi^{1/2}(v + w_0 + r_0)}}{v} dv$$

$$\chi = -\int_0^{r_0} e^{2a\varphi^{1/2} u} du - (w_0 + r_0) e^{2a\varphi^{1/2}(w_0 + r_0)} \int_{-(w_0 + r_0)}^{-w_0} \frac{e^{2a\varphi^{1/2} v}}{v} dv \qquad \text{S29}$$

Yet another substitution, $t = -2a\varphi^{1/2} v$, yields

$$\chi = -\int_0^{r_0} e^{2a\varphi^{1/2} u} du - (w_0 + r_0) e^{2a\varphi^{1/2}(w_0 + r_0)} \int_{2a\varphi^{1/2}(w_0 + r_0)}^{2a\varphi^{1/2} w_0} \frac{e^{-t}}{t} dt \qquad \text{S30}$$

$$\chi = -\int_0^{r_0} e^{2a\varphi^{1/2}u} du - (w_0 + r_0)e^{2a\varphi^{1/2}(w_0+r_0)} \left[\int_{2a\varphi^{1/2}(w_0+r_0)}^{\infty} \frac{e^{-t}}{t} dt - \int_{2a\varphi^{1/2}w_0}^{\infty} \frac{e^{-t}}{t} dt \right]$$

The first integral can be integrated directly to give:

$$\chi = \frac{1}{2a\varphi^{1/2}} \left[1 - e^{2a\varphi^{1/2}r_0}\right] - (w_0 + r_0)e^{2a\varphi^{1/2}(w_0+r_0)} \left[\int_{2a\varphi^{1/2}(w_0+r_0)}^{\infty} \frac{e^{-t}}{t} dt - \int_{2a\varphi^{1/2}w_0}^{\infty} \frac{e^{-t}}{t} dt \right] \qquad \text{S31}$$

The other two integrals are "exponential integrals" of the form:

$$E_1(x) = \int_x^{\infty} \frac{e^{-t}}{t} dt \qquad \text{S32}$$

χ can then be rewritten as:

$$\chi = \frac{1}{2a\varphi^{1/2}} \left\{1 - e^{2a\varphi^{1/2}r_0} + 2a\varphi^{1/2}(w_0 + r_0)e^{2a\varphi^{1/2}(w_0+r_0)} \left[E_1(2a\varphi^{1/2}w_0) - E_1(2a\varphi^{1/2}[w_0 + r_0])\right]\right\} \qquad \text{S33}$$

For typical parameter values, this can be further simplified to:

$$\chi = \frac{e^{2a\varphi^{1/2}r_0}}{2a\varphi^{1/2}} \left\{2a\varphi^{1/2}(w_0 + r_0)e^{2a\varphi^{1/2}w_0} E_1\left(2a\varphi^{1/2}w_0\right) - 1\right\} \qquad \text{S34}$$

since $E_1(2a\varphi^{1/2}w_0) \gg E_1(2a\varphi^{1/2}[w_0 + r_0])$ and $e^{2a\varphi^{1/2}r_0} \gg 1$. A simple analytical form for E_1 is then desired over typical values for $2a\varphi^{1/2}w_0$. For $2a\varphi^{1/2} \approx 1$ Å^{-1} and 1 Å $< w_0 <$ 100 Å, an approximation for E_1 over the range $1 < x < 100$ would suffice. This can be accomplished by fitting E_1 over by a function of the form:[6]

$$E_1(x) = \frac{e^{-x}}{x} \left(\frac{p_0 + p_1 x + p_2 x^2 + p_3 x^3 + \cdots}{q_0 + q_1 x + q_2 x^2 + q_3 x^3 + \cdots} \right) \qquad \text{S35}$$

A simple two parameter fit is sufficient for the desired accuracy level over the range considered (ca. 1 % error):

$$E_1(x) = \frac{e^{-x}}{x}\left(\frac{x + 0.486}{x + 1.451}\right) \qquad \text{S36}$$

Incorporating this into χ yields:

$$\chi = \frac{e^{2a\varphi^{1/2}r_0}}{2a\varphi^{1/2}}\left[\frac{w_0 + r_0}{w_0}\left(\frac{2a\varphi^{1/2}w_0 + 0.486}{2a\varphi^{1/2}w_0 + 1.451}\right) - 1\right] \qquad \text{S37}$$

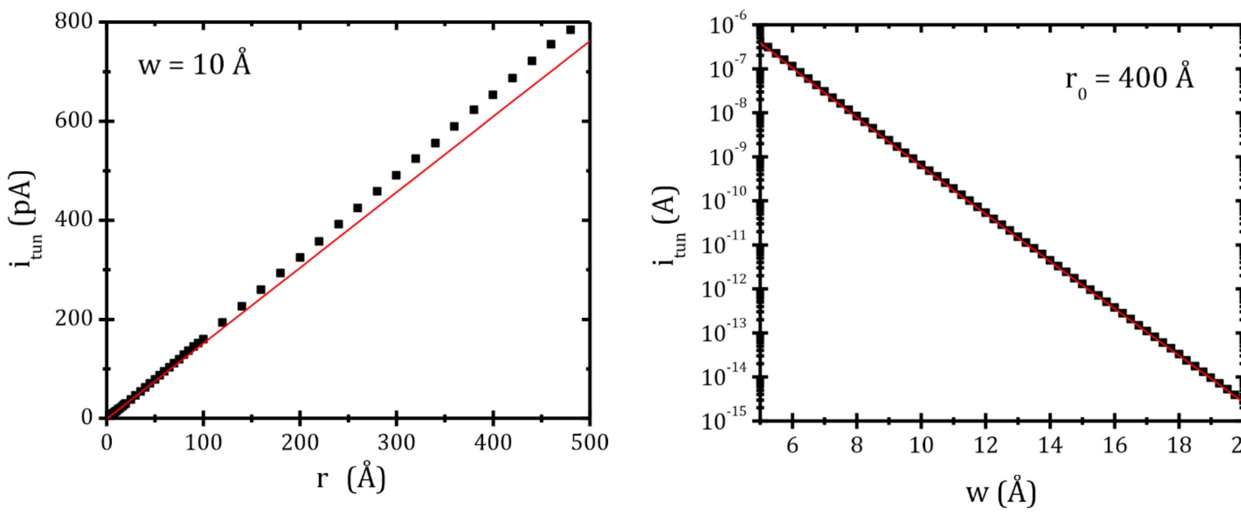

Figure S1. Comparison of the analytical approximation of i_{tun} (red line) to numerical calculations including full angular resolution of tunneling between the electrode and NP (black points) for various values of r_0 and w_0. φ = 1.3eV, η = −100 mV.

Finally, i_{tun} is then:

$$i_{tun} = -\frac{q^2\eta}{2h}\left[\frac{w_0 + r_0}{w_0}\left(\frac{2a\varphi^{1/2}w_0 + 0.486}{2a\varphi^{1/2}w_0 + 1.451}\right) - 1\right]e^{-2a\varphi^{1/2}w_0} \qquad \text{S38}$$

Or, if normalized by the NP area:

$$j_{tun} = \frac{i_{tun}}{4\pi r_0^2} = -\frac{q^2\eta}{8\pi h r_0^2}\left[\frac{w_0 + r_0}{w_0}\left(\frac{2a\varphi^{1/2}w_0 + 0.486}{2a\varphi^{1/2}w_0 + 1.451}\right) - 1\right]e^{-2a\varphi^{1/2}w_0} \qquad \text{S39}$$

The validity of this approximate form for j_{tun} was checked by comparing calculated values to numerical calculations which account explicitly for the dependence of tunneling distance on the angle of the exiting electron path:

$$J(r) = \frac{2mq}{h^3} \iiint [f_1(E) - f_2(E - q\eta)]\, P_t(E, \theta, \phi, r) E \sin 2\theta \; dE d\theta d\phi$$

$$P_t(E, \theta, \phi, r) = e^{-2a w_t(\theta,\phi,r)\left[E_b + \frac{q\eta}{2} - E\cos^2\theta\right]^{1/2}} \qquad \text{S41}$$

$$w_t(\theta, \phi, r) = \{\gamma(\theta, \phi, r) - [\gamma(\theta, \phi, r)^2 - r^2 - w_0^2 - 2r_0 w_0]\} \cos\theta$$

$$\gamma(\theta, \phi, r) = r \sin\theta \cos\phi + (w_0 + r_0)\cos\theta$$

The results are summarized in **Figure S1**. Over the range of interest, the derived analytical form of i_{tun} was found to deviate less than 10 % from the numerical calculations.

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1. Bard, A. J.; Faulkner, L. R., Electrochemical Methods, Fundamentals and Applications, 2nd ed.; John Wiley & Sons: New York, 2001; p 341.
2. Simmons, J. G. Generalized Formula for the Electric Tunnel Effect between Similar Electrodes Separated by a Thin Insulating Film. *J. Appl. Phys.* **1963**, *34*, 1793.
3. Wolf, E.L. *Principles of Tunneling Spectroscopy*, 2nd ed.; Oxford University Press, New York, 2012.
4. This is due to the fact that for a negative overpotential, $f(E) - f(E - q\eta)$ will be 1 when $(E_F + q\eta) < E \leq E_F$ and 0 otherwise.
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6. Tseng, P. H.; Lee, T. C. Numerical Evaluation of Exponential Integral: Theis Well Function Approximation. *J. Hydrol.* **1998**, *205*, 38.