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An interpretation of small values of transfer coefficient at conducting polymers

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Abstract

The electrochemical oxidation of electronically conducting polymers has shown values of the anodic transfer coefficient closed to zero at the Tafel equation rather than 0.5. This experimental result is interpreted in this report as a difference between the ionic conductance in the reactant with the neutral state and the electric conductance in the product with the polaron state. Since the electric conductance generates a lower electric field for the charged activated complex than the ionic conductance in the reaction coordinate, it compels the activated complex to move less toward the reactant than toward the product. The asymmetry of the activation potential hill makes the anodic transfer coefficient small. This concept is demonstrated by use of the Langevin equation for the activated complex at the activation energy hill. The transfer coefficient is expressed in terms of the thermal fluctuation the conductance, and the current density. The Tafel plot deviates convexly from a straight line, and depends on applied potential, as is consistent with experimental results.

key words: conducting polymers, transfer coefficient, Tafel plot, activated complex, conductance

1. Introduction

Attractive features of conjugated conducting polymers are not only exhibition of intrinsically electrical conduction but also the coupling of the conduction state with the redox state [1]. Consequently, a redox reaction alters the conduction state. When conducting polymers are formed on an electrode, their conduction state can be controlled by the electrochemical potential [2], exemplified by the polyaniline film in which the semi-conducting state of the neutral leucoemeraldine is oxidized to the electrically conducting state at the threshold potential of ca. 0.2 V vs. SCE [3].

When a conducting polymer with the insulating state is switched electrochemically into the conducting state in sufficient concentrations of dopant ion, the conducting zone grows clearly from the electrode at the expense of the insulating domain [4-11]. The growth occurs in the direction normal to the electrode. However, it is rarely noticed at conventionally electropolymerized films because of poor spatial resolution of the conducting species in the direction normal to the film surface. A very thick film has allowed us to observe the growth from the electrode [7]. The growth can readily be observed at a self-standing conducting film, one end of which is connected with an electrode on an insulating substrate [6]. When the film is not uniform, the growth occurs like nuclei formation [12]. Detection techniques used include chronoamperometry [8], cyclic voltammetry [13], time-variation of absorbance [9], microband arrays [14], and optical array detectors [15,16]. The growth is caused by the successive conversion of the insulating zone to the conducting zone by electrochemical oxidation, starting from the electrode|film interface toward the film|solution interface [8,17,18]. This concept has been suggested by Lacroix and Diaz [19] before these detailed experimental results. It has been realized theoretically from a view point of mass transport [11,13,20].

Since the propagation is caused by the electrode reaction, propagation rate should be

related with the electrode reaction rate, as has been demonstrated with the linear relationship between the propagation rate and the current [9]. The rate is predicted to be expressed by the Tafel or the Butler-Volmer equation. When the Tafel type equation was applied to the relation between the propagation rate and the electrode potential, the transfer coefficient evaluated from the plot of the logarithms of propagation rate against the applied potential was close to 0.1 for polypyrrole [8,21] as well as polyaniline [4,5]. This value is extraordinarily small in comparison with conventional values close to 0.5 [22]. The small value suggests asymmetry of the potential dependence in the oxidation and the reduction. More precisely, the energy profile for the activated complex along the reaction coordinate should be asymmetric, with a less slope toward the oxidized state than the reduced state, as illustrated in Fig.1. Since a medium with higher conduction generates a lower electric field, the asymmetry is expected to be ascribed to difference in conduction between the two phases.

Heterogeneous electrode kinetics for one-step one-electron reactions has conventionally been expressed by the Butler-Volmer equation with the standard rate constant and the transfer coefficient. In order to associate the two kinetic parameters with properties and structure of reacting species and media, we need microscopic interpretation of the electrode kinetics. Well-known microscopic interpretations [23] are Marcus theory and the distribution of energy states. However, both theories do not define the transfer coefficient so that microscopic properties may be reflected on the transfer coefficient. For example, the Marcus theory assumes overlap of two parabolic potential energies, which have been introduced *a priori* on the basis of the harmonic oscillation. This parabolic form fails to represent specifically the microscopic properties relevant to the transfer coefficient.

In this paper, the anodic transfer coefficient is represented as the ratio of the velocity in the forward direction for the redox activated complex to that in the backward direction near the potential maximum. The velocity is estimated from the Langevin equation for the activated complex, which contains the electric energy and other potential energies as acceleration terms. Since the transfer coefficient varies with the velocity or the current, the

Tafel plot shows non-linear variation.

2. THEORY

The outline of the theory is to introduce a Langevin equation for an activated complex at the top of the activate potential profile (see Fig.1), to derive the average velocities on both the reactant and the product sites, to define the transfer coefficient by use of the velocity, to introduce the electric force in the media of the both sites, to represent the electric field as the conductance of media, and to estimate the dependence of the transfer coefficient on the conductance.

We consider the one-electron oxidation of a *p*-doped conducting polymer:

$$R\ (\text{insulator}) \leftrightarrow O\ (\text{conductor}) + e^- \qquad (1)$$

where R is the neutral and electrically insulating species, and O is the doped and electrically conducting species. The activated complex here is defined as an intermediate between R and O. It may be in a polymer strand when the reaction occurs within the polymer (Fig.2A), or it may be at the edge of a strand in contact with the other strand (Fig.2B). The former corresponds to an intra-molecular reaction, proceeding through a vibration between nearest two segments, while the latter belongs to the intermolecular reaction which has more freedom in motion than for the former. Both are essentially the same except for a degree of the freedom. Once the oxidation proceeds at the interface between the conducting and the insulating zone, the oxidized species is captured in the conducting zone, leading to the development of the front of the conducting zone.

When the activated complex is at the top of the reaction potential profile, the feasibility of the complex of running to the reactant side or the product side depends on external forces, *f*, acting on the complex. In order to evaluate the probability of running toward each side, we

begin with a Langevin equation. When the complex with mass m and velocity $v(x)$ at x on the reaction coordinate is influenced by the external force, $f(x)$, and the thermal fluctuation force, $g(x)$, in the viscous medium with viscosity, ξ, then the Langevin equation is given by:

$$m[\mathrm{d}v(x,t)/\mathrm{d}t] + m\xi v(v,t) = f(x) + g(t) \qquad (2)$$

The solution for $v(x, t)$ has been obtained in a form of the time-average $\bar{v}(x,t)$, which has converted the randomness in $g(t)$ into the thermal energy term [24]. The time-averaged velocity for a long time is expressed by [24]

$$\bar{v}(x) = \left(k_{\mathrm{B}}T/m\right)^{1/2} + f(x)/m\xi \qquad (3)$$

where k_{B} is Boltzmann's constant. Possible sources of the external force are the electric force, f_{E}, and the other complicated force, f_{C}, such as by orientation of solvent, the difference in vibration modes on the reactant and the product sides, and a contribution of dopant ions. Letting the electric field at x be $E(x)$ and the charge of the activated complex be q, then Eq.(3) can be rewritten as

$$\bar{v}(x) = \left(k_{\mathrm{B}}T/m\right)^{1/2} + f_{\mathrm{C}}(x)/m\xi + qE(x)/m\xi \qquad (4)$$

The origin of x is set to be at the top of the potential hill, as is shown in Fig.1. Then, $x > 0$ and $x < 0$ denote the oxidation and the reduction side, respectively. The anodic transfer coefficient is defined by the probability for the activated complex of going toward the oxidation side along the reaction coordinate. It is proportional to the velocity, and hence the anodic transfer coefficient is expressed by

$$\alpha = \bar{v}(x)/\left[\bar{v}(x) + \bar{v}(-x)\right] \qquad (5)$$

The first term on the left hand side of Eq.(4) represents thermal fluctuation and hence is independent of x. Inserting Eq.(4) into Eq.(5) yields

$$\alpha = \frac{\xi(mk_{\mathrm{B}}T)^{1/2} + f_{\mathrm{C}}(x) + qE(x)}{2\xi(mk_{\mathrm{B}}T)^{1/2} + f_{\mathrm{C}}(x) + f_{\mathrm{C}}(-x) + q\{E(x) + E(-x)\}} \qquad (6)$$

The most conspicuous difference in properties between O and R lies in the conductivity rather than difference in chemical properties. For example, the ratio of the conductivity of polyaniline films can be varied over fifteen orders of magnitudes [25], whereas the *p*-doped state and the neutral state have similar solubility, density, hydrophilicity and ion permeability in comparison with the conductivity difference. Therefore, we have $|E(x)| >> |E(-x)|$ and $|f_C(x)| \sim |f_C(-x)|$. This relation is independent of charge carriers, electrons or holes. The electric field can be expressed by the product of the current density, j, and the resistivity, ρ, i.e., $E = j\rho$. Then, Eq.(6) is reduced under the assumption of $f_C(x) = f_C(-x)$ to

$$\alpha = 1/(2+h) \qquad (7)$$

where

$$h = \frac{qj\{\rho(-x)-\rho(x)\}}{\xi(mk_BT)^{1/2} + f_C + qj\rho(x)} = \frac{\rho(-x)/\rho(x)-1}{\{\xi(mk_BT)^{1/2} + f_C\}/qj\rho(x)+1} \qquad (8)$$

The parameter h is a function of conductivity. If conductivity of the phases of R and O is identical, we have $\rho(-x) = \rho(x)$ and hence $h = 0$, leading to $\alpha = 0.5$. In contrast, values of α decrease with an increase in $\rho(-x)/\rho(x)$, depending on values of $\{\xi(mk_BT)^{1/2} + f_C\}/qj\rho(x)$, as shown in Fig.3. If values of $\rho(-x)/\rho(x)$ are much larger than those of $\{\xi(mk_BT)^{1/2} + f_C\}/qj\rho(x)$, α becomes zero. Unfortunately, it is quite difficult to estimate f_C and q, because neither molecular structure of the activated complex or reaction coordinate can be specified, and hence values of $\{\xi(mk_BT)^{1/2} + f_C\}/qj\rho(x)$ are unknown.

The experimental results ($\alpha \approx 0$) [4,5,8,21] suggest large values of h, according to Eq.(7). If $\rho(x)$ and $\rho(-x)$ represent the bulk resistivity of the conducting and the insulating species, respectively, values of h are so large that $\rho(-x)/\rho(x)$-1 in Eq.(8) is regarded as $\rho(-x)/\rho(x)$. It is assumed that $\{\xi(mk_BT)^{1/2} + f_C\}/qj\rho(x) >> 1$ in Eq.(8). Then h is approximated as $h = qj\rho(-x)/[\xi(mk_BT)^{1/2} + f_C]$. This form does not include the term $\rho(x)$, which is specific to conducting polymers. Therefore, values of $\{\xi(mk_BT)^{1/2} + f_C\}/qj\rho(x)$ should be of the same order as 1 or smaller than 1. So, values of h are mostly determined by $\rho(-x)/\rho(x)$. Applying the

minimum and the maximum values for typical bulk conducting polymers to $\rho(-x)$ and $\rho(x)$, respectively, we estimate $\rho(-x)/\rho(x) = 10^{15}$ as a maximum value [25]. However, the solution resistivity is obviously much smaller than the resistivity of the dried insulating species because the insulating species is surrounded with dopant ion for the electrochemical reaction. We try to regard $\rho(-x)$ as the resistivity of the solution including 1 M electrolyte, for example, KCl. Then the ratio $\rho(-x)/\rho(x)$ becomes 10-100 for the typical conductivity of conducting polymers (1 Ω cm). Even for the underestimation of $\rho(-x)/\rho(x)$, values of α are smaller than 0.5, as shown in Fig.3.

In order to evaluate the transfer coefficient from the growth experiment of the conducting zone, we have measured distances of the conducting front from the electrode at various electrolysis time after a given electrode potential is applied to the electrode [4,5,6,16]. The current density should be proportional to the velocity of the moving front if the growing domain is rectangular. Then the Tafel's type kinetic equation:

$$\ln j = \ln j^{o} + \alpha\left[F(\phi - \phi^{o})/RT\right] \qquad (9)$$

can be rewritten as

$$\ln(u/u^{o}) = F(\phi - \phi^{o})/RT(2+h) \qquad (10)$$

where j^{o} is the exchange current density at the standard potential ϕ^{o}, and u^{o} is the growth speed corresponding to j^{o}. Since h is a function of j or u through Eq.(8), it cannot be regarded as a constant for variation of j. Consequently, the variation of ln u (or ln j) with ϕ may deviate from a linear relationship. Figure 4 shows an example of the dependence of the logarithm of the velocity on the applied potential, calculated from Eq.(8) and (10). The plot is always deviated convexly. The deviation is obvious if Eq.(6) is rewritten as the roughly approximated form:

$$\alpha \approx \frac{A + j\rho(x)}{2A + j\rho(-x)} \approx \frac{A}{2A + j\rho(-x)} \qquad (11)$$

where $A = \{\xi(mk_BT)^{1/2} + f_C\}/q$ under the assumption of $\rho(-x) >> \rho(x)$. A physical meaning of this variation is that the term, $\bar{v}(-x)$ has a larger variation with the current than $\bar{v}(x)$ because of the stronger electric field effect in the more resistive domain. This deviation has been found in the plots for polyaniline [4,5] and polypyrrole films [6,8], as shown in Fig.4.

A question arises about whether the conductivity can be used reasonably for the microscopic model of charge transfer reactions. Conductivity is obviously a quantity which is temporally and spatially averaged over a macroscopic domain, and hence should be different from that near the activated complex. However, the bulk conductivity should alter the conductivity in the microscopic domain near the activated complex, and hence $\rho(x)$ and $\rho(-x)$ may be close to values in the bulk conducting and the bulk insulating zones, respectively.

Conclusion

An extraordinarily small value of the anodic transfer coefficient of electronically conducting polymers was interpreted as a difference between the ionic conductance in the reactant with the neutral state and the electric conductance in the product with the conducting state. In other words, the asymmetry of the potential profile for the activated complex is caused by the difference in the conductivity. This behavior is specific to conducting polymers, in which switching of conductivity is coupled with the redox reaction. The difference in the conductivity deviates the Tafel plot from a straight line to a convex curve, as demonstrated by experimental results. Detailed verification of this concept might require elaborate experimental data under various combinations of conductivities. The concept presented here is so general that it can be applied to any redox systems including conductivity change.

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Figure Captions

Figure 1. Potential profile for the electrode reaction of a conducting polymer from the neutral (insulating) state to the doped (conducting) state along the reaction coordinate.

Figure 2. Image of the activated complex which takes an intermediate state between the neutral and insulating (I) state and the doped and conducting (C) state when it lies within a polymer strand (A) and at the edge of a strand in contact with the other strand (B).

Figure 3. Variation of the anodic transfer coefficient with $\rho(-x)/\rho(x)$, evaluated from Eq.(7) and (8) for $\{\zeta(mk_BT)^{1/2} + f_C\}/qj\rho(x)$ = (a) 0.1, (b) 1, (c) 10, and (d) 100.

Figure 4. Variation of logarithm of the velocity of the moving front with the applied potential, calculated from Eq.(8) and (10) for $\{\zeta(mk_BT)^{1/2} + f_C\}/q\rho(x)$ = 1 mA cm^{-2} and $\rho(-x)/\rho(x)$ = 33. Circles are experimental data for polypyrrole from Fig.8 [6].

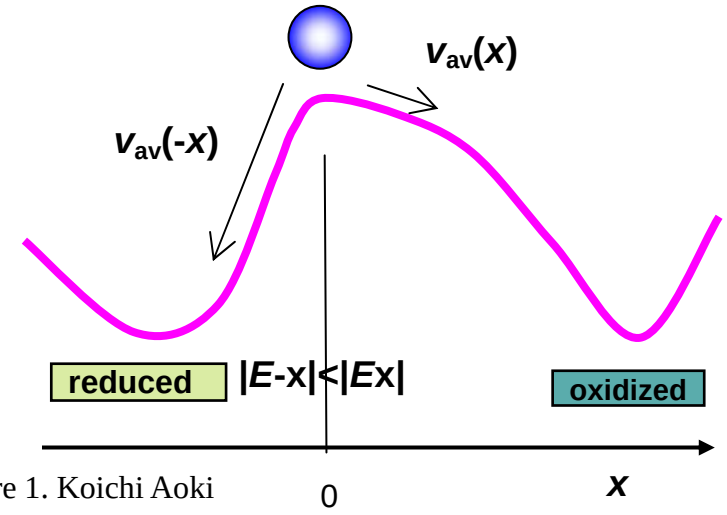

Figure 1. Koichi Aoki

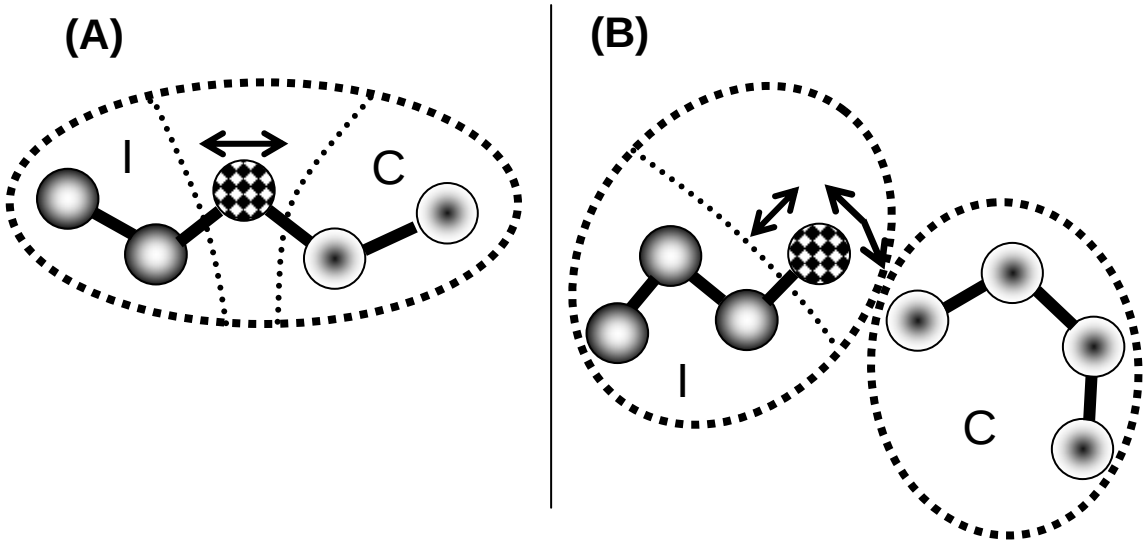

Figure 2 Koichi Aoki

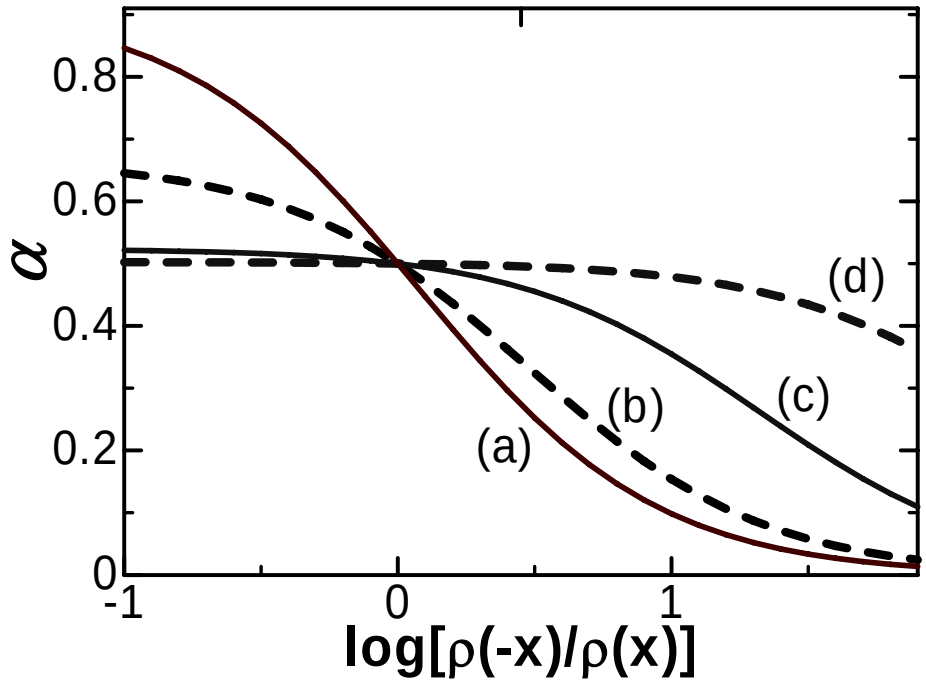

Figure 3. Koichi Aoki

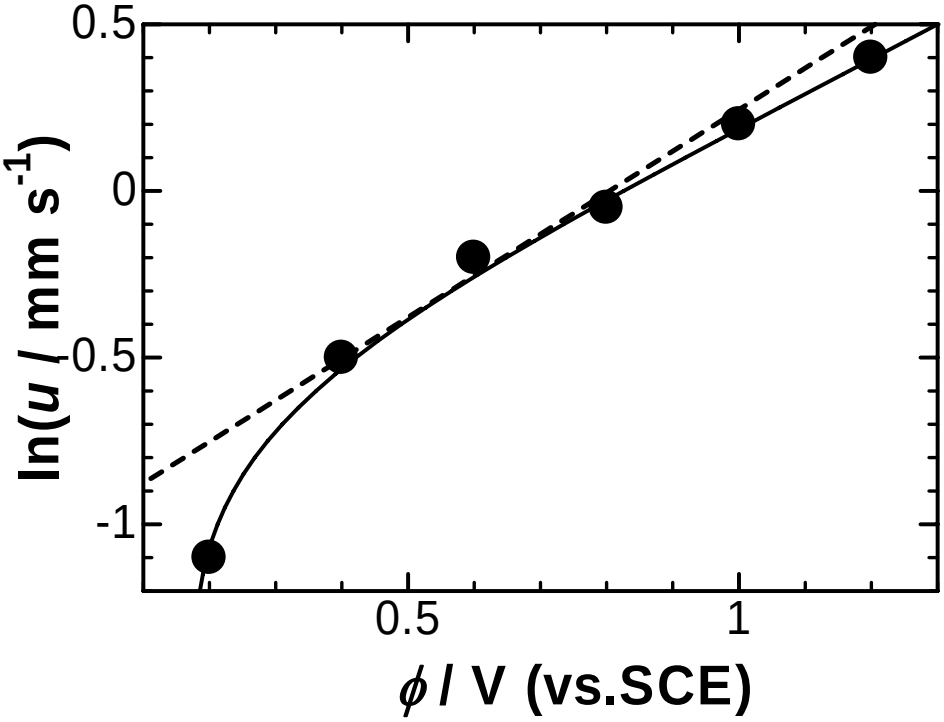

Figure 4. Koichi Aoki