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Diffusion-controlled current with memory

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Abstract

The diffusion equation complicated by a delay of a concentration flux, J, from the formation of a concentration gradient, $\partial c/\partial x$, was formulated in the context of electrochemical measurements. In contrast with the Fick's first law, $J = -D\partial c/\partial x$, the flux at a short time is known to be delayed owing to a finite propagation speed of the gradient, called the memory effect or the second sound for thermal diffusivity. The modified Fick's law contained the second time-derivative of the concentration multiplied by the relaxation time, τ, additive to the conventional diffusion equation. It was applied to chronoamperometry. The current-time curve was smoother than that for the Cottrell equation. The current at a short time was almost constant owing to the rate-determining step of the propagation velocity, $(D/\tau)^{1/2}$, and then decays obeying the Cottrell equation. This variation was similar to the curve mixed with the Butler-Volmer kinetics. The relaxation time was estimated from the period during which a diffusing particle can recognize the concentration gradient by collision with the nearest diffusing particle. The propagation velocity was of the order of some cm s^{-1}, which is similar to the maximum values of the measurable charge transfer rate constant.

key words: diffusion, memory effect, chronoamperometry, Butler-Volmer kinetics, Fick's law, second sound

1. Introduction

Irreversible thermodynamics has derived the Fick's first law by balancing the force of the gradient of chemical potential with the frictional force which acts on the flowing particle in a Newtonian fluid [1]. Consequently the flux of the diffusing particle is proportional to the concentration gradient with a diffusion coefficient as a constant of the proportionality. The proportionality of the flux to the gradient is also found in a heat flux caused by temperature gradients with a thermal conductivity, in a momentum flux caused by fluid velocity gradient with a viscosity, and in an electric current caused by the electric field [2]. These proportionalities can be generalized in terms of a relation between a cause (gradient) and an effect (flux). In general, an effect is realized necessarily after a delay of a cause rather than a simultaneous response. However, these fluxes have been assumed to appear simultaneously at the onset of the gradients at an infinite propagation velocity [3-5] without any delay. This unrealistic point has been resolved by the concept of the second sound or the memory effect in the field of heat transport [6-8].

We consider an example of the unrealistic diffusion from the electrochemical viewpoint. A concentration profile of an redox active species controlled by diffusion at chronoamperometry is expressed by the error function, $\text{erf}[x/2(Dt)^{1/2}]$, where x is the distance from the electrode, t is the electrolysis time and D is the diffusion coefficient of the electroactive species [9]. It varies asymptotically [10] in the form of $2\pi^{-1/2}[(Dt)^{1/2}/x]\exp(-x^2/4Dt)$. When one mole is generated at the electrode, one particle can be detected necessarily at such x and t that $1/N_A = 2\pi^{-1/2}[(Dt)^{1/2}/x]\exp(-x^2/4Dt)$ is satisfied, where N_A is the Avogadro constant. This equation yields $x/(Dt)^{1/2} = 14.4$, leading to the velocity $x/t = 210$ m s^{-1} of transferring the particle for $x = 1$ nm and $D = 10^{-5}$ cm^2 s^{-1}. The velocity is close to the value of the ideal gas $(2RT/w_M)^{1/2} = 220$ m s^{-1} for the species with molecular weight $w_M = 100$ g mol^{-1} at 25°C. The particle collides with solvent molecules so many times within 1 nm (3 times of the molecular distance in

water) that it cannot keep the velocity 210 cm s^{-1}. Thus it cannot reach the position of 1 nm. This contradiction is ascribed to the assumption of the simultaneous occurrence of the flux with the concentration gradient. The Fick's first law is invalid at a short time. The contradiction has been long discussed in the field of heat transfer, including a number of debates [8].

We take into account in this report a delay of the flux of electrochemical diffusion by use of the simplest relaxation that has been developed in the field of heat transfer. The diffusion equation including the delay, called diffusion with memory, will be solved under chronoamperometric conditions. The current is predicted to show a slower decay than the Cottrell equation. The delayed current may be similar to the current partially controlled by the charge transfer reaction, and hence the participation in the memory effect may be mistaken for a sluggish charge transfer reaction. The degree of the participation will be estimated to be close to the maximum values of the reaction rate constant.

2. Diffusion equation with memory

Classical mechanics mentions that a gradient of potential is equivalent to a force, and hence the force of a gradient of the chemical potential of a given species acts on the particles to drive them at velocity v. When the particle is a sphere in radius a, it is subjected to the frictional force, $6\pi\eta av$, in the medium of the viscosity, η, according to the Stokes' law. The driven particle is accelerated until the gradient of the chemical potential, -grad μ, is balanced with $6\pi\eta av$. Let the concentration of the particle be so low that the chemical potential per particle is expressed by $\mu^{\mathrm{o}} + k_{\mathrm{B}}T\ln(c/c^{\mathrm{o}})$, where μ^{o} is the standard chemical potential, k_{B} is the Boltzmann constant, and c^{o} is the standard concentration. Then the force of the one-dimensional gradient is given by $-(k_{\mathrm{B}}T/c)(\partial c/\partial x)$. Letting the molar flow rate of the species be $J = cv$, the balance of the forces is given by

$$-(k_{\mathrm{B}}T/c)(\partial c/\partial x)=6\pi\mu a(J/c) \tag{1}$$

Applying the Stokes-Einstein relation [1] $D = k_{\mathrm{B}}T/6\pi\eta a$ to Eq.(1), we obtain the Fick's first law

$$J = -D(\partial c/\partial x) \tag{2}$$

This derivation is based on the assumption that the onset of the flux occurs simultaneously with the formation of the gradient. Indeed, both hand sides in Eq.(2) do not include any time variable explicitly, indicating the simultaneous occurrence.

If a gradient is an external field like gravity or electricity, a particle in the field can read the magnitude of the gradient without any delay and respond simultaneously to the gradient. The diffusing particle, in contrast, forms itself the gradient. In order to recognize the gradient of the diffusing particle, the particle has to collide with at least the closest neighboring particles (Fig.1 (a), (b)). Once it recognizes the gradient, it can move and gain the velocity corresponding to the gradient (Fig.1 (c)). During the recognition period, τ, the amount proportional to the difference, $(-D\partial c/\partial x) - J(t)$ is supplied to the flux at $t+\Delta t$ as an excess. The amount of the supplied flux is also proportional to $\Delta t/\tau$. Consequently, the flux at $t+\Delta t$ is given by

$$J(t+\Delta t) = J(t) + (\Delta t/\tau)[(-D\partial c/\partial x) - J(t)]$$

Expanding $J(t+\Delta t)$ in the Taylor series and taking the limit of $\Delta t \to 0$, we obtain the equation for the first order relaxation [6]

$$\tau(\partial J/\partial t) = -(J + D\partial c/\partial x) \tag{3}$$

where τ is the relaxation time during which the Fick's first law (Eq.(2)) holds.

Equation (3) is now combined with the equation for one-dimensional continuum:

$$\partial c/\partial t = -\partial J/\partial x \tag{4}$$

Carrying out differentiation of Eq.(3) with respect to x and of Eq.(4) with respect to t leads to

$$\tau\frac{\partial^2 J}{\partial t\partial x}+\frac{\partial J}{\partial x}=-D\frac{\partial^2 c}{\partial x^2} \tag{5}$$

$$\frac{\partial^2 c}{\partial t^2}=-\frac{\partial^2 J}{\partial x\partial t} \tag{6}$$

Eliminating J from Eq.(5) by use of Eq.(4) and (6), we obtain

$$\tau \frac{\partial^2 c}{\partial t^2} + \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \tag{7}$$

This corresponds to the Fick's second law containing the memory effect.

Equation (7) obviously tends to the Fick's second law at $\tau = 0$. When τ is so large that the second term in Eq.(7) is smaller than the first term, in contrast, Eq.(7) tends to

$$\frac{\partial^2 c}{\partial t^2} - \frac{D}{\tau} \frac{\partial^2 c}{\partial x^2} = 0 \tag{8}$$

This is a hyperbolic differential equation or a wave equation. It has a solution

$$c = A \sin\left(t/\tau - x/\sqrt{D\tau} \right) \tag{9}$$

which expresses a wave propagating at the velocity $(D/\tau)^{1/2}$. Consequently, Eq.(7) contains properties of both time-evolving diffusion and propagating waves. If a concentration distribution is uniform in Eq.(7), the concentration is given by the first order transient, $c = A_1 + A_2 \exp(-t/\tau)$, regardless of any boundary conditions. This irrational behavior is a limitation of Eq.(3), as has been stated [8].

3. Estimation of relaxation time

The relaxation time includes not only the time of the recognition of the next neighboring redox particles but also a delay by inertia of the particle to gain a given velocity. It may also include deviation from Stokes force, $6\pi\eta a v$. These factors are discussed here.

The present model of the molecular motion in solution is a number of imaginary collisions of a redox particle with solvent molecules by transferring the distance between the closest neighboring solvent molecules, as is illustrated as thin arrows in Fig.1(a). In other words, the redox particle translates between two molecules at the

velocity corresponding to the thermal energy, k_BT, changes the direction of the motion randomly by collision at a site of a solvent molecule, and follows these processes iteratively. The redox particle cannot recognize the concentration until it has any communication with other redox particles. The simplest communication is collision of the particle with the closest neighboring redox particles (broad arrows in Fig.1 (a)) rather than the solvent molecules. The lower is the concentration of the redox species, the lower is the probability of the collision. The collision probability may be close to the probability of finding a redox particle at a given point. If the redox species is in an aqueous solution with molar concentration, c, the probability is given by $c/(1000/18)$. Letting the weight of the redox particle be m, the translational velocity by the thermal fluctuation is expressed by the velocity for an ideal gas, $\sqrt{2k_BT/m}$. Consequently the average velocity of the collision between two redox particles is given by

$$v = [c/(1000/18)]\sqrt{2k_BT/m} = (c/55.6)\sqrt{2RT/w_M} \tag{10}$$

where the unit of c is mol dm^{-3}, and w_M is the molar weight of the redox species. Then the relaxation time is expressed by

$$\tau = D/v^2 = Dw_M/2RT(c/55.6)^2 \tag{11}$$

The inertia of the redox particle might influence the relaxation time. The effect of the inertia can be represented by the kinetic energy. When a redox particle with molecular weight 200 (g mol^{-1}) gains the velocity of 1 cm s^{-1} by the diffusion force, the kinetic energy is 10^{-5} J mol^{-1}. This is much smaller than the thermal energy, 2.5 kJ mol^{-1} at 25°C and hence the effect of the inertial can be sufficiently negligible. Another possible source of the delay is the deviation of the friction force from the Stokes' law at high velocity. The deviation is reportedly negligible when $av\rho/\eta < 0.05$ [11] for the density ρ of a sphere. This contribution is ca 10^{-10} at $v = 1$ cm s^{-1}, and hence the deviation from Stokes' law has no effect on τ.

As a result, the velocity and the relaxation time are given by Eq.(10) and (11) respectively. A typical value of the velocity and the relaxation time are, respectively, 0.56 cm s^{-1} and 31μs for $c = 1$ mM, $w_M = 50$ (g mol^{-1}) and $D = 10^{-5}$ cm^2 s^{-1}. This

velocity is close to a maximum value of the standard charge transfer rate constants that can be evaluated by fast transient electrochemical measurements, as will be discussed later. Lower concentration increases largely the relaxation time. For example, concentration 1 μM yields 31 s, which may provide extraordinary voltammetric behavior. Domains of v and τ for conventionally used electrochemical measurements are

$$0.023\,\mathrm{cm\,s^{-1}} < v < 7.3\,\mathrm{cm\,s^{-1}},\ 0.19\,\mathrm{\mu s} < \tau < 19\,\mathrm{ms} \tag{12}$$

for 30 g mol^{-1} < w_M < 300 g mol^{-1} and 0.1 mM < c < 10 mM at $D = 10^{-5}$ cm^2 s^{-1}.

4. Chronoamperometry

We apply Eq.(7) to chronoamperometry on the assumption that the relaxation time is independent of the concentration. When the potential is stepped to the diffusion-controlled domain so that the surface concentration becomes zero, the initial and boundary conditions are given by

$$c = c^*, J = 0 \ \text{ for } t = 0 \text{ and } x \to \infty \tag{13}$$

$$c = 0 \ \text{ for } x = 0 \tag{14}$$

The current equivalent to the flux at $x = 0$ is given by setting x to be zero in Eq.(3)

$$\tau(\partial J_{x=0}/\partial t) = -D(\partial c/\partial x)_{x=0} - J_{x=0} \tag{15}$$

The boundary condition is expressed by this differential equation with respect to t. Carrying out the Laplace transformation of Eq.(15) for t, we have

$$\tau s \bar{J}_{x=0} = -D(\mathrm{d}\bar{c}/\mathrm{d}x)_{x=0} - \bar{J}_{x=0}$$

or

$$\bar{J}_{x=0} = -D(\mathrm{d}\bar{c}/\mathrm{d}x)_{x=0}/(1+\tau s) \tag{16}$$

where the upper bar means the Laplace transformation and s is the transformed variable. The Laplace transform of Eq.(7) with condition (13) is given by

$$\tau\left(s^2\bar{c} - sc^*\right) + s\bar{c} - c^* = D\left(\mathrm{d}^2\bar{c}/\mathrm{d}x^2\right)$$

The solution of the above equation including conditions (13) and (14) is

$$\bar{c} = c^*/s\left(1 - \exp\left[-\sqrt{s(\tau s+1)/D}\,x\right]\right) \tag{17}$$

When the differentiation of Eq.(17) at $x = 0$, i.e., $\left(\mathrm{d}\bar{c}/\mathrm{d}x\right)_{x=0} = c^*\sqrt{(\tau s+1)/sD}$ is inserted into Eq.(16), we obtain

$$\bar{J}_{x=0} = -c^*\sqrt{D/s(\tau s+1)} \tag{18}$$

Carrying out the inverse Laplace transformation of $[s(\tau s+1)]^{-1/2}$ by use of a table of the Laplace transformation, the current density, j ($= -FJ$) is expressed by

$$j/F = c^*\sqrt{D/\tau}\exp(-t/2\tau)\,\mathrm{I}_0(t/2\tau) \tag{19}$$

where $\mathrm{I}_0(z)$ is the modified Bessel function of the first kind with the 0-th order [12].

The modified Bessel function has the asymptotic form [12]:

$$\mathrm{e}^{-z}\mathrm{I}_0(z) = (2\pi z)^{-1/2}\left[1 + 1/8z + 9/128z^2 + \Lambda\right]$$

and hence the long term variation of the current is expressed by

$$j/F = c^*\sqrt{D/\pi t}\left(1 + \tau/4t + 9\tau^2/32t^2 + \Lambda\right) \tag{20}$$

When $\tau \ll t$, this equation tends to the Cottrell equation. In contrast, the ascending series of the modified Bessel function [12]

$$\mathrm{I}_0(z) = 1 + z^2/4 + z^4/64 + \Lambda$$

rewrites $\mathrm{e}^{-z}\mathrm{I}_0(z)$ as

$$\mathrm{e}^{-z}\mathrm{I}_0(z) = \left(1 - z + z^2/2 - \Lambda\right)\left(1 + z^2/4 + \Lambda\right) = 1 - z + 3z^2/4 - \Lambda$$

Hence Eq.(19) is expressed by

$$j/F = c^*\sqrt{D/\tau}\left(1 - t/2\tau + 3t^2/16\tau^2 - \Lambda\right) \tag{21}$$

The current at a very short time is a constant, $Fc^*\sqrt{D/\tau}$, determined by the propagation velocity, $\sqrt{D/\tau}$. The constancy of the current at $t \to 0$ resolves the irrationality of the infinite current at $t \to 0$ for the Cottrell equation. Figure 2 shows variation of the dimensionless chronoamperometric curve for Eq.(19) by use of the approximate equation for $\mathrm{I}_0(z)$ [12]. The current for $t/\tau < 0.53$ is less than the Cottrell current owing to the finite propagation velocity. The suppressed current is retrieved for $0.53 < t/\tau < 0.7$. The current for $0.61 < t/\tau$ is regarded as the Cottrell current within 5 % errors.

Figure 3 shows the dimensionless plot of the current against $t^{-1/2}$ (Cottrell plot) computed from Eq.(19). There are three domains of showing approximate linearity, the proportionality for $(\tau/t)^{1/2} < 0.3$, linearity with a negative intercept for $0.5 < (\tau/t)^{1/2} <$

1.0, and linearity with a positive intercept for $1.5 < (\tau/t)^{1/2}$. The plot for a long time ($\tau/t)^{1/2} < 0.3$) is the same as the Cottrell variation, and the slope of j vs. $t^{-1/2}$ gives $Fc^*(D/\pi)^{1/2}$. The current in the middle domain is larger than the Cottrell values owing to the higher terms in Eq.(20). Observed linearity depends on a selected time domain.

It is interesting to see concentration profiles especially in the light of the wave propagation. Unfortunately, there is no simple expression for inverse Laplace transform of Eq.(17). We derived the inverse Laplace transform approximately in Appendix 1 and obtained the approximate equation for small values of $x^2/D\tau$.

$$c/c^* \approx 1 - e^{-x/2\sqrt{D\tau}} I_0\left(x/2\sqrt{D\tau}\right) U\left(t/\tau - x/\sqrt{D\tau}\right) \qquad \text{for small } x^2/Dt \qquad (22)$$

where $U(x)$ is a step function ($U = 0$ for $x < 0$, $U = 1$ for $x > 0$). Figure 4 shows concentration profiles for $t/\tau =$ (a1) 0.3 and (b1) 3.0 calculated from Eq.(22), exhibiting the stepwise variations of the concentration. The dimensionless distances, $x(D\tau)^{-1/2}$, of the step from the electrode are 0.3 and 3.0 for curve (a1) and (b1), respectively. These profiles are quite different from those of Cottrell current, expressed by $c/c^* = \text{erf}[x/2(Dt)^{1/2}]$, as shown in (a2) and (b2). In order to support the validity of the concentration profiles, we obtained the numerical solution of the boundary value problem by mean of the explicitly finite difference method. The technique is described briefly in Appendix 2. The computed values are plotted in Fig.4, confirming the variation of Eq.(22).

The current at a short time in Fig.2 is smaller than the Cottrell current. Conventionally, small deviation from the Cottrell current has been ascribed to sluggish charge transfer kinetics. As an example of the charge transfer kinetics, we use here the irreversible charge transfer rate of one-electron obeying the Butler-Volmer equation:

$$j/F = (c)_{x=0} k_s \exp\left(\alpha F(E - E^o)/RT\right) \qquad (23)$$

where α is the anodic transfer coefficient, and k_s is the standard charge transfer rate constant. Eliminating the surface concentration in Eq.(23) by use of solution of the diffusion equation, $\partial c/\partial t = D\partial^2 c/\partial x^2$, we have [13]

$$(j/c^*F)\sqrt{\tau/D} = \lambda \exp(\lambda^2 z)\,\text{erfc}\left(\lambda\sqrt{z}\right) \qquad (24)$$

where

$$\lambda = k_s \exp\left(\alpha F(E - E^o)/RT\right)\sqrt{\tau/D} \tag{25}$$

Variations of Eq.(24) are shown in Fig.2 (c)-(e) for some values of λ. Since the Taylor expansion of Eq.(24) has the form $\lambda - 2\lambda\sqrt{t/\pi\tau} + \Lambda$, the current density decays from λ with the $t^{1/2}$-dependence. The variation of Eq.(24) is similar to that for the memory effect in that the current decreases from a constant value. It may not easy to discern real chronoamperometric curves with the Butler-Volmer kinetics from those for the memory effect. If one interprets curve (a) for the memory effect as curve (e) for the electrode kinetics, one obtains $k_s = 2(D/\tau)^{1/2} = 1.1$ cm s^{-1} for $c^* = 1$ mM and $\tau = 31$ μs. This value is close to that of limit of the rate constant to be evaluated at fast transient electrochemical techniques.

5. Conclusion

The diffusion with memory was introduced to the electrochemical mass transport problem. In contrast with the Fick's first law that contains no explicit time-variation, the flux with memory shows the first order time-relaxation, approaching $-D\partial c/\partial x$. This diffusion is expressed as an additional term of the second derivative of the concentration with the time to the Fick's second law. The relaxation time corresponds to the period of recognizing the gradient for a redox particle by searching the closest neighboring redox particles. It is inversely proportional to the square of the concentration. The delay of the diffusion-controlled current was revealed in the chronoamperometric curve as a finite value at a short time. The finite value represents the velocity, $(D/\tau)^{1/2}$, of the propagation of the relaxation front, as was demonstrated in the concentration profiles. It is of 1 cm s^{-1} order of magnitude. This rate is close to maximum limiting values of the standard rate constants that have been evaluated by fast electrochemical techniques. Thus, data analysis of fast electrochemical responses requires consideration of not only electrode kinetics but diffusion with memory.

The above treatment can resolve not only the infinity of the Cottrell current

immediately after the potential step but also the irrationally fast propagation velocity of the diffusion front. However, it raises other three problems: (a) the decay of the concentration under the uniform distribution, regardless of boundary conditions, as has been described section 3, (b) ambiguity of the relaxation time by the simple estimation, and (c) the neglect of the concentration dependence on the relaxation time when solving Eq.(7). Since the three problems are independent, each will require its own resolution. In order to apply this concept to real systems, we have not only to examine problem (c) in details but also to develop theoretically techniques of analyzing voltammetric data of linear sweep, ac, pulse and microelectrode voltammetry.

6. Appendix

6.1. Approximate equation

The approximate equation (22) is derived in this appendix. When $|s\tau|$ is large, the term $[s(s\tau+1)]^{1/2}$ in the exponential of Eq.(17) can be expanded into

$$\sqrt{s(s\tau+1)} = s\sqrt{\tau(1+1/s\tau)} = s\sqrt{\tau} + 1/2\sqrt{\tau} - 1/8\tau^{3/2}s + \Lambda \qquad (A1)$$

Retaining the first three terms in $[s(s\tau+1)]^{1/2}$, Eq.(17) is rewritten as

$$\frac{\bar{c}}{c^*} = \frac{1}{s} - \frac{1}{s}\exp\left[-\frac{x}{\sqrt{D}}\left(s\sqrt{\tau} + \frac{1}{2\sqrt{\tau}} - \frac{1}{8\tau^{3/2}s}\right)\right] \qquad (A2)$$

We apply to Eq.(A2) the correspondence $F(s)e^{-ks} \Leftrightarrow f(t-k)U(t-k)$ and $(1/s)e^{a/s} \Leftrightarrow I_0(2(at)^{1/2})$ between the transformed function $F(s)$ and the original function $f(t)$. The first term of the exponential argument of Eq.(A2) works as a shift by $-x(\tau/D)^{1/2}$ from t. The shift indicates the propagation at the constant velocity, $(D/\tau)^{1/2}$. The result of the transformation yields Eq.(22). The error in Eq.(22) is due to a loss of the higher terms in Eq.(A1).

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6.2. Finite difference method

The time and the space in Eq. (7) were digitized with an equi-interval and an equi-space, respectively. The second time-derivative of c was represented by the central differences at t and x, i.e.,

$$\partial^2 c / \partial t^2 \approx \left(c(t+\Delta t) - 2c(t) + c(t-\Delta t)\right)/\left(\Delta t\right)^2 \tag{A3}$$

In contrast, the first derivative in Eq.(7) was expressed as the forward difference

$$\partial c / \partial t \approx \left(c(t+\Delta t) - c(t)\right)/\Delta t \tag{A4}$$

The space-derivative was expressed by the central differences. Values of $c(t+\Delta t)$ were evaluated from $c(t)$ and $c(t-\Delta t)$ explicitly at a given x. A problem of applying the finite difference method lies in the inconsistency of the central and the forward method in Eq.(A3) and (A4). However, there was no significant errors of the concentration when values of $D(\Delta x)^2/\Delta t$ were varied.

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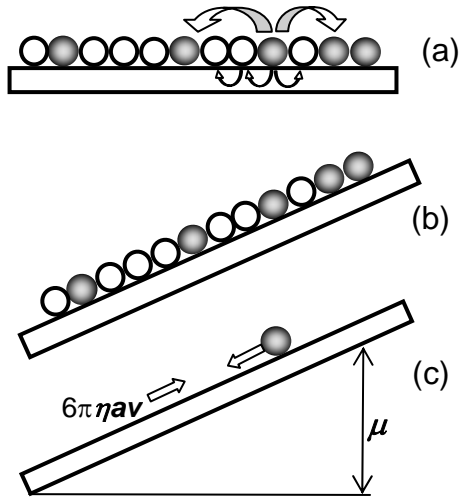
Fig.1 K. Aoki
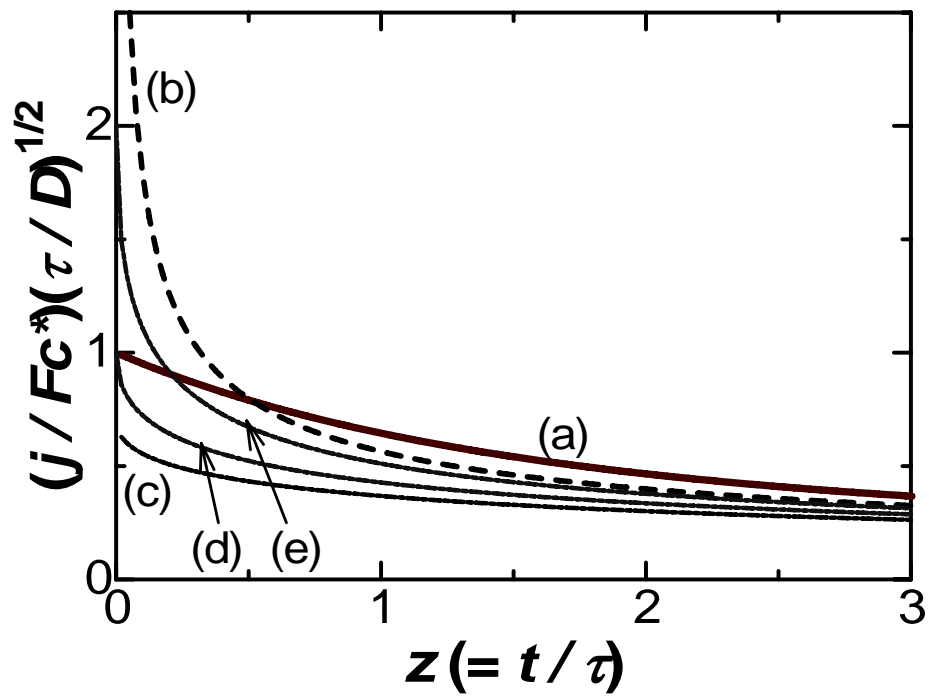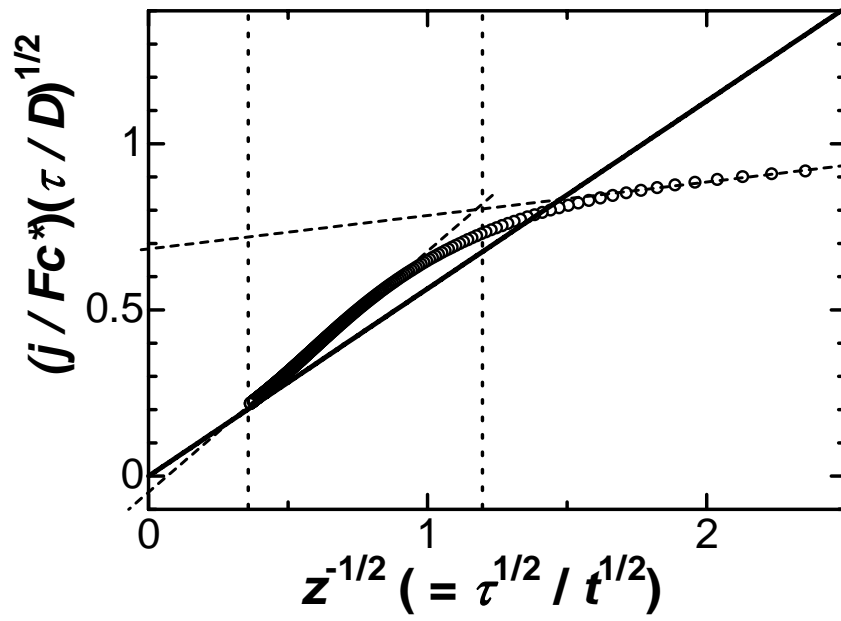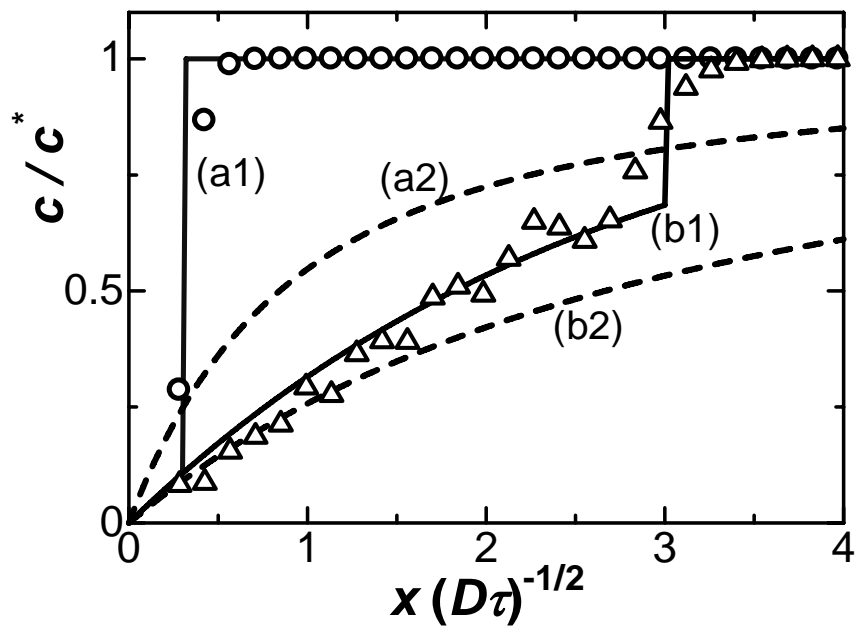

Fig.2 K. Aoki

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Fig.3 K. Aoki

Fig. 4 K. Aoki

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Figure captions

Fig.1. Illustration of (a) recognition of the concentration gradient by collision between the redox particles (black balls), (b) formation of concentration gradient, and (c) generation of the flow of the particle. The collision (broad arrows in (a)) is realized by a number of replacement (thin arrows in (a)) between the redox particle and solvent molecules.

Fig.2. Dimensionless chronoamperometric curves for (a) the memory effect calculated from Eq.(19), (b) the Cottrell equation, and charge transfer kinetics at (c) $\lambda = 0.7$, (d) 1.0 and (e) 2.0 calculated from Eq.(24).

Fig.3. Dimensionless Cottrell plot for the chronoamperometric curve with the memory effect. There are three domains of exhibiting a line.

Fig.4. Concentration profiles at (a1) $t/\tau = 0.3$ and (b1) 3.0, calculated from Eq.(22). The dashed curves are for the conventional concentration profiles, evaluated from the error function. Circles at $t/\tau = 0.3$ triangles at 3.0 are by the explicit finite difference method.