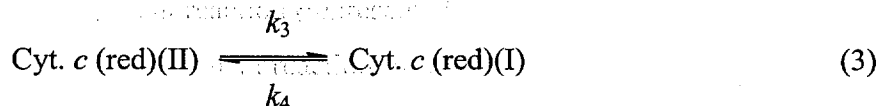
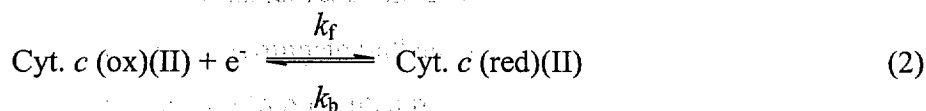
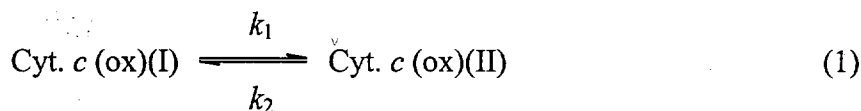


April 6 #34

Supplemental Material

In the proposed model, the electron transfer reaction (2) between the electrode and cyt. *c* (which is immobilized on the carboxylic acid terminated-alkanethiol SAM) follows a preceding configurational rearrangement reaction (represented by reaction (1)), and is in turn followed by a second configurational rearrangement reaction (represented by the reaction (3)). Reaction (1) represents the configurational rearrangement reaction from the binding form (binding complex, which is energetically the most stable form) to the form which facilitates the most efficient ET pathway (ET complex). Reaction (2) represents the ET reaction. Reaction (3) represents the configurational rearrangement from the ET complex to the binding complex.



It is assumed that the surface binding energies of Cyt. *c* (ox)(I) and Cyt. *c* (ox)(II) are equal to those of Cyt. *c* (red)(I) and Cyt. *c* (red)(II), respectively. This assumption is justified on the basis that the binding between the lysine residues and the carboxylate group on the SAM is electrostatic, which is a short range force, and that the effect of the oxidation states of Cyt. *c* would be insignificant. Therefore, it is reasonable to assume that the equilibria of reactions (1) and (3) are symmetrical and that $k_1 = k_4$ and $k_2 = k_3$.

At the equilibrium condition

$$(\Gamma_2/\Gamma_1) = (k_1/k_2) \text{ and } (\Gamma_4/\Gamma_3) = (k_3/k_4) = (k_2/k_1) \quad (4)$$

$$(I_2/I_1) = (I_3/I_4) \quad (5)$$

where I represents the surface concentration and subscripts 1, 2, 3 and 4 represent Cyt. *c* (ox)(I), Cyt. *c* (ox)(II), Cyt. *c* (red)(II) and Cyt. *c* (red)(I), respectively.

At the formal potential of the ET reaction (2)

$$E = E^{\circ'}$$

$$I_1 + I_2 = I_3 + I_4, \quad I_2 = I_3 \text{ and } I_1 = I_4 \quad (6)$$

The transfer coefficient of the ET reaction given by eq. (2) is very close to 0.5

$$k_f = k_s \exp [(-F/2RT)(E - E^{\circ'})] \quad (7a)$$

$$k_b = k_s \exp [(F/2RT)(E - E^{\circ'})] \quad (7b)$$

where k_s is the standard ET reaction rate constant at the binding site between cyt. *c* and the carboxylate at the formal potential.

The ET rate constant at the terminal is given by the Marcus expression

$$k_s = k_{(n=0)} \exp (-\beta n) \quad (8)$$

where $k_{(n=0)}$ represent the ET rate constant at the binding site at the alkanethiol terminus with alkyl chains having no methylene groups.

The electrode potential is modulated by ac at the formal potential of the reaction (2) with the amplitude of ΔE_{ac}

$$E - E^{\circ'} = \eta = \Delta E_{ac} e^{j\omega t}$$

where $j = (-1)^{1/2}$ and ω is the angular frequency of modulation.

When $(F/2RT)\eta \ll 1$, equations (7a) and (7b) can be written as

$$k_f = k_s (1 - \eta F/2RT) \quad (9a)$$

$$k_b = k_s (1 + \eta F/2RT) \quad (9b)$$

The material balance caused by the potential modulation (angular velocity ω and potential η at

the formal potential) is given by the following equations

$$d\Gamma_1/dt = -k_1\Gamma_1 + k_2\Gamma_2 \quad (10a)$$

$$d\Gamma_2/dt = -d\Gamma_1/dt - (k_f\Gamma_2 - k_b\Gamma_3) \quad (10b)$$

$$d\Gamma_3/dt = k_f\Gamma_2 - k_b\Gamma_3 - k_3\Gamma_3 + k_4\Gamma_4 = k_f\Gamma_2 - k_b\Gamma_3 - d\Gamma_4/dt = k_f\Gamma_2 - k_b\Gamma_3 - d\Gamma_1/dt \quad (10c)$$

$$d\Gamma_4/dt = k_3\Gamma_3 - k_4\Gamma_4 = k_2\Gamma_2 - k_1\Gamma_1 = d\Gamma_1/dt \quad (10d)$$

The variation in the surface concentrations of 1, 2 and 3 are given by eqs. (11-a, -b, -c) when the electrode potential is modulated by ac with the amplitude of ΔE_{ac} at E^0

$$\Gamma_1 = \Gamma_1^{dc} + \Gamma_1^{ac}(t) = \Gamma_1^{dc} + A_1 e^{j\omega t} \quad (11a)$$

$$\Gamma_2 = \Gamma_2^{dc} + \Gamma_2^{ac}(t) = \Gamma_2^{dc} + A_2 e^{j\omega t} \quad (11b)$$

$$\Gamma_3 = \Gamma_3^{dc} + \Gamma_3^{ac}(t) = \Gamma_3^{dc} + A_3 e^{j\omega t} \quad (11c)$$

where superscript "dc" represents the dc component, "ac" represents the ac component, and A_1 , A_2 and A_3 are time independent terms.

Substituting eqs. (11-a, -b, and -c) into eqs. (10-a, -b and -c) yields the following equations

$$d\Gamma_1^{ac}/dt = -k_1\Gamma_1^{ac} + k_2\Gamma_2^{ac} \quad (12a)$$

$$d\Gamma_2^{ac}/dt = -d\Gamma_1^{ac}/dt - d\Gamma_3^{ac}/dt = k_1\Gamma_1^{ac} - k_2\Gamma_2^{ac} - k_f\Gamma_2 + k_b\Gamma_3 \quad (12b)$$

$$\begin{aligned} d\Gamma_3^{ac}/dt &= k_f\Gamma_2 - k_b\Gamma_3 + (k_1\Gamma_1^{ac} - k_2\Gamma_2^{ac}) \\ &= k_s(\Gamma_2 - \Gamma_3) - k_s(\eta F/2RT)(\Gamma_2 + \Gamma_3) + (k_1\Gamma_1^{ac} - k_2\Gamma_2^{ac}) \end{aligned} \quad (12c)$$

Substitution of eqs. (11-a, -b, -c) after differentiation into eqs. (12-a, -b, -c) yields eqs. (13-a, -b and -c). At $E = E^0$, $\Gamma_2 = \Gamma_3$ since $\Gamma^{dc} \gg \Gamma^{ac}$.

$$j\omega A_1 e^{j\omega t} = -k_1 A_1 e^{j\omega t} + k_2 A_2 e^{j\omega t} \quad (13a)$$

$$j\omega A_2 e^{j\omega t} = k_1 A_1 e^{j\omega t} - k_2 A_2 e^{j\omega t} - k_s A_2 e^{j\omega t} + k_s A_3 e^{j\omega t} + (k_s F \Delta E_{ac} e^{j\omega t} / 2RT)(\Gamma_2 + \Gamma_3) \quad (13b)$$

$$j\omega A_3 e^{j\omega t} = k_s A_2 e^{j\omega t} - k_s A_3 e^{j\omega t} - (k_s F \Delta E_{ac} e^{j\omega t} / 2RT)(\Gamma_2 + \Gamma_3) + k_1 A_1 e^{j\omega t} - k_2 A_2 e^{j\omega t} \quad (13c)$$

$$j\omega A_1 = -k_1 A_1 + k_2 A_2 \quad A_1 = \{k_2/(k_1 + j\omega)\} A_2 \quad (14a)$$

$$j\omega A_2 = -j\omega A_3 - 2j\omega A_1 \quad (14b)$$

$$j\omega A_3 = k_s A_2 - k_s A_3 - (k_s F \Delta E_{ac} / 2RT)(\Gamma_2 + \Gamma_3) + k_1 A_1 - k_2 A_2$$

$$= k_s A_2 - k_s A_3 - (k_s F \Delta E_{ac} / 2RT)(\Gamma_2 + \Gamma_3) - j\omega A_1 \quad (14c)$$

$$K = \{k_2/(k_1 + j\omega)\} \quad (15)$$

$$A_1 = K A_2 \quad (16a)$$

$$A_2 = -A_3 - 2A_1 = -A_3 - 2K A_2$$

$$A_2 = -A_3 / (1 + 2K) \quad (16b)$$

$$A_1 = -K A_3 / (1 + 2K) \quad (16a')$$

Substituting eqs. (16-a and -b) into eq. (14c) yields

$$j\omega A_3 = k_s A_2 - k_s A_3 - (k_s F \Delta E_{ac} / 2RT)(\Gamma_2 + \Gamma_3) - j\omega A_1$$

$$= -k_s A_3 / (1 + 2K) - k_s A_3 - (k_s F \Delta E_{ac} / 2RT)(\Gamma_2 + \Gamma_3) + j\omega K A_3 / (1 + 2K) \quad (17)$$

$$A_3 \{j\omega + k_s / (1 + 2K) + k_s - j\omega K / (1 + 2K)\} = - (k_s F \Delta E_{ac} / 2RT)(\Gamma_2 + \Gamma_3) \quad (18)$$

$$A_3 = (k_s F \Delta E_{ac} / 2RT) (\Gamma_2 + \Gamma_3) \xi(k_s, k_1, k_2, \omega) \quad (19)$$

$$\xi(k_s, k_1, k_2, \omega) = 1 / \{j\omega + k_s / (1 + 2K) + k_s - j\omega K / (1 + 2K)\}$$

The ac current, i_{ac} , can be represented by eq. (20) because $k_f \Gamma_2 - k_b \Gamma_3 \gg d\Gamma_1/dt$, so that

$$d\Gamma_3/dt \approx k_f \Gamma_2 - k_b \Gamma_3$$

$$i_{ac} = F d\Gamma_3/dt = F d\Gamma_3^{ac}/dt = j\omega A_3 F e^{j\omega t} = i_{ac}^o e^{j\omega t} \quad (20)$$

then

$$i_{ac}^o = j\omega A_3 F = j\omega (k_s F^2 \Delta E_{ac} / 2RT)(\Gamma_2 + \Gamma_3) \xi(k_1, k_2, k_s, \omega) \quad (21)$$

$$i_{ac}^o / \Delta E_{ac} = (R_{et} + 1/j\omega C_a)^{-1} \quad (22).$$

By combining eqs. (21) and (22)

$$(R_{et} + 1/j\omega C_a) = \Delta E_{ac}/i_{ac}^0 = (2RT/k_s F^2)/(\Gamma_2 + \Gamma_3) \{j\omega \xi(k_1, k_2, k_s, \omega)\} \quad (23)$$

$$1/j\omega \xi(k_1, k_2, k_s, \omega) = \{j\omega + k_s/(1 + 2K) + k_s - j\omega K/(1 + 2K)\}/j\omega \quad (24)$$

$$\begin{aligned} 1/\xi(k_1, k_2, k_s, \omega) &= j\omega + k_s/(1 + 2K) + k_s - j\omega K/(1 + 2K) = j\omega + k_s + (k_s - j\omega K)/(1 + 2K) \\ &= [(j\omega + k_s)(1 + 2K) + (k_s - j\omega K)]/(1 + 2K) = [j\omega + k_s + 2j\omega K + 2Kk_s + k_s - j\omega K]/(1 + 2K) \\ &= [j\omega + 2k_s + K(2k_s + j\omega)]/(1 + 2K) \\ &= \{j\omega(2k_s + k_1 + k_2) + 2k_s(k_1 + k_2) - \omega^2\}/(k_1 + 2k_2 + j\omega) \end{aligned} \quad (25).$$

Then

$$\begin{aligned} 1/j\omega \xi(k_1, k_2, k_s, \omega) &= \{j\omega(2k_s + k_1 + k_2) + 2k_s(k_1 + k_2) - \omega^2\}/j\omega(k_1 + 2k_2 + j\omega) \\ &= \{j\omega(2k_s + k_1 + k_2) + 2k_s(k_1 + k_2) - \omega^2\}/\{j\omega(k_1 + 2k_2) - \omega^2\} \end{aligned} \quad (26).$$

Usually, the rate constants k_s , k_1 and $k_2 \gg \omega^2$

$$1/j\omega \xi(k_1, k_2, k_s, \omega) = \{j\omega(2k_s + k_1 + k_2) + 2k_s(k_1 + k_2)\}/j\omega(k_1 + 2k_2) \quad (26')$$

Substituting eq. (26') into eq. (23)

$$(R_{et} + 1/j\omega C_a) = 2RT/\{k_s F^2(\Gamma_2 + \Gamma_3) j\omega \xi(k_1, k_2, k_s, \omega)\} \quad (27).$$

At $E = E^0$, $\Gamma_2 = \Gamma_3$ since $\Gamma^{dc} \gg \Gamma^{ac}$, $\Gamma_2 + \Gamma_3 = 2\Gamma_2$

$$(R_{et} + 1/j\omega C_a) = RT/\{j\omega k_s F^2 \Gamma_2 \xi(k_1, k_2, k_s, \omega)\} \quad (27').$$

Substituting eq. (26') and $\Gamma_2 = \Gamma/2(1 + k_2/k_1)$ into eq. (27')

$$(R_{et} + 1/j\omega C_a) = (2RT/k_s F^2 \Gamma) \{(k_1 + k_2)/k_1\} \{(2k_s + k_1 + k_2)/(k_1 + 2k_2) + 2k_s(k_1 + k_2)/j\omega(k_1 + 2k_2)\} \quad (28).$$

From eq. (28), one can obtain R_{et} and C_a

$$R_{et} = (2RT/k_s \Gamma F^2) \{(k_1 + k_2)(2k_s + k_1 + k_2)/k_1(k_1 + 2k_2)\} \quad (29).$$

The apparent charge transfer rate constant k_{app} is defined by eq. (30)

$$R_{et} = (2RT/\Gamma_t F^2)(1/k_{app}) \quad (30)$$

$$k_{app} = k_s k_1 (k_1 + 2k_2) / \{(k_1 + k_2)(2k_s + k_1 + k_2)\} \quad (31)$$

and the capacitive component is given by eq. (32)

$$1/C_a = (2RT/\Gamma_t F^2)[2(k_1 + k_2)^2 / \{k_1(k_1 + 2k_2)\}] \quad (32).$$

For the ET reaction through short alkyl chains (i.e., when the ET rate is limited by the preceding configurational rearrangement reaction), it is reasonable to assume that $k_s \gg k_1, k_2$ and $k_1 \gg k_2$

$$\begin{aligned} k_{app} &= k_s k_1 (k_1 + 2k_2) / \{(k_1 + k_2)(2k_s + k_1 + k_2)\} \\ &= k_1 k_s (k_1 + 2k_2) / \{2k_s (k_1 + k_2)\} = k_1/2 \end{aligned} \quad (33).$$

For the ET reaction through long alkyl chains (i.e., when the ET rate is limited by the ET resistance through the alkyl chain), it is reasonable to assume that $k_1, k_2 \gg k_s$

$$\begin{aligned} k_{app} &= k_s k_1 (k_1 + 2k_2) / \{(k_1 + k_2)(2k_s + k_1 + k_2)\} = k_s k_1 (k_1 + 2k_2) / (k_1 + k_2)^2 \\ &= k_s [\{1 + 2(k_2/k_1)\} / \{1 + (k_2/k_1)\}^2] \end{aligned} \quad (34)$$

$$\ln k_{app} = \ln \{1 + 2(k_2/k_1)\} - 2 \ln (1 + k_2/k_1) + \ln k_{(n=0)} - n\beta - (r - r_o)\beta_r \quad (35).$$