April, 1989] Bull. Chem. Soc. Jpn., 62, 1023—1031 (1989)

Charge-Transfer Rates in Thin Polyelectrolyte Films Incorporating a Redox Molecule with Two Separate Electroactive Centers Having Different Redox Potentials. An Alizarine Red S-Cationic Perfluoropolymer Film System

Takeo Ohsaka, Youko Takahira, Osamu Hatozaki, and Noboru Oyama*
Department of Applied Chemistry for Resources, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184

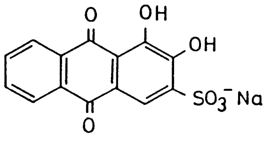
(Received October 13, 1988)

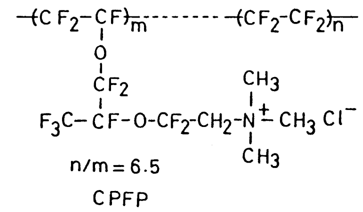
The diffusion coefficients for the charge-transport processes through 9,10-dihydro-3,4-dihydroxy-9,10-dioxo-2-anthracenesulfonate (Alizarine Red S, **1**)-incorporating cationic perfluoropolymer (CPFP) polyelectrolyte films on electrodes undergoing oxidation or reduction of two separate electroactive centers with different redox potentials, i.e., the two-electron reduction of **1** to 3,4,9,10-tetrahydroxy-2-anthracenesulfonate (**2**) and the two-electron oxidations of **2** to **1** and **1** to 3,4,9,10-tetrahydro-3,4,9,10-tetraoxo-2-anthracenesulfonate (**3**) were measured by potential-step chronoamperometry and chronocoulometry. The apparent diffusion coefficients for **1** to **2**, **2** to **1**, and **1** to **3** processes where the first two processes are reversible and the **1** to **3** process is irreversible, represented as $D^{\mathrm{rev}}_{\mathrm{app}}(1\rightarrow2)$, $D^{\mathrm{rev}}_{\mathrm{app}}(2\rightarrow1)$ and $D^{\mathrm{irrev}}_{\mathrm{app}}$ $(1\rightarrow3)$, respectively, decreased with increasing the concentration (C_{film}) of **1** (or **2**) in the CPFP film, and for a given C_{film} they were found to be in the following order: $D_s' \gg D^{\mathrm{rev}}_{\mathrm{app}}$ $(1\rightarrow2) \sim D^{\mathrm{rev}}_{\mathrm{app}}(2\rightarrow1) > D^{\mathrm{irrev}}_{\mathrm{app}}$ $(1\rightarrow3)$, where D_s' represents the diffusion coefficients corresponding to the diffusion of supporting electrolyte ions coupled to electron transfer and molecular motion of reactant itself. It became apparent that the difference in $D^{\mathrm{rev}}_{\mathrm{app}}(1\rightarrow2)$ (or $D^{\mathrm{rev}}_{\mathrm{app}}(2\rightarrow1)$) and $D^{\mathrm{irrev}}_{\mathrm{app}}$ $(1\rightarrow3)$ can be attributed to different contributions of electron exchange between electroactive centers to the overall charge-transport rates. The results demonstrate that the contributions from molecular motion of reactant itself and electron exchange between reactants to the overall charge-transport rates can be estimated depending upon which redox center is employed in an electrochemical measurement of diffusional rates.

Charge transport through thin films (thicknesses are typically ca. 10^{-6}—10^{-3} cm) of redox polymers with electroactive mobile reactants or fixed sites, which are coated on electrode surfaces and are well-swollen with solvent/electrolyte, has been a subject of much interest in recent years.[1—20] The mechanisms of charge transport are generally reasonably well-understood, but in any particular case it is often difficult to determine the rate-determining step, especially in the case[2a,3,4f,5,6a,9,12,14,15,17] where the electroactive reactants incorporated in films are not part of the polymeric structure or permanently attached to functional groups present in the films. In this case, the diffusion of electroactive reactants within the polymeric matrix can include contributions from both molecular motion[1b,2a—c,3a,b,d,e,g,4b,c,f,g,5,9,12,14,15] and electron exchange between adjacent pairs of the oxidized and reduced reactants.[1a,b,2c—e,3b,c,f,g,4a,d,e,5g—i,12,21,22] The diffusion is also usually accompanied by migration of electrolyte ions to maintain electroneutrality, motion of solvent and segmental motion of polymeric chain. Thus, it has been generally known that the rates of charge transport, which has been proved to be treated in many cases[1—5,7a,8a,9a,b,12—15,17—20] as a Fickian diffusion process, depend on the polymer matrix, the electroactive reactant incorporated into it, the concentration of the reactant, the supporting electrolyte and its concentration, pH of solution, solvent, etc.

A variety of redox polymer film systems have been ever used as models for the fundamental elucidation of charge-transfer process within thin films on electrodes.[1—9,12,14,15,17—20] Among these, a system, where a molecule with two separate electroactive centers having different redox potentials is incorporated in a polyelectrolyte film on electrodes, is of particular interest as originally pointed out by Tsou and Anson,[3f] because one could obtain new information on charge transport that is not obtained or is different from that obtained for cases where a kind of redox species is incorporated in a film or two kinds of redox species are simultaneously incorporated in it. Tsou and Anson have measured the diffusion coefficients of the hetero-binuclear metal complex $(NH_3)_5RuC_5H_4N$-$CH_2NHC(=O)$-CpFeCp (C_5H_4N=4-pyridyl, Cp=cyclopentadienide or substituted cyclopentadienide) within Nafion coatings in all three of its possible redox states (i.e., $Ru^{II}LFe^{II}$, $Ru^{III}LFe^{II}$, $Ru^{III}LFe^{III}$) and have explained successfully possible origins of the differences of the diffusional rates corresponding to these three oxidation states and their concentration dependences on the basis of intermolecular electron self-exchange, single-file diffusion and electrostatic cross linking. More recently, we[23] also have reported the preliminary results concerning the charge-transport rates for the oxidation and reduction of the two separate electroactive centers-containing molecule/thin polymer film system, i.e., 9,10-dihydro-3,4-dihydroxy-9,10-dioxo-2-anthracenesulfonate (which is often called Alizarine Red S dye and is abbreviated as ARS in this paper)-incorporating perfluoropolymer (CPFP) film system. ARS contains two separate electroactive centers, i.e., 3,4-dihydroxy and 9,10-dioxo groups, and the electrode reactions of 3,4-dihydroxy and 9,10-dioxo groups are irreversible and reversible, respectively.[23,24] Thus, if the electron exchange between electroactive centers contributes significantly to the overall charge-transport rates, we could observe different charge-transport rates for the oxidation (or reduction) process of these two kinds of the electroactive centers. This is the first reason why we chose ARS as an electroactive molecule to be incorporated in films. The electroinactive functional group (i.e., SO_3^- group) serves as a counter anion site of the fixed cationic quaternized ammonio groups of CPFP and the net charge on ARS does not change before and after the oxidation or reduction of the electroactive centers. This is another reason for using ARS. In a previous paper,[23] it has been suggested that the contributions from molecular motion of reactant itself and electron exchange between reactants to the overall charge-transport rates can be estimated depending upon which redox center is employed in an electrochemical measurement of diffusional rates.

In this study, in addition to the fundamental redox behavior of ARS incorporated in CPFP films, we examined in more detail the charge-transport process within ARS-incorporating CPFP films undergoing oxidation or reduction of 3,4-dihydroxy and 9,10-dioxo groups, e.g., the dependences of the diffusional charge-transport rates on the concentration of ARS in films and the differences between these rates and the diffusional rates corresponding to the physical diffusion of counter ions which is necessarily, for charge neutrality, coupled to electron transfer (i.e., the homogeneous oxidation-reduction reaction of the electroactive groups in the CPFP films). The results obtained are reported in this paper.


Alizarine Red S



CPFP

Experimental

Materials. 9,10-Dihydro-3,4-dihydroxy-9,10-dioxo-2-anthracenesulfonate (abbreviated as ARS) of reagent grade was obtained from Wako Pure Chemical Industries, Ltd., and was recrystallized three times from $H_2O-C_2H_5OH$ mixture (volume ratio=1 : 1), then dried at 100 °C. A stock solution of cationic perfluoropolymer (abbreviated as CPFP) was prepared as described previously.[25] The concentration of CPFP stock solution (solvent: $H_2O-C_2H_5OH$-2-propanol (volume ratio=1 : 1 : 1)) was 10.5 mg ml^{-1}. $[Co(tpy)_2]Cl_2 \cdot 2H_2O$ (tpy: 2,2′ : 6′,2″-terpyridine) was prepared and purified according to the literature.[26] NaI was of reagent grade (Tokyo Kasei Co., Ltd.). Basal-plane pyrolytic graphite (BPG, Union Carbide Co.) and In-Sn oxide conducting glass (ITO, Matsuzaki Shinku Co.) were used as working electrodes. Unless otherwise noted, the areas of BPG and ITO electrodes used were 0.19 and 0.25 cm^2, respectively. A platinum wire was used as a counter electrode. The supporting electrolyte solutions were 0.2 M (1 M=1 mol dm^{-3}) CF_3COONa, prepared from CF_3COOH (Aldrich) and NaOH, adjusted to the desired pH's with CF_3COOH, NaOH and/or the commonly used buffer solutions: citric acid/Na_2HPO_4 buffer solutions (at pH 3, 5, and 7), $Na_2B_4O_7$/HCl buffer solution (pH 9) and Na_2HPO_4/NaOH buffer solution (pH 11). Aqueous solutions were prepared from doubly distilled water. Other chemicals were of reagent grade and were used as received.

Apparatus and Procedures. A standard three-electrode, electrochemical cell was used for all the electrochemical experiments. The electrode assembly consisted of an uncoated or a CPFP film-coated BPG (or ITO) as the working electrode, a sodium chloride saturated calomel electrode (SSCE) as the reference electrode, and a platinum wire as the counter electrode.

For cyclic voltammetry (CV), potential-step chronoamperometry (PSCA) and potential-step chronocoulometry (PSCC), a homemade instrument was employed. Positive feedback circuitry was employed to compensate the resistances associated with the polymer films as much as possible. PSCA and PSCC data (i.e., current-time responses and charge-time responses) were monitored and stored on a Nicolet digital oscilloscope (model 3091). These data were then transferred to the laboratory's minicomputer (NEC, PC-9801VE), where calculation was performed, and then graphically presented on an X-Y recorder (Graphtec Co.). Rotating-disk voltammograms were obtained with standard, previously described procedures and apparatus.[27]

The preparation of CPFP film-coated electrodes and the measurement of the film thickness (typically 1.0 μm) were carried out by the same procedure as before.[25] The CPFP film-coated electrodes were equilibrated with 0.01—0.1 mM solutions (pH 1.0) (containing 0.2 M CF_3COONa) of ARS in order to achieve the incorporation of desired quantities of ARS into the films. During the incorporation of several hours, the electrode potential was repeatedly cycled between −0.6 and 0.2V vs. SSCE, and simultaneously the solution was stirred. The quantity (Γ) of ARS incorporated into the CPFP films on the electrodes was estimated (in mol cm^{-2}) by measuring the area of cyclic voltammograms for the oxidation of ARS obtained at slow potential scan rates (1—5 mV s^{-1}). In this case, the electrode potential was held at −0.6 V vs. SSCE for ca. 5—20 min and then the potential was scanned from −0.6 to 0.2 V vs. SSCE. The concentration (in mol cm^{-3}) of the incorporated ARS was calculated from the Γ value thus obtained using the measured film thickness. All experiments were run under a nitrogen atmosphere at laboratory temperature (25±1 °C). The potentials were measured and are quoted with respect to the SSCE.

Results

Incorporation of ARS into CPFP Films Coated on Electrodes. Figure 1 shows typical cyclic voltammograms demonstrating the incorporation of ARS into the CPFP film (thickness: 1.0 μm) coated on an ITO electrode in a 0.2 M CF_3COONa aqueous solution (pH 1.0) containing 0.1 mM ARS. The incorporation of ARS by anion exchange with Cl^- ions, which are initially present in the film as the counteranions of the fixed cationic quaternized ammonio groups, continued for about 90 min (Fig. 1B). No further increases

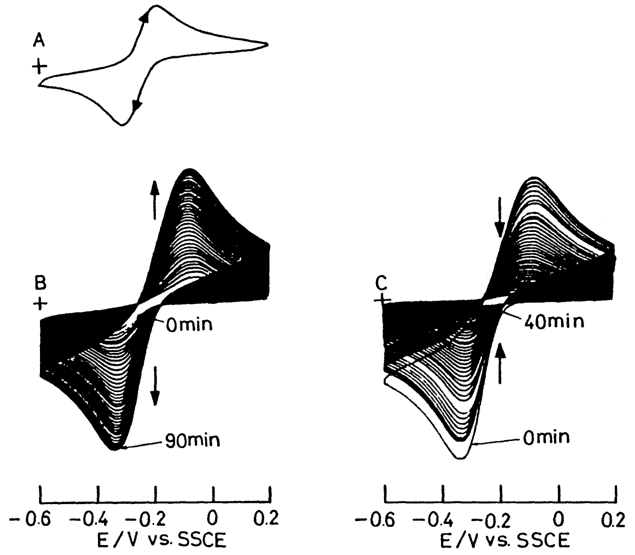


Fig. 1. (A) Cyclic voltammogram of ARS at an uncoated ITO electrode in 0.2 M CF$_3$COONa solution (pH 1.0) containing 0.1mM ARS. (B) Cyclic voltammograms demonstrating the incorporation of ARS into the CPFP film coated on an ITO electrode in the same solution as used in A. Thickness of the CPFP film: 1.0 μm. Volume concentration of the quaternized ammonium site in the CPFP film: 1.7 M. (C) Cyclic voltammograms obtained when the electrode used in B was transferred to a 0.2 M CF$_3$COONa solution (pH 1.0). Immersion time is indicated on the voltammograms. In every case, scan rate was 50 mV s^{-1} and electrode area was 0.25 cm^2.

in peak current were observed with scanning time longer than 90 min. The peak current at the coated electrode was about 2.5 times that at an uncoated electrode (Fig. 1A), and the concentration of the incorporated ARS was 0.46 M. This indicates that the quantity of the incorporated ARS corresponds to ca. 27% of the total amount (1.7 M)[25] of the quaternized ammonium site in the CPFP film. When the CPFP-coated electrode was removed from the incorporating solution and replaced in the pure supporting electrolyte, the ARS anions leached gradually from the CPFP film, and thus the peak current decreased with scanning time. After about 40 min, most of the ARS anions were lost from the film (Fig. 1C). However, the steady-state currents shown in Fig. 1B remained substantially unchanged in the incorporating solution containing 0.1 mM ARS for a period of several hours, even when the electrode was rotated at rotation rates of 100—4900 rpm in the hydrodynamic voltammetric experiments using rotating-disk electrodes (as mentioned below).

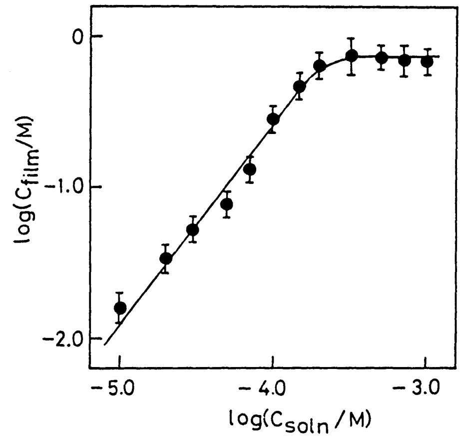


Fig. 2. Equilibrium distribution curve of ARS in the bulk of 0.2 M CF$_3$COONa solutions (pH 1.0) and in the CPFP films (thickness: 1.0 μm) coated on electrodes. C_soln and C_film refer to the concentrations of ARS in the bulk of CF$_3$COONa solution and the CPFP film, respectively.

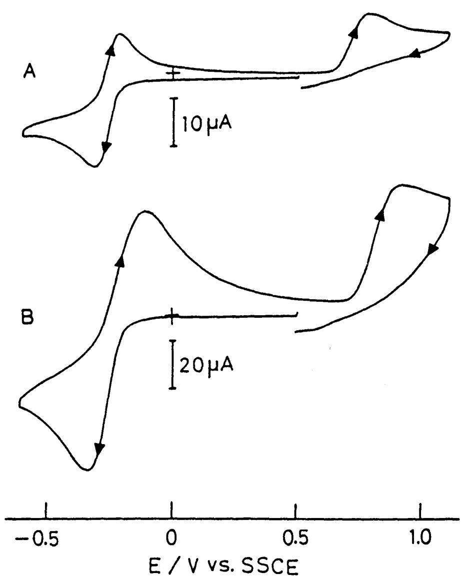


Fig. 3. (A) Cyclic voltammogram of ARS at an uncoated ITO electrode in 0.2 M CF$_3$COONa solution (pH 1.0) containing 0.1 mM ARS. Scan rate: 20 mV s^{-1}. (B) Cyclic voltammogram of ARS confined in the CPFP film (thickness: 1.0 μm) coated on ITO electrode in the same solution as used in A. Scan rate: 50 mV s^{-1}. In both cases, the electrode areas were 0.22 cm^2.

The equilibrium distribution curve for ARS partitioned into the CPFP film from 0.2 M CF$_3$COONa solution (pH 1.0) is shown in Fig. 2, where the logarithm of the concentration (C_film) of ARS incorporated into the films is plotted against the logarithm of the concentration (C_soln) of ARS in the incorporating solutions over the concentration range 10^{-5} to 10^{-3} M. It is apparent from this figure along with Fig. 1 that ARS is incorporated and concentrated into CPFP film on electrode. The C_film vs. C_soln plot is almost linear at $C_\mathrm{soln}<0.14$ mM and the equilibrium distribution coefficients, defined as $C_\mathrm{film}/C_\mathrm{soln}$, are estimated to be $(1—3)\times10^3$ at $C_\mathrm{soln}=10^{-5}$—10^{-4} M.

Cyclic Voltammetry of ARS in Solution and CPFP Film. The cyclic voltammetric behavior of ARS confined in CPFP film was found to be essentially the

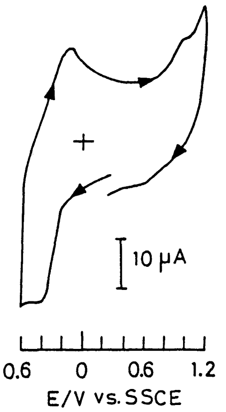


Fig. 4. Cyclic voltammogram for ARS confined in the CPFP film (thickness: 1.0 μm) coated on ITO electrode in 0.2 M CF_3COONa (pH 1.0) containing 0.025 mM ARS. Scan rate: 10 $V s^{-1}$.

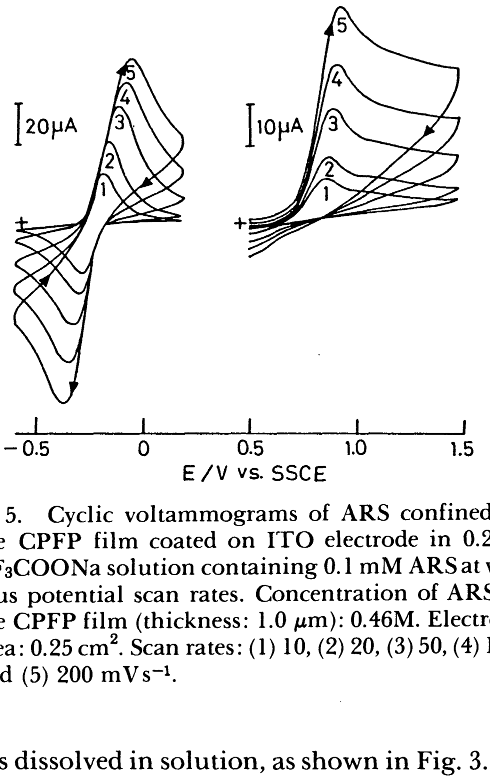


Fig. 5. Cyclic voltammograms of ARS confined in the CPFP film coated on ITO electrode in 0.2 M CF_3COONa solution containing 0.1 mM ARS at various potential scan rates. Concentration of ARS in the CPFP film (thickness: 1.0 μm): 0.46M. Electrode area: 0.25 cm^2. Scan rates: (1) 10, (2) 20, (3) 50, (4) 100, and (5) 200 $mV s^{-1}$.

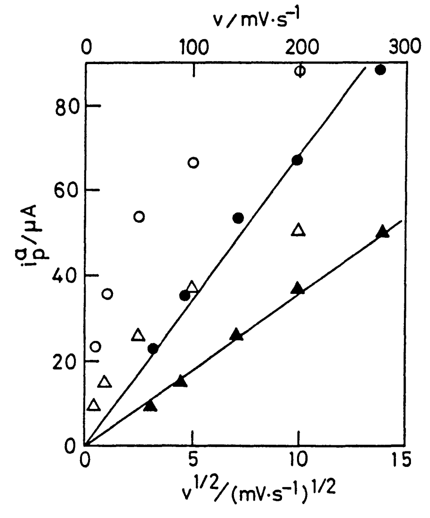
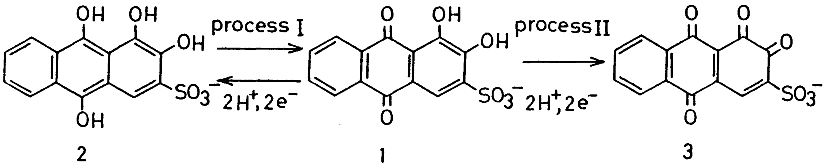


Fig. 6. Dependences of the anodic peak currents, i_p^a, for the oxidations of ARS confined in the CPFP film upon potential scan rate, v. The plots correspond to the data used in Fig. 5. (○, △): i_p^a vs. v plots, (●, ▲): i_p^a vs. $v^{1/2}$ plots. (○, ●): oxidation of **2** to **1**, (△, ▲): oxidation of **1** to **3**.

same as dissolved in solution, as shown in Fig. 3. That is to say, the reversible and irreversible redox responses can be observed at ca. −0.27 and ca. 0.8 V vs. SSCE, which correspond to the oxidation-reduction reaction of 9,10-dioxo group and the oxidation of 3,4-dihydroxy group, respectively. The data in Fig. 3 were obtained with ITO electrodes. Almost similar results were also obtained with BPG electrodes, but in this case an adsorption of ARS on uncoated BPG electrode substrates was observed. The reversibility of the electrode reactions of 9,10-dioxo and 3,4-dihydroxy groups seemed essentially unchanged on the time scale (ca. 1—40 ms) of the potential-step experiments from which the diffusion coefficients for the diffusional charge-transport processes were obtained (mentioned below), as seen from the cyclic voltammograms shown in Fig. 3 and obtained at a scan rate of 10 $V s^{-1}$ (Fig. 4). The time scale of 10 $V s^{-1}$ at CV approximately corresponds to ca. 1 ms at PSCA and PSCC.[28] Plots of the peak currents (i_p) for the oxidation and/or reduction of 9,10-dioxo and 3,4-dihydroxy groups of ARS incorporated in the CPFP film against the square root of potential scan rate, $v^{1/2}$, were nearly linear in the range of v from 10 to 200 $mV s^{-1}$ (as shown typically in Figs. 5 and 6), indicating that charge transport through the CPFP film is apparently diffusional and obeys Fick's law.[28]

The formal redox potentials ($E^{\circ\prime}$) (estimated as the average of the anodic and cathodic peak potentials) for the oxidation-reduction reaction of the 9,10-dioxo group of ARS in both solution and CPFP film shifted to negative potentials with increasing pH, and the slope of the $E^{\circ\prime}$ vs. pH plot was about −56 mV/pH. Thus, protons and electrons were found to take part in the electrode reaction in a 1/1 ratio. On the basis of the above-mentioned and previously reported results,[23,24] the mechanism of the electrode reaction of ARS confined in the CPFP film on electrodes can be represented as follows.



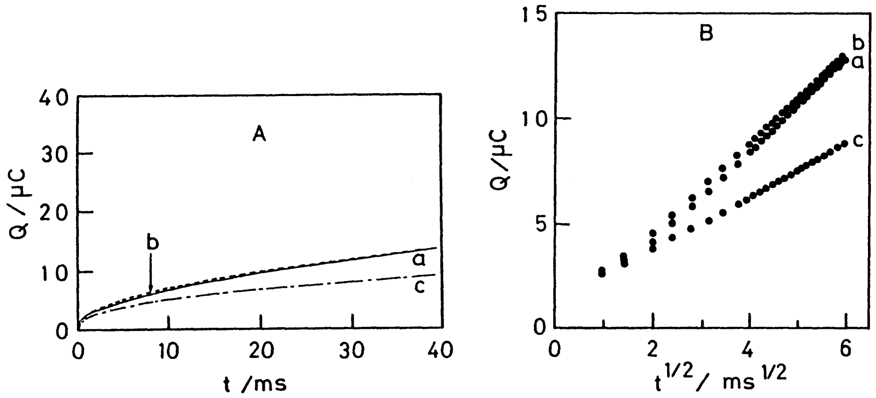


Fig. 7. (A) Typical potential-step chronocoulometric responses for (a) the reduction of **1** to **2**, and the oxidations of (b) **2** to **1** and (c) **1** to **3** of ARS confined in the CPFP film coated on ITO electrode (0.25 cm^2) in 0.2 M CF_3COONa solution (pH 1.0) containing 0.01 mM ARS. Concentration of ARS in the CPFP film (thickness: 1.0 μm): 35 mM. The electrode potentials were stepped from (a) 0.2 to −0.6, (b) −0.6 to 0.2, and (c) 0.2 to 1.3 V vs. SSCE. (B) Chronocoulometric Cottrell plots for the data in A.

Potential-Step Chronoamperometry and Chronocoulometry. Figure 7A shows typical potential-step chronocoulometric responses for an ITO/CPFP, ARS electrode where the electrode potentials were stepped from (a) 0.2 to −0.6, (b) −0.6 to 0.2, and (c) 0.2 to 1.3 V vs. SSCE. Responses a and b correspond to process I and response c corresponds to process II. The chronocoulometric Cottrell plots (i.e., Q vs. $t^{1/2}$ plots) are shown in Fig. 7B. The data gave almost linear Q-$t^{1/2}$ plots in the examined range of t from ca. 1 to 40 ms, and thus the slopes of these plots yielded the apparent diffusion coefficients (D_{app}) for the diffusion-like charge-transport processes within the films. The D_{app} values were also obtained by potential-step chronoamperometry. The results thus obtained are summarized in Fig. 8 and Table 1. In this paper, for convenience, we will represent D_{app}'s for the reversible process I and the irreversible process II as D_{app}^{rev} and D_{app}^{irrev}, respectively. It should be noted that the D_{app} values changed slightly from one electrode to another, even when the experimental conditions (e.g., C_{film} and step-potential in PSCA and PSCC experiments) were the same. For this reason, the values of D_{app}^{rev}, D_{app}^{irrev}, and κD_s (D_s: diffusion coefficients for I^- and $[Co(tpy)_2]^{2+}$ in CPFP films, κ: partition coefficient, mentioned below) at a given C_{film}, summarized in Table 1, were obtained at the same electrode. From Fig. 8 and Table 1, we can see that D_{app}^{rev} and D_{app}^{irrev} decrease with increasing C_{film} and that $D_{app}^{rev} > D_{app}^{irrev}$ for a given C_{film}.[35)]

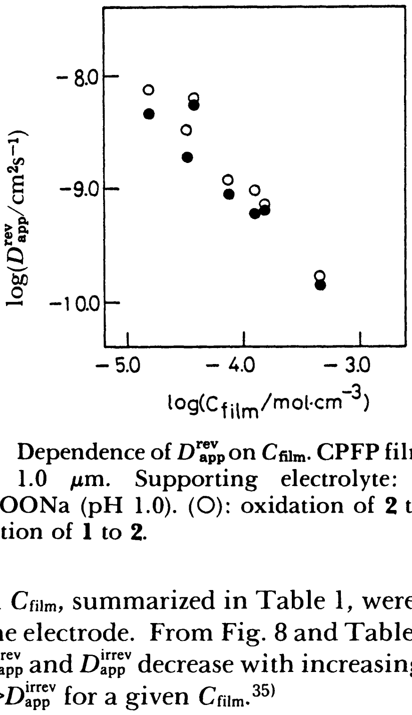


Fig. 8. Dependence of D_{app}^{rev} on C_{film}. CPFP film thickness: 1.0 μm. Supporting electrolyte: 0.2 M CF_3COONa (pH 1.0). (○): oxidation of **2** to **1**; (●) reduction of **1** to **2**.

Rotating-Disk Voltammetry. In order to estimate the diffusion coefficients coresponding to the diffusion of supporting electrolyte ions which is necessarily, for

Table 1. Comparison of D_{app}'s for ARS with κD_s's for $[Co(tpy)_2]^{2+}$ and I^- [a,b)]

C_{film}/M	D_{app}^{rev}/cm^{2}s^{-1} [c)]	D_{app}^{irrev}/cm^{2}s^{-1} [c)]	κD_s/cm^{2}s^{-1}	
			$[Co(tpy)_2]^{2+}$ [d)]	I^- [d)]
0.035	(5.6±0.5)×10^{-9}(Red) (5.7±0.5)×10^{-9}(Ox)	(2.0±0.2)×10^{-9}(Ox)	(3.7±0.6)×10^{-8}	(6.3±0.5)×10^{-6}
0.46	(1.5±0.2)×10^{-10}(Red) (1.6±0.1)×10^{-10}(Ox)	(6.1±0.1)×10^{-11}(Ox)	(2.6±0.4)×10^{-8}	(1.2±0.1)×10^{-6}

a) Supporting electrolyte: 0.2 M CF_3COONa (pH 1.0). CPFP film thickness: 1.0 μm. b) See the text for the definition of C_{film}, D_{app}^{rev}, D_{app}^{irrev}, and κD_s. c) Ox: oxidation process, Red: reduction process. d) The D_{soln} values of $[Co(tpy)_2]^{2+}$ and I^- in 0.2 M CF_3COONa solutions (pH 1.0) were estimated to be (3.8±0.2)×10^{-6} and (2.4±0.2)×10^{-5} cm^{2}s^{-1}, respectively.

charge neutrality, coupled to electron transfer (i.e., redox reactions of electroactive groups of ARS), the redox ions, which are electroactive in such a potential region (ca. 0—0.7 V vs. SSCE) that the redox response of ARS is not substantially observed, are required owing to electroinactivity (under the experimental conditions employed in this study) of the supporting electrolyte ions used (Na^+ and CF_3COO^-). For this purpose, I^- and $[Co(tpy)_2]^{2+}$ were chosen. Figure 9 shows typical steady-state current-potential curves for the oxidation of I^- at both bare and CPFP film-coated rotating BPG disk electrodes in a 0.2M CF_3COONa solution (pH 1.0) containing 0.01 mM ARS and 0.5 mM NaI. In this case, the CPFP film-coated electrode was previously equilibrated with a 0.01 mM ARS solution containing no I^-, and then the hydrodynamic voltammetric experiments were conducted. Note that the oxidation of I^- is not thermodynamically mediated by ARS incorporated in the CPFP film, as seen from the comparison of formal redox potentials ($E^{\circ\prime}$) of ARS and I_2/I^- couple, i.e., the $E^{\circ\prime}$'s of ARS (for process I) and I_2/I^- couple are −0.27 and 0.44 V vs. SSCE, respectively, in 0.2 M CF_3COONa aqueous solution (pH 1.0). The oxidation of I^- might be mediated by the I_2/I^- couple present within the CPFP film, since it is an anion-exchanging film and thus the trapping of I^- in the film is possible. However, this possibility may be ignored from the following fact. After the above-mentioned rotating-disk voltammetric experiments, the electrode was transferred into a 0.2 M CF_3COONa solution (pH 1.0) containing no ARS and I^- and the cyclic voltammetric response was examined as soon as possible. Consequently, we observed a well-defined redox response of ARS, but no redox response corresponding to I_2/I^- couple was obtained. Thus, the observed anodic currents correspond to the oxidation of I^- ions that penetrate the ARS-containing CPFP films to reach the electrode surface. Figure 10A shows the Levich plots[29] of limiting current, i_{lim} vs. (rotation rate, $\omega)^{1/2}$ obtained from the steady-state current-potential curves such as those shown in Fig. 9. The deviations of the limiting currents with CPFP-coated electrodes from the straight line obtained with a bare BPG electrode reflect the different diffusion rates of I^- ion in the bulk of the solution and the swollen, ARS-containing CPFP films.

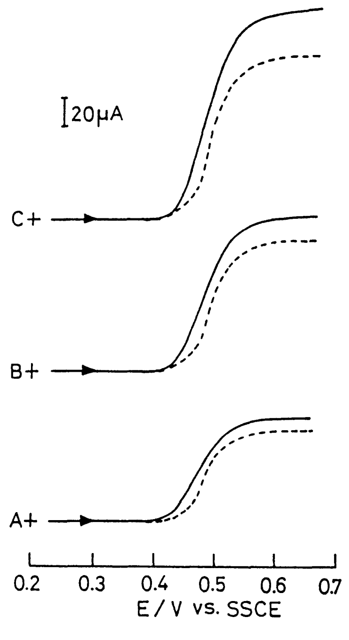


Fig. 9. Typical steady-state current-potential curves for the oxidation of iodide ion at uncoated and ARS-containing CPFP film-coated BPG disk electrodes. (——): at an uncoated BPG electrode in 0.2 M CF_3COONa solution (pH 1.0) containing 0.5 mM NaI; (----): at an ARS-containing CPFP film-coated BPG electrode in 0.2 M CF_3COONa solution (pH 1.0) containing 0.01 mM ARS and 0.5 mM NaI. Concentration of ARS in the CPFP film (thickness: 1.0 μm): 35 mM. Electrode areas: 0.19 cm². Potential scan rate: 2 mV s⁻¹. Electrode rotation rate: (A) 400, (B) 900, (C) 1600 rpm.

The quantitative analysis of this problem was made according to the Koutecky-Levich equation as described previously:[28,30)]

$$\frac{1}{i_{\text{lim}}} = \frac{1}{i_{\text{Lev}}} + \frac{1}{i_{\text{s}}} \tag{1}$$

with

$$i_{\text{Lev}} = 0.62\, nFAD_{\text{soln}}{}^{2/3}\, \nu^{-1/6}\, C_{\text{soln}}\, \omega^{1/2} \tag{2}$$

$$i_{\text{s}} = nFA\kappa C_{\text{soln}} D_{\text{s}} \phi^{-1} \tag{3}$$

where i_{Lev} is the Levich current,[29] i_{s} is the "permeation current"[7c,28,31,32] of I^- ion through the CPFP film, D_{soln} is the diffusion coefficient of I^- ion in a bulk solution, D_{s} is the diffusion coefficient of I^- ion in the film, ν is the kinematic viscosity of the solution, C_{soln} is the bulk concentration of I^- ion, ϕ is the film thickness, and κ is the partition coefficient of I^- ion between in the film and in the bulk of the solution. The Koutecky-Levich plots of $i_{\text{lim}}{}^{-1}$ vs. $\omega^{-1/2}$ for the data of Fig. 10A were linear, as expected from Eq. 1, and the slopes matched that at a bare electrode (Fig. 10B). Thus, from the data shown in Fig. 10B, the values of D_{soln} and κD_{s} for I^- ion were estimated (Table 1).

The values of D_{soln} and κD_{s} for $[Co(tpy)_2]^{2+}$ ion ($E^{\circ\prime}$ of $[Co(tpy)_2]^{2+/3+}$ couple=0.035 V vs. SSCE in 0.2 M CF_3COONa solution (pH 1.0)) were also estimated according to the same way as mentioned above (Table 1). We can see that the diffusion rates of I^- and $[Co(tpy)_2]^{2+}$ ions in the swollen CPFP film of a given C_{film} are different and that they change with C_{film}.

Discussion

Dependence of $D_{\text{app}}^{\text{rev}}$ on C_{film}. The decrease of apparent diffusion coefficients (D_{app}) for charge-transport processes within electroactive films with increasing the concentration (C_{film}) of electroactive species confined in the films has been previously

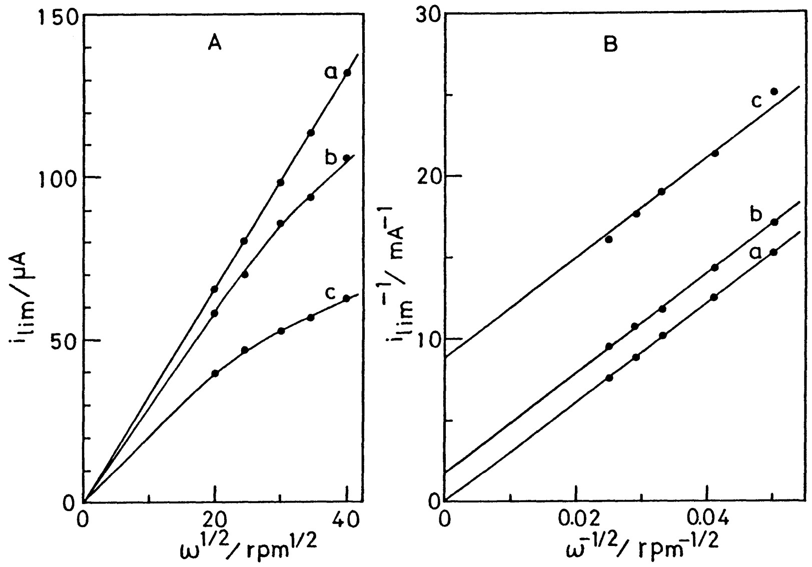


Fig. 10. (A) Levich plots of limiting current, i_{lim}, vs. (rotation rate, $\omega)^{1/2}$ for the oxidation of iodide ion at (a) uncoated and (b,c) ARS-containing CPFP film-coated BPG electrodes. (B) Koutecky–Levich plots of i_{lim}^{-1} vs. $\omega^{-1/2}$ for the data used in A. Solution compositions: (a) 0.2 M CF_3COONa (pH 1.0)+0.5 mM NaI; (b) 0.2 M CF_3COONa (pH 1.0)+0.5 mM NaI+0.01 mM ARS; (c) 0.2 M CF_3COONa (pH 1.0)+0.5 mM NaI+0.1 mM ARS. Other experimental conditions are the same as in Fig. 9.

observed in many cases[3,5a–f,j)] where multiply-charged electroactive species are electrostatically confined in oppositely charged polymer films. In these cases, the decrease of D_{app} with increasing C_{film} has been explained in terms of an electrostatic cross-linking of the polymer film[2,3,4b,c,f,g,5a–f,j,25)] and a single-file diffusion.[3c,f,33,34)] That is to say, an increase of the electrostatic cross linking with increasing C_{film} causes a decrease in the diffusion rate of electroactive species itself as well as decreases in the rates of the charge-compensating counterion motion which is necessarily coupled to electron transfer, the motion of solvent and/or the segmental motion of the polymeric chain. Also, the diffusion species which must move between more or less fixed sites within a polymeric matrix are considered to have their rate of motion limited by the decreasing availability of sites as C_{film} of diffusing species increases ("single-file diffusion effect"[34)]). These result in the decrease of the overall rate of the charge transport with an increase in C_{film}.

However, the same explanation seems not to be straightforwardly applicable to the case of the ARS-CPFP film system examined in this study (though the decrease of $D_{\mathrm{app}}^{\mathrm{rev}}$ with increasing C_{film} was observed (Fig. 8), because ARS bears only a single negative charge as SO_3^- group and thus replacing Cl^- anions initially present in the film by ARS anions can not be expected to produce a cross linking based on an electrostatic interaction alone. A possible explanation for the result obtained is that a hydrophobic interaction between the aromatic ring of ARS and the large fluorocarbon component of the CPFP coating as well as an electrostatic interaction between the SO_3^- group and the cationic quaternized ammonio group in the film concurrently contribute to the trapping of ARS anion in the film and such a combined interaction operates in the same manner as an electrostatic interaction[3,5a–f,j)] between multiply-charged species and oppositely charged polyelectrolyte films. A similar hydrophobic interaction has been realized in the incorporation of electroactive compounds into polyelectrolyte films on electrode surfaces.[3c,h,33,36)] A relatively high concentration of ARS anions into the CPFP coating (shown in Figs. 1 and 2), which is almost comparable to that of multiply-charged species into polyelectrolyte films by electrostatic interactions,[3,5a–f,j)] may support this explanation.

Differences in Rates of Various Diffusional Processes and Their Physical Significance. Prior to considering differences in rates of various diffusional processes, it seems to be useful in developing the discussion to mention some reasons for use of ARS as an electroactive species incorporated in the CPFP film on electrodes: (i) ARS contains two separate electroactive centers with different $E^{\circ\prime}$'s and different reversibility of their electrode reactions, (ii) the electroinactive functional group (i.e., SO_3^- group) other than the electroactive ones (i.e., 3,4-dihydroxy and 9,10-dioxo groups) serves as a counteranion site of the fixed cationic quaternized ammonio groups in the CPFP film domain, and (iii) the net charge on ARS does not change before and after the oxidation or reduction of the electroactive centers.

As can be seen from Table 1, the diffusion coefficients for processes I and II and for the physical diffusion of I^- and $[Co(tpy)_2]^{2+}$ in the film are in the following order: $\kappa D_s \gg D_{app}^{rev}$ $(1 \rightarrow 2) \sim D_{app}^{rev}$ $(2 \rightarrow 1) > D_{app}^{irrev} (1 \rightarrow 3)$, where D_{app}^{rev} $(1 \rightarrow 2)$, D_{app}^{rev} $(2 \rightarrow 1)$, and D_{app}^{irrev} $(1 \rightarrow 3)$ correspond to **1** to **2**, **2** to **1**, **1** to **3** processes, respectively. The diffusion coefficients (D_s') for the diffusion of supporting electrolyte ions used (Na^+ and CF_3COO^-) in the CPFP film have been unknown. The diffusion coefficients (D_s) of I^- and $[Co(tpy)_2]^{2+}$ in the ARS-containing CPFP film were estimated by hydrodynamic voltammetry using rotating disk electrodes. These ions were chosen based on the fact that they are electroactive in the potential region where the redox response of ARS is not substantially observed. The mean ionic diameters (a) of Na^+ and CF_3COO^- ions can be assumed to be between those of I^- and $[Co(tpy)_2]^{2+}$ ions: a's of I^-, Na^+, CF_3COO^- and $[Co(tpy)_2]^{2+}$ are roughly considered to be ca. 3, 4.5, 5, and >6 Å, respectively.[37)] Thus, D_s's for I^- and $[Co(tpy)_2]^{2+}$ ions were obtained as a rough measure of D_s''s for Na^+ and CF_3COO^- ions. Based on these considerations and the obtained values of κD_s, D_{app}^{rev}, and D_{app}^{irrev}, it can be expected that $D_s' \gg D_{app}^{rev} > D_{app}^{irrev}$. This suggests that the rate of the charge transport in the film is not substantially controlled by motion of the counterion (supporting electrolyte ion) in the polymer matrix which is coupled to electron transfer and molecular motion of ARS itself undergoing electrolysis.

The different values of D_{app}^{rev} and D_{app}^{irrev} seem to be instructive in understanding the charge transport mechanism as pointed out in a previous paper.[23)] In general, the D_{app} value can include contributions from both molecular motion (physical diffusion of reactant in film) and electron exchange between reactants, which will be represented as D_o and D_{ex} (in units of $cm^2\,s^{-1}$), respectively:[2d,e,3b,c,f,4c,d,5h,21–23)]

$$D_{app} = D_o + D_{ex} \tag{4}$$

According to Dahms and Ruff,[21,22)] D_{ex} is expressed by Eq. 5.

$$D_{ex} = (\pi/4)\, k_{ex} \delta^2 C \tag{5}$$

where k_{ex} is the second-order electron-exchange rate constant for the redox couple, δ is the distance between the reactants when the electron transfer occurs, and C is the concentration of reactants (the sum of the concentrations of the oxidized and reduced forms of the redox couple). In **1** to **2** and **1** to **3** processes, the contribution (D_o) from molecular motion should be the same, because the same molecule takes part in both processes. Thus, based on Eq.4 the difference in D_{app}^{rev} $(1 \rightarrow 2)$ and D_{app}^{irrev} $(1 \rightarrow 3)$ at a given C_{film} may be considered to originate from that in D_{ex}'s. As can be readily seen from Eq.5, the degree of the contribution from electron exchange to the overall charge-transport rate depends on the electron self-exchange rate constant between electroactive reactants, i.e., homogeneous electron self-exchange rate constant (k_{ex}): The larger k_{ex} is, the larger is D_{ex}, and thus the larger is the contribution of electron exchange. Alternatively, k_{ex} can be correlated to the heterogeneous electron-transfer rate constant (k°)[38)], i.e., in a qualitative sense to the reversibility of the electrode reaction: For the redox system with large k_{ex}, the k° value is large. As seen from Fig. 3, process I is reversible, while process II is irreversible. Thus, the k° value for process I should be larger than that for process II. Based on these considerations, the difference in D_{app}'s for processes I and II can be attributed to different contributions of electron exchange between electroactive centers to the overall charge-transport rates.

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Area of "Dynamic Interactions and Electronic Processes of Macromolecular Complexes" No. 62612504, for N. Oyama, from the Ministry of Education, Science and Culture.

References

1) a) F. B. Kaufman and E. M. Engler, *J. Am. Chem. Soc.*, **101**, 547 (1979). b) F. B. Kaufman, A. H. Schroeder, and J. Q. Chamber, *ibid.*, **102**, 483 (1980).

2) a) I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.*, **103**, 5007 (1981). b) P. J. Peerce and A. J. Bard, *J. Electroanal. Chem.*, **122**, 97 (1980). c) P. J. Peerce and A. J. Bard, *J. Electroanal. Chem.*, **114**, 89 (1980). d) H. S. White, J. Leddy, and A. J. Bard, *J. Am. Chem. Soc.*, **104**, 4811 (1982). e) C. R. Martin, I. Rubinstein, and A. J. Bard, *ibid.*, **104**, 4817 (1982).

3) a) N. Oyama and F. C. Anson, *J. Electrochem. Soc.*, **127**, 640 (1980). b) D. A. Buttry and F. C. Anson, *J. Electroanal. Chem.*, **130**, 333 (1981). c) D. A. Buttry and F. C. Anson, *J. Am. Chem. Soc.*, **105**, 685 (1983). d) F. C. Anson, T. Ohsaka, and J. M. Savéant, *J. Phys. Chem.*, **87**, 640 (1983). e) D. D. Montgomery and F. C. Anson, *J. Am. Chem. Soc.*, **107**, 3431 (1985). f) Y. M. Tsou and F. C. Anson, *J. Phys. Chem.*, **89**, 3818 (1985). g) D. A. Buttry, J. M. Savéant, and F. C. Anson, *ibid.*, **88**, 3086 (1984). h) Y. M. Tsou and F. C. Anson, *J. Electrochem. Soc.*, **131**, 595 (1984). i) N. Oyama and F. C. Anson, *Anal. Chem.*, **52**, 1192 (1980).

4) a) R. Nowak, F. A. Schultz, M. Umana, R. Lam, and R. W. Murray, *Anal. Chem.*, **52**, 315 (1980). b) P. Daum, J. R. Lenhard, D. Rolison, and R. W. Murray, *J. Am. Chem. Soc.*, **102**, 4649 (1980). c) J. Facci and R. W. Murray, *J. Phys. Chem.*, **85**, 2870 (1981). d) J. Facci, R. H. Schmehl, and R. W. Murray, *J. Am. Chem. Soc.*, **104**, 4959 (1982). e) R. Schmehl and R. W. Murray, *J. Electroanal. Chem.*, **152**, 97 (1983). f) J. Facci and R. W. Murray, *ibid.*, **124**, 339 (1981). g) K. Kuo and R. W. Murray, *ibid.*, **131**, 37 (1982). h) B. J. Feldman and R. W. Murray, *Inorg. Chem.*, **26**, 1702 (1987).

5) a) N. Oyama, T. Ohsaka, M. Kaneko, K. Sato, and H. Matsuda, *J. Am. Chem. Soc.*, **105**, 6003 (1983). b) N. Oyama, T. Ohsaka, and T. Ushirogouchi, *J. Phys. Chem.*, **88**, 5274 (1984). c) T. Ohsaka, H. Yamamoto, M. Kaneko, A. Yamada, M. Nakamura, S. Nakamura, and N. Oyama, *Bull. Chem. Soc. Jpn.*, **57**, 1844 (1984). d) T. Ohsaka, K. Sato, H. Matsuda, and N. Oyama, *J. Electrochem. Soc.*, **132**, 1871

(1985). e) T. Ohsaka, T. Ushirogouchi, and N. Oyama, *Bull. Chem. Soc. Jpn.*, **58**, 3252 (1985). f) T. Ohsaka, T. Okajima, and N. Oyama, *J. Electroanal. Chem.*, **215**, 191 (1986). g) K. Chiba, T. Ohsaka, and N. Oyama, *ibid.*, **217**, 239 (1987). h) N. Oyama, T. Ohsaka, H. Yamamoto, and M. Kaneko, *J. Phys. Chem.*, **90**, 3850 (1986). i) T. Ohsaka, H. Yamamoto, and N. Oyama, *ibid.*, **91**, 3775 (1987). j) N. Oyama, T. Ohsaka, K. Chiba, and K. Takahashi, *Bull. Chem. Soc. Jpn.*, **61**, 1095 (1988).

6) a) D. C. Bookbinder, J. A. Bruce, R. N. Dominey, N. S. Lewis, and M. S. Wrighton, *Proc. Natl. Acad. Sci. U. S. A.*, **77**, 6280 (1980). b) D. J. Harrison, K. A. Daube, and M. S. Wrighton, *J. Electroanal. Chem.*, **163**, 93 (1984).

7) a) C. P. Andrieux and J. M. Savéant, *J. Electroanal. Chem.*, **111**, 377 (1980). b) C. P. Andrieux, J. M. Dumas-Bouchiat, and J. M. Savéant, *ibid.*, **131**, 1(1982). c) C. P. Andrieux and J. M. Savéant, *ibid.*, **142**, 1 (1982).

8) a) E. Laviron, *J. Electroanal. Chem.*, **112**, 1 (1980). b) K. M. O'connell, E. Waldner, L. Roullier, and E. Laviron, *ibid.*, **162**, 77 (1984).

9) a) M. Majda and L. R. Faulkner, *J. Electroanal. Chem.*, **137**, 149 (1982). b) M. Majda and L. R. Faulkner, *ibid.*, **169**, 77 (1984).

10) A. N. K. Lau, L. L. Miller, and B. Zinger, *J. Am. Chem. Soc.*, **105**, 5278 (1983).

11) W. T. Yap, R. A. Durst, E. A. Blubaugh, and D. D. Blubaugh, *J. Electroanal. Chem.*, **144**, 69 (1983).

12) a) K. Doblhofer, H. Braun, and R. Lange, *J. Electroanal. Chem.*, **206**, 93 (1986). b) R. Lange and K. Doblhofer, *ibid.*, **237**, 13 (1987).

13) G. Inzelt, J. Q. Chambers, J. F. Kinstle, and R. W. Day, *J. Am. Chem. Soc.*, **106**, 3396 (1984).

14) I. Rubinstein, *J. Electroanal. Chem.*, **188**, 227 (1985).

15) M. W. Espenscheid and C. R. Martin, *J. Electroanal. Chem.*, **188**, 73 (1985).

16) W. J. Albery, M. G. Boutelle, P. J. Golby, and A. R. Hillman, *J. Electroanal. Chem.*, **133**, 135 (1982).

17) B. Lindholm, M. Sharp, and R. D. Armstrong, *J. Electroanal. Chem.*, **235**, 169 (1987).

18) C. J. Miller and M. Majada, *J. Am. Chem. Soc.*, **108**, 3118 (1986).

19) O. Haas and B. Sandmeier, *J. Phys. Chem.*, **91**, 5072 (1987).

20) C. M. Elliott and J. G. Redepenning, *J. Electroanal. Chem.*, **181**, 137 (1984).

21) a) I. Ruff, *Electrochim. Acta*, **15**, 1059 (1970). b) I. Ruff and V. Friedrich, *J. Phys. Chem.*, **75**, 3297 (1971). c) I. Ruff and V. Friedrich, *J. Phys. Chem.*, **76**, 2954 (1972).

22) H. Dahms, *J. Phys. Chem.*, **72**, 362 (1968).

23) T. Ohsaka, Y. Takahira, S. Nakamura, and N. Oyama, *J. Electroanal. Chem.*, **247**, 339 (1988).

24) H. E. Zittel and T. M. Florence, *Anal. Chem.*, **39**, 320 (1967).

25) N. Oyama, T. Ohsaka, and T. Okajima, *Anal. Chem.*, **58**, 979 (1986).

26) R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, **1962**, 341.

27) T. Ohsaka, T. Hirokawa, H. Miyamoto, and N. Oyama, *Anal. Chem.*, **59**, 1758 (1987).

28) For example, A. J. Bard and L. R. Faulkner, "Electrochemical Methods, Fundamentals and Applications," Wiley, New York (1980).

29) V. G. Levich, "Physicochemical Hydrodynamics," Prentice-Hall, Englewood Cliffs, NJ. (1962).

30) J. Koutecky and V. G. Levich, *Zh. Fiz. Khim.*, **32**, 1565 (1956).

31) D. A. Gough and J. K. Leypoldts, *Anal. Chem.*, **51**, 439 (1979).

32) N. Oyama, Y. Ohnuki, T. Ohsaka, and H. Matsuda, *Nippon Kagaku Kaishi*, **1983**, 949.

33) N. Oyama, T. Ohsaka, T. Ushirogouchi, S. Sanpei, and S. Nakamura, *Bull. Chem. Soc. Jpn.*, **61**, 3103 (1988).

34) K. Heckmann, "Biomembranes," ed by A. L. Manson, Plenum Press, New York (1972), Vol. 3, p. 127.

35) Preliminary experiments revealed that the D_{app} values obtained at pH 1 and 5 were almost the same within experimental error.

36) N. Oyama, T. Ohsaka, K. Sato, and H. Yamamoto, *Anal. Chem.*, **55**, 1429 (1983).

37) J. Kielland *J. Am. Chem. Soc.*, **59**, 1675 (1937).

38) For example, R. A. Marcus, *Electrochim. Acta*, **13**, 995 (1968).