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DETERMINATION OF THE REARRANGEMENT ENERGY BY USING TUNNEL ELECTRODE

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An expression of the potential dependence of cathodic current at an n-type semiconductor tunnel electrode is derived. By applying a tunnel electrode, the rearrangement energy can be determined without ambiguity from the plot of the transfer coefficient against electrode potential.

When a highly doped n-type semiconductor is used as an electrode, tunneling of electrons through the space charge layer sometimes contributes significantly in the current,[1] so that such an electrode can be a new useful means for elucidating electron transfer mechanisms in polar solvents. This communication presents an expression of the dependence of the cathodic tunnel current on the electrode, by means of which the rearrangement energy can be determined.

The cathodic tunnel current density at a potential more positive than the flat band potential is given by[2]

$$i_c = -e\, C_{ox}\, \Delta x \int W_{if}(\varepsilon)\rho(\varepsilon)f(\varepsilon)\, d\varepsilon \qquad (1)$$

where C_{ox} is the number of oxidant devided by the volume of the solution, Δx is the effective length for the electron transfer, e is the elementary charge, W_{if} represents the transition probability per unit time, $\rho(\varepsilon)$ is the state density of the conduction band, $f(\varepsilon)$ is the Fermi distribution function, and ε is the energy of electron. In a highly doped n-type semiconductor, the carriers are in a degenerate state and the Fermi level is located near the bottom of the conduction band, so we can approximate $\rho(\varepsilon)f(\varepsilon)$ as follows:

$$\rho(\varepsilon)f(\varepsilon) = N\, \delta(\varepsilon + eV) \qquad (2)$$

where N is the number of carriers in the semiconductor, $\delta(\varepsilon)$ is the Dirac-delta function, and V is the electrode potential. By inserting Eq(2) into Eq(1), we have

$$i_c = -e\, C_{ox}\, \Delta x\, N\, W_{if}(-eV) \qquad (3)$$

Thus the cathodic current directly reflects the transition probability $W_{if}(-eV)$ in contradistinction to the anodic tunnel current in which the electron transfer processes from the reductant to various vacant levels of the conduction band are involved. Hence, only the cathodic tunnel current is dealt with in the present work.

The transition probability W_{if} is derived on the basis of the harmonic approximation for the solvent polarization, the linear approximation for the interaction between the solvent and the electron,[3] and the high temperature approximation.[4] Thus

$$W_{if}(-eV) = \frac{(2\pi)^2}{h} |\langle\phi_i'|V_{int}|\phi_f\rangle|^2 Pr(V) \left(\frac{1}{4\pi kT\lambda_s}\right)^{\frac{1}{2}} \exp\left[-\frac{(-eV + eV_0 - \lambda_s)^2}{4kT\lambda_s}\right] \quad (4)$$

where λ_s is the rearrangement energy, V_0 is the equilibrium electrode potential, ϕ_i' and ϕ_f respectively represent the electronic wave function at the semiconductor surface and that in the ion, V_{int} represents the interaction which causes the electron transfer, and Pr represents the tunnel probability through the space charge layer in the semiconductor. With the WKB[6] approximation and the Schottky type barrier, the tunnel probability Pr is given by

$$Pr(V) = \exp\left[-\frac{4\pi}{h}\left(\frac{m^*\varepsilon_{sc}\varepsilon_0}{n}\right)^{\frac{1}{2}}(V - V_{fb})\right] \quad (5)$$

where m* is the effective mass of the electron, n is the number of carriers per volume of the semiconductor, ε_{sc} is the relative permittivity of the semiconductor, ε_0 is the permittivity of vacuum, and V_{fb} denotes the flat band potential. Therefore, the final expression for the cathodic tunnel current is written as

$$i_c = -\frac{(2\pi)^2}{h} e C_{ox} \Delta x N |\langle\phi_i'|V_{int}|\phi_f\rangle|^2 \left(\frac{1}{4\pi kT\lambda_s}\right)^{\frac{1}{2}} \exp\left[-\frac{(-eV + eV_0 - \lambda_s)^2}{4kT\lambda_s}\right]$$
$$\times \exp\left[-\frac{4\pi}{h}\left(\frac{m^*\varepsilon_{sc}\varepsilon_0}{n}\right)^{\frac{1}{2}}(V - V_{fb})\right] \quad (6)$$

The matrix element, $\langle\phi_i'|V_{int}|\phi_f\rangle$, strongly depends on the shape and height of the barrier in the Helmholtz layer. At the tunnel electrode the variation of the field strength at the electrode surface is small, so the potential barrier in the Helmholtz layer is independent of the electrode potential. Then, the transfer coefficient is given by

$$\alpha = \frac{kT}{e}\frac{4\pi}{h}\left(\frac{m^*\varepsilon_{sc}\varepsilon_0}{n}\right)^{\frac{1}{2}} + \frac{eV - eV_0 + \lambda_s}{2\lambda_s} \quad (7)$$

Eq(7) indicates that α - V plot is a straight line with the slope of $e/2\lambda_s$ and shifts upward with the decrease in n. We can thus obtain the rearrangement energy λ_s from the slope of the experimental α - V plot. Hitherto, the rearrangement energy has been estimated from the electron transfer rate by assuming the transmission coefficient to be unity.[5] However, this assumption is not always adequate, so the quantitative estimation of λ_s has been very difficult. On the other hand, by using a tunnel electrode, the value of λ_s can be determined without ambiguity. Since the small tunnel probability ensures that the cathodic current is not limited by diffusion even at a high overvoltage, it will be possible to elucidate the electron transfer mechanism in a wide potential range by utilizing a tunnel electrode.

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