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Tips of Voltammetry

Koichi Jeremiah Aoki and Jingyuan Chen

Abstract

Theories of cyclic voltammetry, AC-impedance techniques, and the double-layer capacitive currents are described concisely to touch their principles. Applications of the theory to experimental data do not always lead to reasonable interpretation consistent with other techniques. Several tips are presented not only in the experimental viewpoint but also in a perspective of the data analysis. Most of them are devoted to cyclic voltammetry. They include shape of voltammograms, information from peak currents and peak potentials, criteria of diffusion and adsorption controls, the static and the dynamic numbers of electrons, handling of reference and counter electrodes, usage of AC impedance, concepts of heterogeneous charge-transfer rates, and combination with data by scanning probe microscope. They belong partially to recommendation and prohibition.

Keywords: current-voltage curves, cyclic voltammetry, AC impedance, double-layer capacitance, diffusion control, surface wave

1. Introduction

Voltammetry is an electrochemical technique for current-voltage curves, from which electrode reactions at electrode-solution interfaces can be interpreted. Since current-voltage curves, called voltammograms, include sensitive properties of solution compositions and electrode materials, their analysis provides not only chemical structures and reaction mechanisms on a scientific basis but also electrochemical manufacture on an industrial basis. The voltammograms vary largely with measurement time except for steady-state measurements, and so it is important to pay attention to time variables. Voltage is a controlling variable in conventional voltammetry, and the current is a measured one detected as a function of applied voltage at a given time.

The equipment for voltammetry is composed of electrodes, solution, and electric instruments for voltage control. Electrodes and electric instruments are keys of voltammetry. Three kinds of electrodes are desired to be prepared: a working electrode, a counter one, and a reference one. The three will be addressed below.

Let us consider a simple experiment in which two electrodes are inserted into a salt-included aqueous solution. When a constant current is applied to the two electrodes, reaction $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ may occur at one electrode, and reaction $2\text{OH}^- \rightarrow \text{H}_2\text{O}_2 + 2\text{e}^-$ occurs at the other. The current is the time variation of the electric charge, and hence it is a kind of reaction rate at the electrode. Since the applied current is a sum of the two reaction rates, one being in the positive direction and the other being in the negative, it cannot be attributed to either reaction rate. A technique of attributing the reactions is to use an electrode with such large area that an uninteresting reaction rate may not become a rate-determining step.

This electrode is called a counter electrode. The current density at the counter electrode does not specifically represent any reaction rate. In contrast, the current density at the electrode with a small area stands for the interesting reaction rate. This electrode is called a working electrode. It is the potential difference, i.e., voltage, at the working electrode and in the solution that brings about the electrode reaction. However, the potential in the solution cannot be controlled with the working electrode or the counter one. The control can be made by mounting another electrode, called a reference electrode, which keeps the voltage between an electrode and a solution to be constant. However, the constant value cannot be measured because of the difference in phases. A conventionally employed reference electrode is silver-silver chloride (Ag-AgCl) in high concentrated KCl aqueous solution.

An electric instrument of operating the three electrodes is a potentiostat. It has three electric terminals: one being a voltage follower for the reference electrode without current, the second being a current feeder at the counter electrode, and the third being at the working electrode through which the current is converted to a voltage for monitoring. A controlled voltage is applied between the working electrode and the reference one. These functionalities can readily be attained with combinations of operational amplifiers. A drawback of usage of operational amplifiers is a delay of responses, which restricts current responses to the order of milliseconds or 10 kHz frequency.

Voltammetry includes various types—linear sweep, cyclic, square wave, stripping, alternating current (AC), pulse, steady-state microelectrode, and hydrodynamic voltammetry—depending on a mode of the potential control. The most frequently used technique is cyclic voltammetry (CV) on a time scale of seconds. In contrast, currently used voltammetry at time as short as milliseconds is AC voltammetry. We describe here the theory and tips for practical use of mainly the two types of voltammetry.

2. Theory

The theory of voltammetry is to obtain expressions for voltammograms on a given time scale or for those at a given voltage. First of all, it is necessary to specify rate-determining steps of voltammograms. There are three types of rate-determining steps under the conventional conditions: diffusion of redox species in solution near an electrode, adsorption on an electrode, and charging processes at the double layer (DL). Electric field-driven mass transport, called electric migration, belongs to rare experimental conditions, and hence it is excluded in this review. When a redox species in solution is consumed or generated at an electrode, it is supplied to or departed from the electrode by diffusion unless solution is stirred. When it is accumulated on the electrode, the change in the accumulated charge by the redox reaction provides the current. Whenever electrode voltage is varied with the time, the charging or discharging of the DL capacitor causes current. Therefore, the three steps are frequently involved in electrochemical measurements.

A mass transport problem on voltammetry is briefly described here. The redox species is assumed to be transported by one-directional (x) diffusion owing to heterogeneous electrode reactions. Then, the flux is given by $f = -D(\partial c/\partial x)$, where c and D are the concentration and the diffusion coefficient of the redox species, respectively. Redox species in solution causes some kinds of chemical reaction through chemical reaction rates, $h(c, t)$. Then the reaction rate is the sum of the diffusional flux and the chemical reaction rate, $\partial c/\partial t = -\partial f/\partial x - h(c, t)$. Here the equation for $h = 0$ is called an equation of continuum. Eliminating f with the above equation on the

assumption of a constant value of D yields $\partial c/\partial t = D(\partial^2 c/\partial x^2) - h(c, t)$. This is an equation for diffusion-chemical kinetics. The expression at $h = 0$ is the diffusion equation. A boundary condition with electrochemical significance is the control of c at the electrode surface with a given electrode potential. If the redox reaction occurs in equilibrium with the one-electron transfer at the electrode, the Nernst equation for the concentrations of the oxidized species, c_o , and the reduced one, c_r , holds.

$$(c_o/c_r)_{x=0} = \exp [F(E-E^o)/RT] \quad (1)$$

where E^o is the formal potential. If there is no adsorption, the zero-flux condition in the absence of accumulation is valid:

$$D_o(\partial c_o/\partial x)_{x=0} + D_r(\partial c_r/\partial x)_{x=0} = 0 \quad (2)$$

The other conditions are concentrations in the bulk ($x \rightarrow \infty$) and the initial conditions.

2.1 Diffusion-controlled current

If the mass transport is controlled only by x -directional diffusion, c_r and c_o are given by the diffusion equations, $\partial c/\partial t = D(\partial^2 c/\partial t^2)$ for $c = c_r$ or c_o . An electrochemically significant quantity is not concentration in any x and t , but a relation between the surface concentrations and the current (the flux at $x = 0$). On the assumption of $D_o = D_r = D$, of the initial and boundary conditions, $(c_r)_{t=0} = c^*$, $(c_o)_{t=0} = 0$, and $(c_r)_{x=\infty} = c^*$, $(c_o)_{x=\infty} = 0$, a solution of the initial-boundary problem is given by [1].

$$(c_o)_{x=0} = (\pi D)^{-\frac{1}{2}} \int_0^t [j(u)/F](t-u)^{-\frac{1}{2}} du \quad (3)$$

where j is the current density. The common value of the diffusion coefficients yields $c_o + c_r = c^*$ for any x and t . Inserting this relation and Eq. (3) into the Nernst equation, $(c_o)_{x=0} = c^*/[1 + \exp[-F(E - E^o)/RT]]$, we obtain the integral equation for j as a function of t or E .

2.1.1 Linear sweep voltammetry by diffusion

When the voltage is linearly swept with the time at a given voltage scan rate, v , from the initial potential E_{in} , Eq. (3) through the combination with the Nernst equation becomes

$$\sqrt{\pi D} c^* F / \left[1 + \exp \left(-\frac{F(E_{in} + vt - E^o)}{RT} \right) \right] = \int_0^t j(u)(t-u)^{-\frac{1}{2}} du \quad (4)$$

The above Abel's integral equation can be solved by Laplace transformation. When the time variation is altered to the voltage variation through $E = E_{in} + vt$, the current density is expressed as

$$j = \frac{c^* F^{3/2}}{4} \sqrt{\frac{Dv}{\pi RT}} \int_{\zeta_i}^{\zeta} (\zeta - u)^{-1/2} \operatorname{sech}^2 \left[\frac{\zeta(u)}{2} \right] du \quad (5)$$

where $\zeta = (E - E^o)F/RT$ and $\zeta_i = (E_{in} - E^o)F/RT$. Evaluation of the integral has to resort to numerical computation. Current at any voltage should be proportional to

$v^{1/2}$, as can be seen in Eq. (5). The voltammogram for $v > 0$ rises up from E_o , takes a peak, and then decreases gradually with the voltage. The decrease in the current is obviously ascribed to relaxation by diffusion. The peak current density is expressed by

$$j_p = 0.446c^*F^{3/2}(Dv/RT)^{1/2} \quad (6)$$

at $E_p = E^o + 0.029$ V at 25°C, where 0.446 comes from the numerical calculation of the integral of Eq. (5).

Practical voltage-scan voltammetry is not simply linear sweep but cyclic voltammetry (CV), at which applied voltage is reversed at a given voltage in the opposite direction. The theoretical evaluation of the voltammogram should be at first represented in the integral form with the time variation and then express the time as the voltage. One of the features of the diffusion-controlled cyclic voltammograms is the difference between the anodic peak potential and the cathodic one, ΔE_p (in **Figure 1**), of which value is 59 mV at 25°C.

2.1.2 AC voltammetry by diffusion

AC voltammetry can be performed when the time variation of voltage is given by $E = E_{dc} + V_0 e^{i\omega t}$, where ω is the frequency of applied AC voltage, i is the imaginary unit, V_0 is its voltage amplitude, and E_{dc} is the DC voltage. A conventional value of V_0 is 10 mV. When this voltage form is inserted into Eq. (3) together with the Nernst equation, the AC component of the current density is represented by [2].

$$j = (1 + i) \left[c^* F^2 (D\omega/2)^{1/2} V_0 e^{i\omega t} / RT \right] \operatorname{sech}^2 \{ (E_{dc} - E^o) / RT \} \quad (7)$$

A voltammogram (j vs. E_{dc}) at a given frequency takes a bell shape, which is expressed by $\operatorname{sech}^2 \{ (E_{dc} - E^o) / RT \}$. The functional form of sech^2 is shown in **Figure 2**. The peak current appears at $E_{dc} = E^o$.

The AC-impedance technique often deals with the real impedance, $Z_1 = 1/2Y_1$ and the imaginary one, $Z_2 = -1/2Y_1$, where Y_1 is the real admittance given by

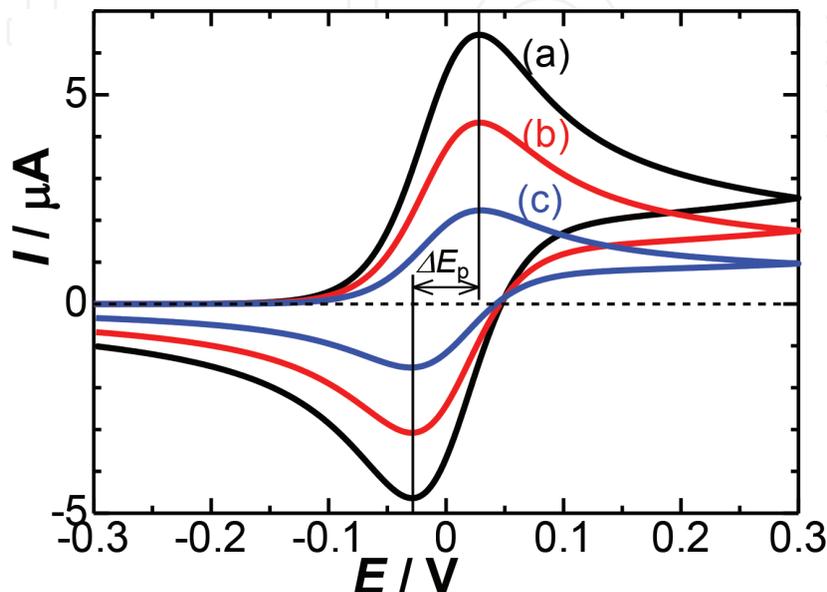


Figure 1. Voltammograms calculated from Eq. (5) for $v =$ (a) 180, (b) 80 and (c) 20 mV s^{-1} .

$$Y_1 = \left[c^* F^2 (D\omega/2)^{1/2} / RT \right] \operatorname{sech}^2[(E_{dc} - E^0)/RT] = Y_2 \quad (8)$$

Here Y_2 is the imaginary admittance, equal to Y_1 . Since $Z_1 = -Z_2$, the Nyquist plot, i.e., $-Z_2$ vs. Z_1 , is a line with the slope of unity. The term $1 + i$ in Eq. (7) has come from $(D\omega)^{1/2}$, originating from $(Di\omega)^{1/2}$. Therefore, it can be attributed to diffusion. In other words, diffusion produces the capacitive component as a delay.

2.2 Adsorption-controlled current

When the redox species with reaction $R = O + e^-$ is adsorbed on the electrode and has no influence from the redox species in the solution, the sum of the surface concentrations of R and O is a constant, Γ^* . Then the surface concentration of the oxidized species, Γ_o , is given by the Nernst equation:

$$\Gamma_o = \Gamma^* / [1 + \exp(-(E - E^0)F/RT)] \quad (9)$$

2.2.1 Linear sweep voltammetry by adsorption

The time derivative of the redox charge corresponds to the current density, $j = d(F\Gamma_o)/dt$. Application of the condition of voltage sweep, $E = E_{in} + vt$, to Eq. (9) yields.

$$j = (F^2\Gamma^*v/4RT) \operatorname{sech}^2(\zeta/2) \quad (10)$$

The voltammogram takes a bell shape (**Figure 2**), of which peak is at $E = E^0$, similar to the AC voltammogram. The current at any voltage is proportional to v . Since the negative-going scan of the voltage provides negative current values, the cyclic voltammogram should be symmetric with respect to the $I = 0$ axis. The peak current is expressed as $j_p = F^2\Gamma^*v/4RT$. The width of the wave at $j_p/2$ is 90 mV at 25°C.

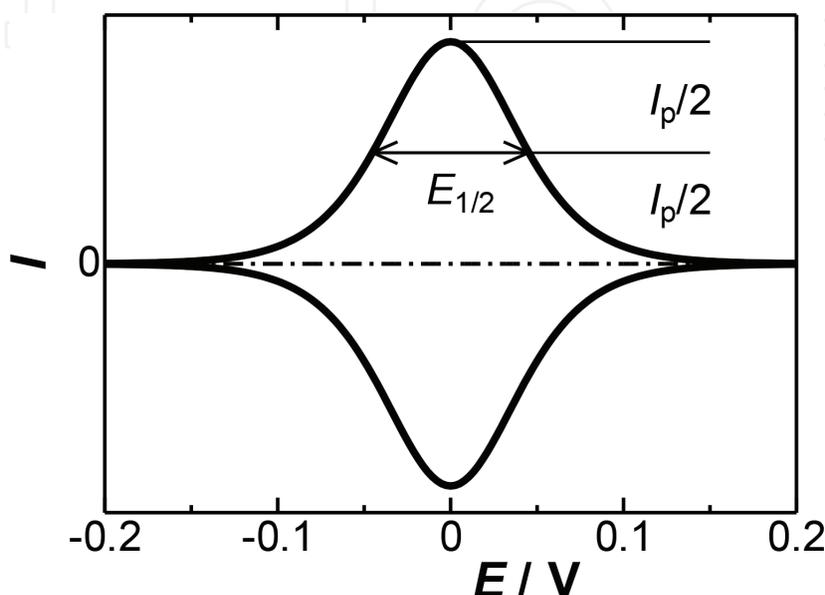


Figure 2.
 Voltammogram calculated from Eq. (10).

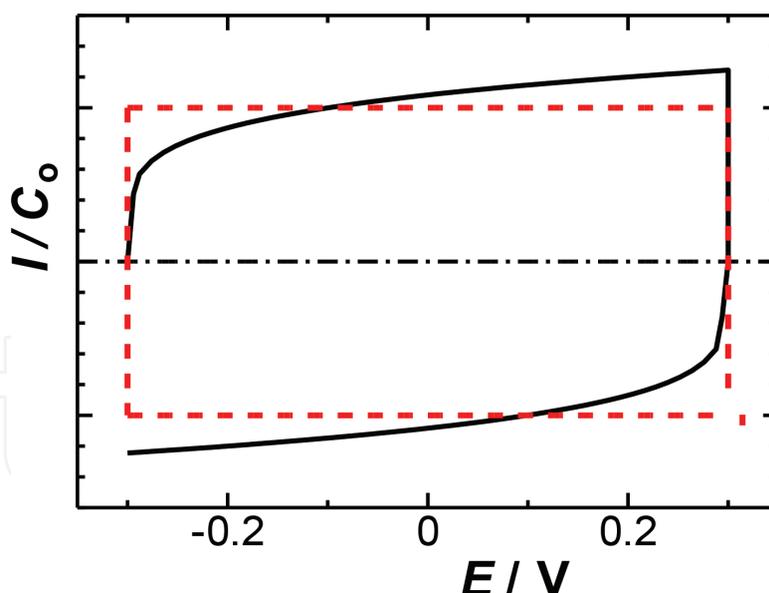


Figure 3. Capacitive voltammograms by CV at $v = 0.5 \text{ V s}^{-1}$ for (dashed lines) the ideal capacitance and for Eq. (13) (solid curves) at $\lambda = 0.2$.

2.3 Capacitive current

Since a phase has its own free energy, contact of two phases provides a step-like gap of the free energy, of which gradient brings about infinite magnitude of force. In order to relax the infinity, local free energy varies from one phase to the other as smoothly as possible at the interface. The large variation of the energy is compensated with spontaneously generated space variations of voltage, i.e., the electric field, which works as an electric capacitor. The capacitance at solution-electrode interface causes orientation of dipoles and nonuniform distribution of ionic concentration, of which layer is called an electric double layer (DL).

When the time variation of the voltage is applied to the DL capacitance, C_d , the definitions of the capacitance ($q = C_d V$) and the current lead

$$I = d(C_d V)/dt = C_d(dV/dt) + V(dC_d/dt) \quad (11)$$

where C_d generally depends on the time. This dependence is significant for understanding experimentally observed capacitive currents.

2.3.1 Capacitance by AC impedance

The DL capacitance has exhibited the frequency dispersion expressed by $C_d = (C_d)_{1\text{Hz}} f^{-\lambda}$, called the constant phase element [3–5] or power law [6, 7], where λ is close to 0.1. Inserting this expression and $V = V_0 e^{i\omega t}$ into Eq. (11) yields

$$I = (i + \lambda)\omega C_d V \quad (12)$$

This is a simple sum of the real part of the current and the imaginary one, indicating that the equivalent circuit should be a parallel combination of a capacitive component and a resistive one, both depending on frequency. Since the ratio, $-Z_2/Z_1$, for Eq. (12) is $1/\lambda$, the Nyquist plots have slopes less than 10 rather than infinity.

2.3.2 Capacitive current by CV

If the capacitive charge is independent of the time, the capacitive current should be $I = d(CV)/dt = C(E - E^0)/v$. Therefore, it takes a horizontal positive ($v > 0$) and a negative line ($v < 0$), as shown in **Figure 3** (dashed lines). When the time dependence of C , i.e., $C_d = (C_d)_0 t^{-\lambda}$, is applied to Eq. (11), for the forward and the backward scans, respectively, we have

$$I = (\lambda + 1)vC_0 t^\lambda, \text{ and } I = (\lambda + 1)vC_0 t^\lambda \quad (13)$$

The variation of CV computed from Eq. (13) (**Figure 3**, solid curves) is similar to our conventionally observed capacitive waves.

3. Tips of voltammetric analysis

Voltammograms can identify an objective species by comparing a peak potential with a table of redox potentials and furthermore determine its concentration from the peak current. Their results are, however, sometimes inconsistent with data by methods other than electrochemical techniques if one falls in some pitfalls of analytical methods of electrochemistry. For example, a peak potential is influenced by a reference electrode and solution resistance relevant to methods. Peak currents are varied complicatedly with mass transport modes as well as associated chemical reactions. Since the theory on voltammetry covers only some restricted experimental conditions, it can rarely interpret the experimental data successfully. This review is devoted to some voltammetric tips which can lead experimenters to reasonable interpretation.

3.1 Understanding outline of voltammograms

It is rare to observe a reversible voltammogram in which both oxidation and reduction waves appear in a symmetric form with respect to the potential axis at a similar peak potential, as in **Figure 1**. Frequently observed voltammograms are irreversible, i.e., either a cathodic or an anodic wave appears; a value of a cathodic peak current is quite different from the anodic one in magnitude; a cathodic peak potential is far from the anodic one. These complications are ascribed to chemical reactions and/or phase transformation after the charge-transfer reaction. A typical example is deposition of metal ions on an electrode. The complications can be interpreted by altering scan rates and reverse potentials.

A wave at a backward scan is mostly attributed to electrode reactions generated by experimenters rather than to species latently present in the solution. That is, it is artificial. It is caused either by the reaction of the wave at the forward scan or the reaction of the rising-up current just before the reverse potential. A source of the backward wave can be found by changing the reverse potentials.

Some voltammograms have more than two peaks at one-directional scan. The appearance of the two can be interpreted as a two-step sequential charge-transfer reaction. However, multiple waves appear also by combinations of chemical reactions and adsorption. The peak current and the charge for this case are quite different from the predicted ones, as will be described in Section 3.2. Change in scan rates may be helpful for interpreting the multiple waves.

3.2 Shape and values of peaks

It is possible to predict theoretically a controlling step of voltammograms from their shape (a bell type corresponding to an adsorption wave or a draw-out type corresponding to a diffusion wave). However, the shape strongly depends on chemical complications, adsorption, and surface treatment of the electrodes. When redox species in solution is partially adsorbed on an electrode, the electrode process is far from a prediction because of very high concentration in the adsorbed state. A draw-out-shaped wave can be observed even for the adsorbed control. It is important to estimate which state the reacting species takes on the electrode. Potentials representing of voltammetric features do not express a controlling step in reality although the theory does. One should pay attention to the current. The peak current controlled by diffusion with one-electron transfer is given by $I_p = 0.27 cAv^{1/2} \mu\text{A}$ (c , bulk concentration mM; A , electrode area mm^2 ; v , potential sweep rate mV s^{-1}). The microelectrode behavior sometimes comes in view at $v < 10 \text{ mV s}^{-1}$, $A < 0.1 \text{ mm}^2$, so the measured current is larger than the estimated value. On the other hand, the peak current controlled by adsorption is given by $I_p = 1.6 Av \text{ nA}$ when one redox molecule is adsorbed at 1 nm^2 on the electrode. The voltammogram by adsorption often differs from the ideal bell shape due to adsorbed molecular interaction and DL capacity. Division of the area of the peak by the scan rate yields the amount of adsorbed electricity. Comparison of this with the anticipated amount of adsorption may be helpful for understanding the electrode process.

3.3 Deviation of ΔE_p from theoretical values

The peak potential difference ΔE_p between the oxidation wave and the reduction wave (**Figure 1**) has been used for a prediction of the reaction mechanism. For example, $\Delta E_p = 60 \text{ mV}$ suggests the diffusion-controlled current accompanied by one-electron exchange, whereas $\Delta E_p = 30 \text{ mV}$ infers a simultaneous reaction with two electrons. Then what would happen for 120 mV which is sometimes found? A half-electron reaction might not be accepted. Potential shift over 60 mV occurs by chemical complications. In contrast, the voltammogram by adsorbed species shows theoretically a bell shape with the width, $E_{1/2} = 90 \text{ mV}$, at the half height of the peak (**Figure 2**). This value is based on the assumption of the absence of interaction among adsorbed species. However, adsorption necessarily yields such high concentrations as strong interaction.

It is necessary to pay attention to the validity of analyzing ΔE_p and $E_{1/2}$. The peak potential is the first derivative of a voltammogram. Since ΔE_p is a difference between the two peaks, it is actually the second-order derivative of the curves in the view of accuracy. In other words, the accuracy of ΔE_p is lower than that of peak current. Furthermore, peak potentials as well as $E_{1/2}$ readily vary with scan rates owing to chemical reactions and solution resistance. One should use the peak current for data analysis instead of the potentials.

3.4 Criteria of diffusion-controlled currents

Voltammograms of a number of redox species have been reported to be diffusion controlled from a relationship between I_p and $v^{1/2}$. The redox species exhibiting diffusion-controlled current is, however, limited to ferrocenyl derivatives under conventional conditions. Voltammograms even for $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and $[\text{Ru}(\text{NH}_3)_6]^{3+}$ are deviated from the diffusion control for a long-time measurement. Why have many researchers assigned voltammograms to be the diffusion-controlled step? The proportionality of I_p to $v^{1/2}$ in Eq. (6) has been confused with

the linearity, $I_p = av^{1/2} + b$ ($b \neq 0$). The plot for the adsorption control ($I_p = kv$) also shows approximately a linear relation for I_p vs. $v^{1/2}$ plot in a narrow domain of v , as shown in **Figure 4B**. The opposite is true (**Figure 4A**). Therefore, it is the intercept that determines a controlling step of either the diffusion or adsorption. Some may say that the intercept can be ascribed to a capacitive current. If so, the peak current should be represented by $I_p = av^{1/2} + bv$, which exhibits neither linear relation with $v^{1/2}$ nor v .

There is a simple method of determining a controlling step either by diffusion or adsorption. Current responding to diffusion-controlled potential at a disk electrode in diameter less than 0.1 mm would become under the steady state after a few seconds [8]. Adsorption-limited current should become zero soon after the potential application. Many redox species, however, show gradual decrease in the current because reaction products generate an adsorbed layer which blocks further electrode reactions.

3.5 Plots of I_p against E_p

It is well known that currents vary not only with applied voltage but also with the time. It is not popular, however, to discuss quantitatively time dependence of CV voltammograms. Enhancing v generally increases the current and causes the peak potential to shift in the direction of the scan. A reason for the former can be interpreted as generation of large current at a shorter time (see Eqs. (6) and (10)), whereas the latter is ascribed to a delay of reaction responses as well as a voltage loss of the reaction by solution resistance. Then the voltage effective to the reaction is lower than the intended voltage, and so the observed current may be smaller than the predicted one. Although I_p is related strongly with E_p , the relationship has rarely been examined quantitatively.

A technique of analyzing the potential shift is to plot I_p against E_p , [9] as shown in **Figure 5**. If the plots on the oxidation side ($I_p > 0$) and the reduction side ($I_p < 0$) fall each on a straight line, the slope may represent conductivity. If values of both slopes are equal, the slope possibly stands for the conductivity of the solution or membrane regardless of the electrode reaction. The potential extrapolated to the zero current on each straight line should be close to the formal potential. Since this plot is simple technically, the analytical result is more reliable than at least discussion of time dependence of E_p .

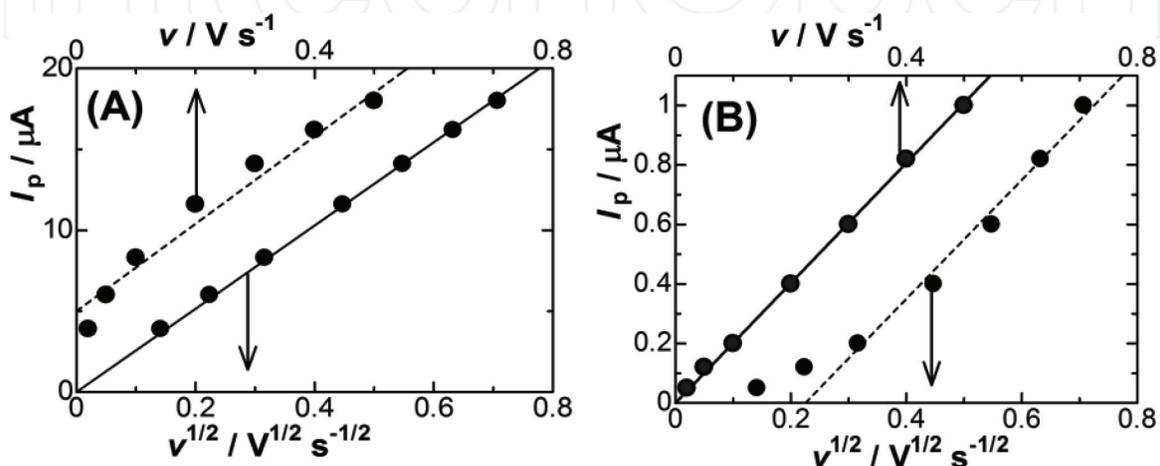


Figure 4.

Plots of I_p of (A) $K_3Fe(CN)_6$ and (B) polyaniline-coated electrode against $v^{1/2}$ and v . Both plots show approximately linear relations.

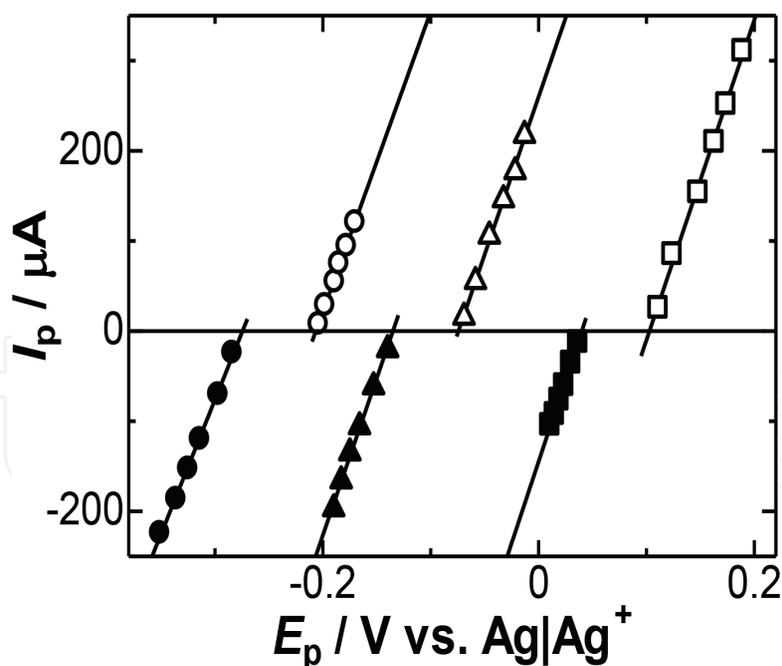


Figure 5.

Plots of I_p vs. E_p by CV of the first (circles) and the second (triangles) peak of tetracyanoquinodimethane (TCNQ), and ferrocene (squares) in 0.2 M $(\text{CH}_3)_4\text{NPF}_6$ included acetonitrile solution when scan rates were varied, where triangles were displayed by 0.4 V shift.

3.6 Meaning of $n^{3/2}$ in the equation for peak current

Most researchers have quoted the Randles-Sevcik equation, $j_p = 0.446 (nF)^{3/2} c^* (Dv/RT)^{1/2}$, for the diffusion-controlled peak current without hesitation, where n is the electron transfer number of the reaction. According to Faraday's law, the electrolytic quantity is proportional to nc^* . Why is the peak current proportional to $n^{3/2}$ instead of n ? Let us consider voltammetry of metal nanoparticles (about 25 nm in diameter) composed of 10^6 metal atoms dispersed in solution. Faraday's law predicts that the current is 10^6 times as high as the current by the one metal atom. However, Randles-Sevcik equation predicts the current further $(10^6)^{1/2} = 1000$ times as large, just by the effect of the potential scan. The order 3/2 is specific to CV. The order of n for AC current and pulse voltammetry is 2 [10]. On the other hand, the diffusion-controlled steady-state currents at a microelectrode and a rotating disk electrode are proportional to n . Comparing the differences in the order by methods, we can predict that the time variation of the voltage increases the power of n .

Let a potential width from a current-rising potential to E_p be denoted by ΔE . When an n -electron transfer reaction occurs through the Nernst equation at which F in Eq. (1) is replaced by nF , the concentration-potential curve takes the slope n times larger than that at $n = 1$ (see $c_o/c_r \cong nF(E - E^o)/RT$ near $E = E^o$ in Eq. (1)). Then we have $(\Delta E)_n = (\Delta E)_{n=1}/n$. The period of elapsing for $(\Delta E)_n$ becomes shorter by $1/n$, as if v might be larger by n times. Then v in Eq. (6) should be replaced by $(nv)^{1/2}$. Combining this result with the flux j/nF , the current becomes $n^{3/2}$ times larger than that at $n = 1$. Therefore, the factor $n^{3/2}$ results from the Nernst equation. This can be understood quantitatively by replacing F in Eq. (3) by nF . There are quite a few reactions for $n \geq 2$ both for Nernst equation and in the bulk as stable species. The term $n^{3/2}$ is valid only for a concomitant charge-transfer reaction, i.e., simultaneous occurrence n -electron transfer rather than a step-by-step transfer. Apparent two-electron transfer reactions in the bulk, for example, Cu, Fe, Zn, and Pb, cause other reactions immediately after the one-electron transfer.

3.7 Area of counter electrode

An electrochemical response is observed as a sum of the half reactions at the two electrodes. In order to extract the reaction at the working electrode, a conventional technique is to increase the area of the counter electrode so that the reaction at the counter electrode can be ignored. If the counter electrode area is increased by 20 times the area of the working electrode, the observed current represents the reaction of the working electrode with an error of 5%. Let us consider the experiment in which nanoparticles of metal are coated on a working electrode for obtaining capacitive currents or catalyst currents. Then, the actual area of the working electrode can be regarded as the area of the metal particles measured by the molecular level. Then, the area will be several thousand times the geometric area so that the observed current may represent the reaction at the counter electrode. This kind of research has frequently been found in work on supercapacitors. On the other hand, if the electrode reaction is diffusion controlled, the current is determined by the projected area of the diffusion layer. Then the current is not affected by the huge surface area of nanoparticles.

It is important to examine whether or not a reaction is controlled by at a counter electrode. A simple method is to coat nanoparticles also on the counter electrode. Then the current in the solution may become so high that the potential of the working electrode cannot be controlled. It is better to use a two-electrode system. Products at the counter electrode are possible sources of contaminants through redox cycling.

3.8 Functionality of reference electrode

The Ag-AgCl electrode is most frequently used as a reference electrode in aqueous solution because of the stable voltage at interfaces of Ag-AgCl and AgCl-KCl through fast charge-transfer steps, regardless of the magnitude of current density. The “fast step” means the absence of delay of the reaction or being in a quasi-equilibrium. The stability without delay is supported with high concentration of KCl.

When an Ag-AgCl electrode is inserted to a voltammetric solution, KCl necessarily diffuses into the solution, associated with oxygen from the reference electrode. Thus, the reference electrode is a source of contamination by salt, dichlorosilver and oxygen. It is interesting to examine how much amount a solution is contaminated by a reference electrode [9]. Time variation of ionic conductivity in the pure water was monitored immediately after a commercially available Ag-AgCl electrode was inserted into the solution. **Figure 6** shows rapid increase in the conductivity as if a solid of KCl was added to the solution. Oxygen included in the concentrated KCl may contaminate a test solution. Even the Ag-Ag₂O electrode, which was formed by oxidizing silver wire, increased also the conductivity, probably because the surface is in the form of silver hydroxide. As a result, no reference electrode can be used for studying salt-free electrode reactions. If neutral redox species such as ferrocene is included in a solution, the potential reference can be taken from redox potential of ferrocene.

3.9 Current flowing through the double layer

When a constant voltage is applied to the ideal capacitance C , the responding current decays in the form of $\exp(-t/RC)$, where R is a resistance in series connected with C . It has been believed that a double-layer capacitance in electrochemical system behaves as an ideal capacitor, where R is regarded as solution

resistance. However, any exponential variation cannot reproduce transient currents obtained at the platinum wire electrode in KCl aqueous solution, as shown in **Figure 7**. The current decays more slowly than by $\exp(-t/RC)$, because it is approximately proportional to $1/t$. The property of non-ideal capacitance is the result of the constant phase element of the DL capacitance, as described in Section 2.3. The dependence of $1/t$ can be obtained approximately by the time derivative of $q = V_0 C_0 t^{-\lambda}$ for the voltage step V_0 .

The slow decay is related with a loss of the performance of pulse voltammetry, in which diffusion-controlled currents can readily be excluded from capacitive currents. The advantage of pulse voltammetry is based on the assumption of the exponential decay of the capacitive current. Since the diffusion current with $1/t^{1/2}$ dependence is close to the $1/t$ dependence, it cannot readily be separated from the capacitive current in reality. A key of using pulse voltammetry is to take a pulse time to be so long as a textbook recommends.

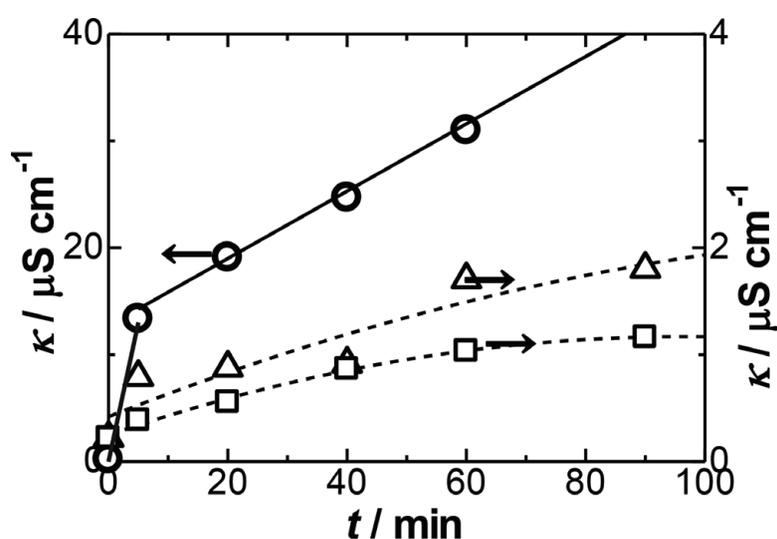


Figure 6. Time-variation of conductivity of water into which (circles) Ag|AgCl, (triangles) Ag|Ag₂O, and (squares) AgCl-coated Ag wire were inserted. Conductivity measurement was under N₂ environment.

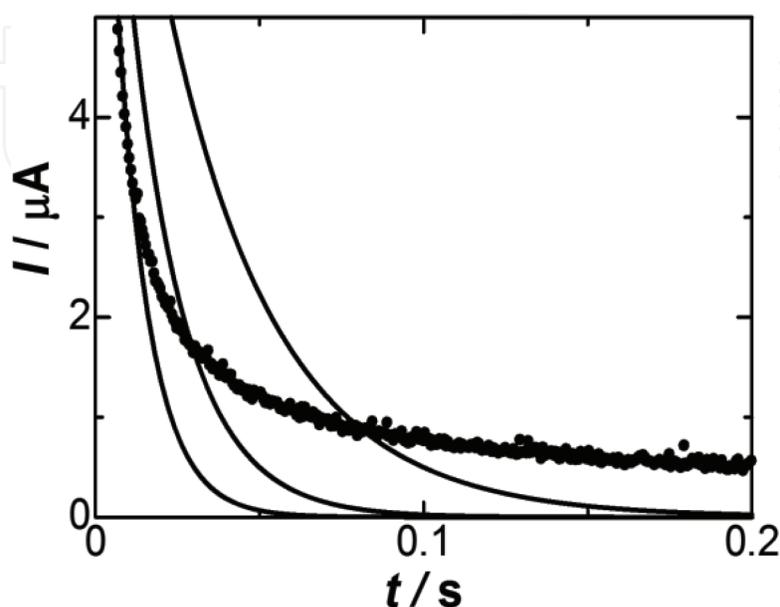


Figure 7. Chronoamperometric curves when 0.2 V vs. Ag|AgCl was applied to a Pt wire in 0.5 M KCl aqueous solution. Solid curves are fitted ones by $\exp(-t/RC)$ for three values of RC.

High-performance potentiostats are equipped with a circuit for compensation of resistance by a positive feedback. Unfortunately, the circuit is merely useful because voltammograms depend on intensity of compensation resistances of the DL capacitance. It should work well if the DL capacitance is ideal.

3.10 Advantages of AC impedance

AC techniques have an advantage of examining time dependence at a given potential, whereas CV has a feature of finding current-voltage curves at a given time. The former shows the dynamic range from 1 Hz to 10 kHz, while the latter does conventionally from 0.01 to 1 Hz. This wide dynamic range of the AC technique is powerful for examining dynamics of electrode reactions. Analytical results by the former are often inconsistent with those by the latter, because of the difference in the time domain. The other scientific advantage of the AC technique is to get two types of independent data set, frequency variations of real components and imaginary ones by the use of a lock-in amplification. The independence allows us to operate mathematically the two data, leading to the data analysis at a level one step higher than CV. An industrial advantage is the rapid measurement, which can be applied to quality control for a number of samples. The analysis of AC impedance necessarily needs equivalent circuits of which components do not have any direction relation with electrochemical variables.

Data of the electrochemical AC impedance are represented by Nyquist (Cole-Cole) plots, that is, plots of the imaginary component (Z_2) of the impedance against the real one (Z_1), as shown in **Figure 8**. The simplest equivalent circuit for electrochemical systems is the DL capacitance C_d in series with the solution resistance R_s . The Nyquist plot for this series circuit is theoretically parallel to the vertical axis (**Figure 8A-a**), but experiments show a slope of 5 or more (**Figure 8A-b**). This behavior, called constant phase element (CPE) and the power law, has been verified for combinations of various materials and solvents [6, 7, 11, 12]. The equivalent circuit for Eq. (12) is a parallel combination of capacitance and resistance (**Figure 8B**). Even without an electrode reaction, current always includes a real component.

The equivalent circuit with the Randles type is a parallel combination of the ideal DL capacitor C_d with the ideal resistance R_{ct} representing the Butler-Volmer-type charge-transfer resistance. Practically, the Warburg impedance (the inverse of

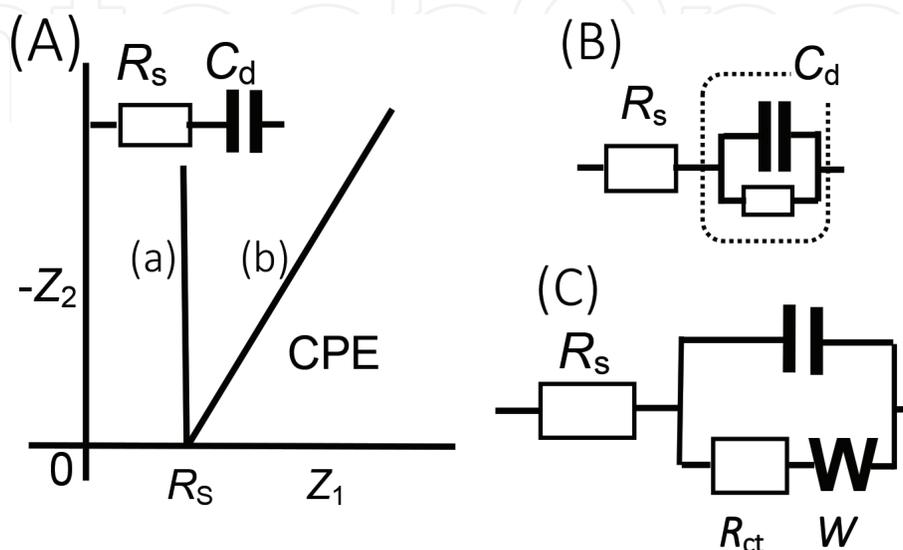


Figure 8.
 (A) Nyquist plots for a RC-series circuit with ideal capacitor (a) and DL capacitor (b). (B) Equivalent circuit with the power-law of C_d . (C) Randles circuit.

Eq. (8)) due to diffusion of redox species is incorporated in a series into R_{ct} (**Figure 8C**). R_{ct} cannot be separated from the DL resistance because of the frequency dispersion. Since even the existence of R_{ct} is in question (Section 3.12), it is difficult to determine and interpret R_{ct} . The usage of a software that can analyze any Nyquist plots will provide values of R and C . Even if analyzed values are in high accuracy, researches should give them electrochemical significance.

3.11 Residual currents depending on surface treatments

Residual current varies with treatments of electrodes such as polishing of electrode surfaces and voltage applications to an extremely high domain. It can often be suppressed to yield reproducible data when the electrode is replaced by simple platinum wire or carbon rod having the same geometric area. Simple wire electrodes are quite useful especially for measurements of DL capacitance and adsorption. One of the reasons for setting off large residual current is that the insulator of confining the active area is not in close contact with the electrode, so that the solution penetrated into the gap will give rise to capacitive current and floating electrode reactions. Since the coefficient of thermal expansion of the electrode is different from that of the insulator, the residual current tends to get large with the elapse from the fabrication of the electrode. This prediction is based on experience, and there are few quantitative studies on residual currents.

Unexpected gap has been a technical problem at dropping mercury electrodes. If solution penetrates the inner wall of the glass capillary containing mercury, observed currents become irreproducible. Water repellency of the capillary tip has been known to improve the irreproducibility in order to reduce the penetration. A similar technique has been used for voltammetry at oil-water interfaces and ionic liquid-water interfaces at present.

3.12 Reversible or irreversible voltammograms

Voltammograms are said to vary with electrode reaction rates, and the rate constants have been determined from time dependence of voltammograms. The fast reaction of which rate is not rate determining has historically been called “reversible.” In contrast, such a slow reaction that a peak potential varies linearly with $\log v$ is called “irreversible.” A reaction between them is called “quasi-reversible.” The distinction among the three has been well known since the theoretical report on the quasi-reversible reaction by Matsuda [1]. This theory is devoted to solving the diffusion equations with boundary conditions of the Butler-Volmer (BV) equation under the potential sweep. As the standard rate constant k_s in the BV equation becomes small, the peak shifts in the direction of the potential sweep from the diffusion-controlled peak. Steady-state current-potential curves in a microelectrode [13] and a rotating disk electrode also shift the potential in a similar way. According to the calculated CV voltammograms in **Figure 9**, we can present some characteristics: (i) if the oxidation wave shifts to the positive potential, the negative potential shift should also be found in the reduction wave. (ii) Both the amounts of the shift should have a linear relationship to $\log v$. (iii) The shift should be found in iterative measurements. (iv) The peak current should be proportional to $v^{1/2}$.

The authors attempted to find a redox species with the above four behaviors. Some redox species can satisfy one of the four requirements, but do not meet the others. Most reaction rate constants have been determined from the potential shift

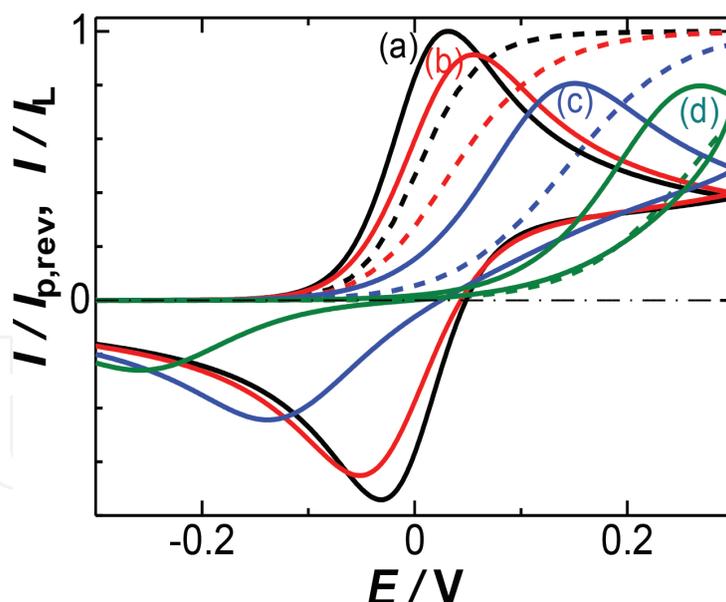


Figure 9. CV voltammograms (solid curves) at a normally sized electrode and steady-state voltammograms (dashed curves) at a microelectrodes in $12 \mu\text{m}$ in diameter, calculated theoretically for $v = 0.5 \text{ V s}^{-1}$, $D = 0.73 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $ks =$ (a) 0.1, (b) 0.01, (c) 0.001, (d) 0.0001 cm s^{-1} . The potential shift of CV is equivalent to the wave-shift at a microelectrode through the relation, $v = 0.4RTD/\alpha Fa^2$ (a : radius).

in a narrow time domain. They are probably caused by follow-up chemical reactions, adsorption, or DL capacitance. For example, CV peak potentials of TCNQ and benzoquinone were shifted at high scan rates, whereas their steady-state voltammograms were independent of diameters of microdisk electrodes even on the nanometer scale [14]. The shift at high scan rates should be due to the frequency dispersion of the DL capacitance, especially the parallel resistance in the DL (**Figure 8B**). Values of the heterogeneous rate constants and transfer coefficients reported so far have depended not only on the electrochemical techniques but also research groups. Furthermore, they have not been applied or extended to next developing work. These facts inspire us to examine the assumptions and validity of the BV formula.

Let us revisit the assumptions of the BV equation when an overvoltage, i.e., the difference of the applied potential from the standard electrode potential, causes the electrode reaction. The rate of the oxidation in the BV equation is assumed to have the activation energy of α times the overvoltage, while that of the reduction does that of $(1 - \alpha)$ times. This assumption seems reasonable for the balance of both the oxidation and the reduction. However, the following two points should be considered. (i) Once a charge or an electron is transferred within the redox species, the molecular structure changes more slowly than the charge transfer itself occurs. The structure change causes solvation as well as motion of external ions to keep electric neutrality. These processes should be slower than the structure change. If the overvoltage can control the reaction rate, it should act on to the slowest step, which is not the genuine charge-transfer process. (ii) Since a reaction rate belongs to the probability theory, the reaction rate (dc/dt) at t is determined with the state at t rather than a state in the future. In other words, the rate of the reduction should have no relation with the oxidation state which belongs to the future state. The BV theory assumes that the α times activation energy for the oxidation is related closely with $1-\alpha$ times one for the reduction. This assumption is equivalent to predicting a state at $t + \Delta t$ from state at $t + 2\Delta t$, like riding on a time machine. This question should be solved from a viewpoint of statistical physics.

3.13 Contradiction of microscopic image with electrochemical data

Development of scanning microscopes such as STM and AFM has allowed us to obtain the molecularly and atomically regulated surface images, which have been used for interpreting electrochemical data. Then the electrochemical data are expected to be discussed on a molecular scale. However, there is an essential problem of applying photographs of regularly arranged atoms on an electrode to electrochemical data, because the former and the latter include, respectively, microscopically local information and macroscopically averaged one. A STM image showing molecular patterns is information of only a part of electrode, at next parts of which no atomic images are often observed but noisy images are found. Electrochemical data should be composed of information both at a part of the electrode showing the molecular patterns and at other parts showing noisy, vague images. Noisy photographs are always discarded for interpreting electrochemical data although the surfaces with noisy images also contribute electrochemical data.

An ideal experiment would be made by taking STM images over all the electrodes that provide electrochemical data and by obtaining an averaged image. However, it is not only impossible to take huge amounts of images, but the averaged image might be also noisy. It may be helpful to describe only a possibility of reflecting the STM-imaged atomic structure on the electrochemical data.

3.14 Surface wave by adsorption

Voltammograms by adsorbed redox species, called surface waves, are frequently different from a bell shape (**Figure 2**). Really observed features are the following: (i) the voltammogram does not suddenly decay after the peak, exhibiting a tail-like diffusional wave; (ii) the peak current and the amount of the electricity are proportional to the power less than the unity of v ; (iii) the oxidation peak potential is different from the reduction one; (iv) the background current cannot be determined unequivocally; and (v) voltammograms depend on the starting potential. Why are experimental surface waves different from a symmetric, bell shape in **Figure 2**?

A loss of the symmetry with respect to the vertical line passing through a peak can be ascribed to the difference in interactions at the oxidized potential domain and at the reduced one. Since redox species takes extremely high concentration in the adsorbed layer, interaction is highly influenced on voltammetric form. When the left-right asymmetry is ascribed to thermodynamic interaction, it has been interpreted not only with Frumkin's interaction [15] but also Bragg-Williams-like model for the nearest neighboring interactive redox species [16]. On the other hand, most surface waves are asymmetric with respect to the voltage axis even at extremely slow scan rates. This asymmetry cannot be explained in terms of thermodynamics of intermolecular interaction, but should resort to kinetics or a delay of electrode reactions. There seems to be no delay in the electrode reaction of the monomolecular adsorption layer, different from diffusion species. The delay resembles the phenomenon of constant phase element (CPE) or frequency power law of DL capacitance, in that the redox interaction may occur two-dimensionally so that the most stable state can be attained. This behavior belongs to a cooperative phenomenon [17]. A technique of overcoming these complications is to discuss the amount of charge by evaluating the area of the voltammogram. It also includes ambiguity of eliminating background current and assuming the independence of the redox charge from the DL charge.

4. Conclusions

The simplest theories for voltammetry are limited to the rate-determining steps of diffusion of redox species and reactions of adsorbed species without interaction. Variation of scan rates as well as a reverse potential is helpful for predicting redox species and reaction mechanisms. Furthermore, the following viewpoints are useful for interpreting mechanisms:

- a. comparison of values of experimental peak currents with theoretical ones, instead of discussing ΔE_p and $E_{1/2}$;
- b. examining the proportionality of I_p vs. v or vs. $v^{1/2}$, i.e., zero or non-zero values of the intercept of the linearity;
- c. a reference electrode and a counter electrode being a source of contamination in solution;
- d. attention to very slow relaxation of DL capacitive currents;
- e. inclusion of ambiguity in the equivalent circuit with the Randles type.

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