Charge Transport at Polypyrrole Film Electrodes: Effect of the Electrolyte Concentration

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From measurements of the a.c. response of polypyrrole film electrodes in KNO_3 solution, we found that solvent swelling of the polymer greatly influences the kinetic behaviors of the polymer film electrodes. Electric migration in bulk film was due to background electrolyte ions which permeated through the film. Inside the film in contact with a supporting electrolyte solution, the mobility of the electrons may be much smaller than that of ions. The charge-transfer resistance of a partially oxidized film decreases along with increasing concentration of the electrolyte solution, because of a resultant increase in the activity of polarons. Such an increased activity of polarons also brings about a smaller Warburg coefficient, and thus a smaller limiting diffusion resistance (R_L). The pseudocapacitance appearing at low frequencies increases along with an increase in the concentration of the electrolyte solution, which is opposed to the change in R_L. These results corroborate that variations in the charge-transport parameters with the electrolyte concentration can be ascribed to an increase in the polaron activity with increasing ion concentration inside the polymer film.

An electroactive polymer film electrode has a characteristic function in the transport of electrons and ions, and in controlling the oxidation–reduction of a solution species. It provides very dense reaction sites compared with a bare metal surface. It has thus received considerable attention because of its possible applications to organic batteries, sensors, electrochromic devices, and electrocatalysis.$^{1,2)}$ Easy electrolytic preparation of polypyrrole films in aqueous media and the facile chemical derivatization of pyrrole make it an attractive new electronic material.$^{3)}$

The fundamentally interesting properties of electrical conducting polymers are related to their novel conductor–insulator transitions induced by electrochemical doping–undoping. The charge transport through the polymer film and the charge transfer at the metal/polymer and polymer/solution interfaces play key roles in the redox kinetics of the polymer coated on a metal. The electrochemical behavior of the polymer film electrodes is very complex, due to the intrinsic inhomogeneity and ionic permeability of the polymer films.$^{4)}$ Electrochemical impedance spectroscopy has been widely applied to the kinetic study of polymer film electrodes,$^{4-7)}$ because this technique can, in principle, give a wealth of information about the systems. There have, however, been serious differences among the interpretations of the data because the nature and dynamics of mobile species remain obscure in conducting polymers in contact with an electrolyte solution.$^{2,6)}$

To elucidate the charge movement through the polymer films from metal to solution, it is necessary to examine the variation in their impedance responses as a function of the experimental variables, such as the electrode potential, film thickness, and electrolyte concentration. We elsewhere discussed the effects of the potential and film thickness on the kinetic parameters of the electrode processes of a polypyrrole film.$^{8)}$ The impedance response of polypyrrole was, then, found to greatly depend on the electrolyte concentration in solutions. In this work we investigate the effect of electrolyte concentrations on the kinetic parameters of the electrode processes by measuring the a.c. response of polypyrrole over a wide range of frequencies.

Experimental

Polypyrrole films were electrolytically deposited on Pt (0.10 or 0.012 cm^2) at a current density of 0.2 $mA\,cm^{-2}$ from a 0.2 M KNO_3 solution containing 0.2 M pyrrole ($M=mol\ dm^{-3}$). Electrochemical experiments were carried out in a two-compartment, three-electrode glass cell at room temperature. An Ag/AgCl/KCl electrode and a large Pt gauze (>10 cm^2) were used as the reference and counter electrodes, respectively. The a.c. impedance of the electrochemical cell was measured on an NF Electronic Instruments (S-5720C) frequency-response analyzer coupled to a Hokuto Denko (HA-501G) potentiostat over the 10^3—10^{-3} Hz frequency range. The amplitude of the applied a.c. signal was 10 mV (peak to peak). The impedance response in the high-frequency range of 10^6—10^2 Hz was examined at an open circuit on an HP 4284A LCR meter, and with the twin electrodes, metal/film/solution/film/metal, where both films were in the same oxidation state. This electrode comprised a pair of cross-sections of Pt wires (diameter 1 mm) sealed into glass tubing. An interdigitated array electrode was purchased from BAS, Inc. (Japan), in which a Pt band has a width of 10 µm and a length of 2 mm, and a band spacing of 5 µm. All of the Pt bands were simultaneously modified with polypyrrole at the same potential. The sandwich-type cell (metal/film/metal), having an additional film/solution interface, was made up by thoroughly rinsing a polymer-covered electrode after polymerization, drying it under a vacuum, and subsequent vacuum-depositing Au on it in stripes. The oxidation level (x) of the polymer, which is the average charge on the polymer chain per pyrrole unit, was calculated from the charge required to oxidize the fully reduced polymer and its mass.

Results and Discussion

When there are large differences in the relaxation times of various electrode processes, complex plane impedance diagrams show some frequency regions that are characteristic of each electrode process. Figure 1 presents typical impedance diagrams of the polypyrrole electrode, which is of an asymmetrical system (metal/film/solution). At low potentials, two regions are noticed: a semicircle in the high-frequency range and a vertical line in the low-frequency range. A thick film, moreover, showed a linear 45° region in the medium-frequency range. At higher potentials than −0.2 V, only a vertical line was observed over the whole range of the measured frequencies.

Electric Migration in Bulk Film. Table 1 shows the ohmic resistance ($R(\infty)$) obtained from the high-frequency intercept of impedance plots with the real axis. The values of $R(\infty)$ decreased along with an increase in the KNO_3 concentration of the solution. The ohmic resistances of the polymer electrode should have increased along with a reduction (i.e., dedoping) of the polymer if electric migration in the bulk film was electronic. They were, however, unvarying with the potential. The polymer-covered electrodes, independent of their film thicknesses, showed $R(\infty)$ values equal to those of a bare electrode. These results indicate that either the film resistance was much smaller than the solution resistances, or that the electric conduction in the bulk film was due to ion migration.

Table 1. The Ohmic Resistances/Ω of Polypyrrole Film Electrode at Different Concentrations of KNO_3 in Solutions[a)]

Potential[b)]	$[KNO_3]$/M		
V vs. Ag/AgCl	2	0.2	0.02
0.2	81 (76)	530 (520)	4000 (4100)
−0.2	81 (78)	530 (540)	4000 (4200)
−0.6	80 (76)	550 (550)	4300 (4200)

a) Numerical values in parenthses show those of a bare Pt electrode. b) The liquid junction potential between 1 M and 0.01 M KNO_3 solutions, which is calculated from limiting ionic mobilities, is about 2 mV. This value indicates that the potential differences between a metal and solutions are kept constant.

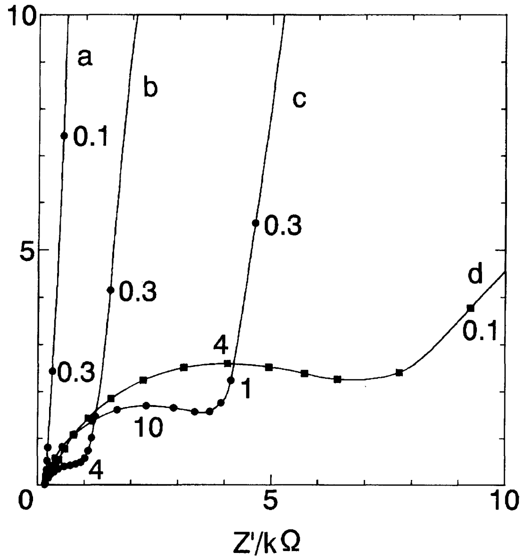

Fig. 1. Typical complex plane impedance diagrams of polypyrrole electrode in 0.2 M KNO_3 solution. Applied potential/V; curve a: 0, b: −0.5, c, d: −0.6. Film thickness/µm; ●: 0.083, ■: 0.67. Numerical values in the figure exhibit frequencies in Hz.

To lessen any contribution of the solution resistance, we examined the impedance response of an interdigitated array electrode. Figure 2 represents three states of the band array electrode and their typically observed respective impedance diagrams. Impedance plots for an electrode covered with a sufficiently thicker film than the band spacing curve back to the real axis at low frequencies; i.e., its impedance becomes purely resistive at zero frequency. Such a behavior indicates that this electrode is symmetrical in the sense that both interfaces of the film are transferable to electrons, where the applied alternating current may pass through only the polymer

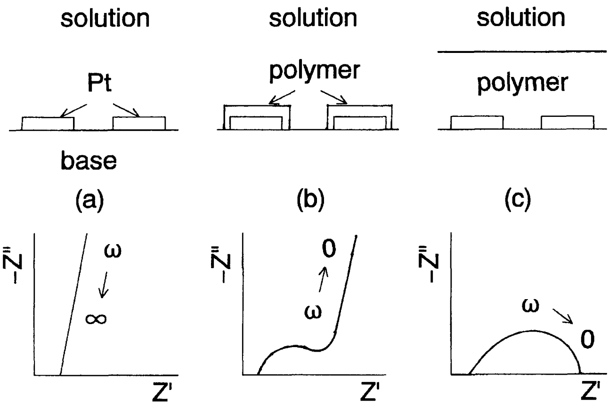

Fig. 2. Three states of band array electrode and their respective impedance diagrams typically observed. (a): a bare Pt (metal/solution/metal). (b): an electrode coated with thin film (metal/polymer/solution/polymer/metal), (c): an electrode covered with sufficiently thick film (metal/polymer/metal).

film. Figure 3 shows the $R(\infty)$ values of the array electrodes in solutions of different KNO_3 concentrations. Variations in the film resistance were noticed at low concentrations of the indifferent electrolyte. The $R(\infty)$ values at a certain film thickness increased along with a reduction of the polymer. As the film was thickend, they decreased slightly at 0.3 V and increased at −0.5 V. For the oxidized film, $R(\infty)$ was almost independent of the electrolyte concentration, which indicates that the electric migration in the bulk film is due to the counterion compensating polymer charges. For the reduced film, it increased along with decreasing concentration of the electrolyte solution, which indicates that the electric migration is caused by the background electrolyte ions permeating through the film.

We also evaluated the values of $R(\infty)$ for the sandwich-type cell (metal/film/metal) having an additional film/solution interface. The oxidized films in contact with the solutions of different KNO_3 concentrations showed the following $R(\infty)$ values: 123 Ω at 1 M, 142 Ω at 0.1 M, 162 Ω at 0.01 M, and 170 Ω at 0.001 M. The values in 1—0.1 M solutions were smaller than the $R(\infty)$ value of 164 Ω for the dry film being in contact with nitrogen gas. This difference, due to the permeation of electrolyte solutions, indicates that the electronic conductivities of the polymer, even in the oxidized state, are small compared with the conductivities of those solutions.

The above results lead to the conclusion that the mobility of electrons is much smaller than that of ions inside the film in contact with a supporting electrolyte solution, because the concentration of the electronic charge of the oxidized film is estimated to be on the order of one mol dm^{-3} based on the density of the film (1.5 g cm^{-3})[9] and its oxidation level. This result originates from solvent swelling of the polymer occurring during electropolymerization, swelling which can cause the ions to easily go into and out of the film.

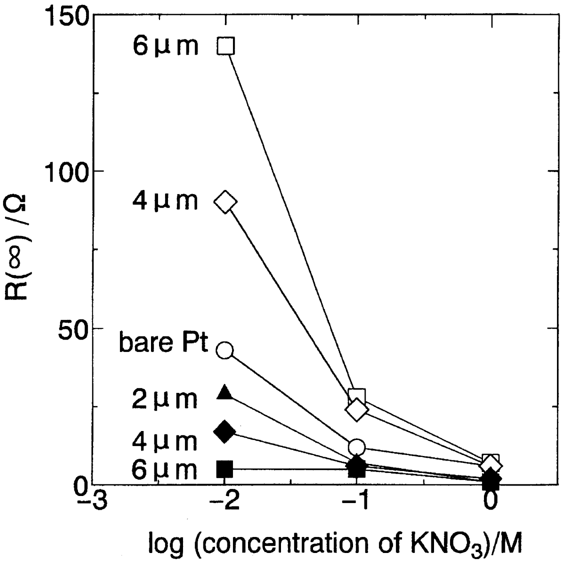

Fig. 3. Changes in ohmic resistance of interdigitated array electrode with KNO_3 concentration in solution at different film thicknesses. Open symbols: −0.5 V, closed symbols: 0.3 V, ○: a bare Pt electrode (unvarying with potential). Film thicknesses are indicated in the figure.

Charge Transfer Process. Figure 4 shows the width of the semicircle observed in asymmetrical systems. The semicircle is due to a parallel RC element: an interfacial charge-transfer resistance (R_c) and double-layer capacitance. The values of R_c greatly increased as the potential was lowered. At a sufficiently high solvent content of the film, the potential drop at the polymer/solution interface is practically constant with varying electrode polarization. It is therefore presumed that R_c (or at least its variations) includes no contribution of the charge-transfer resistance due to ion injection at the polymer/solution interface. Actually, we never observed double semicircles in the impedance diagrams.

Electron-spin resonance studies[6,10] of polypyrrole have demonstrated that stable paramagnetic species are formed during the course of oxidation. Accordingly, the charge-transfer reaction at a metal/conducting polymer interface is expressed as

$$\text{conjugated } \pi \text{ bond} \rightarrow \mathrm{P}^{+\bullet} + \mathrm{e}, \tag{1}$$

where $\mathrm{P}^{+\bullet}$ denotes an electronic charge carrier in the polymer, hereinafter called a polaron. Its flux density across the interface is given by

$$J = k_a(C - C_p) - k_c C_p, \tag{2}$$

where C_p is the concentration of polarons, and C is the concentration of π electrons extractable from the polymer (the maximum concentration of polarons); k_a and k_c are the rate constants of anodic and cathodic processes, respectively. For the present, the concentrations

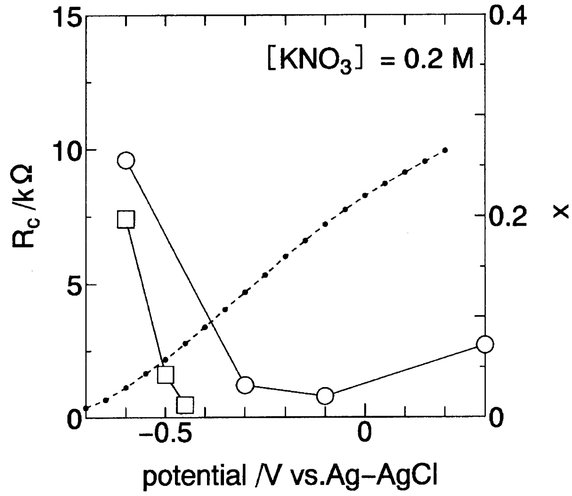

Fig. 4. Changes in width of semicircle with applied potential. ○: twin electrodes, □: electrochemical system (metal/film/solution/reference and counter electrodes), ······: x vs. E curve.

are used in place of the activities, despite the high concentration of electronic charge of the oxidized polymer. R_c is thus given by the following equation:[5)]

$$R_c = RT(F)^{-2}k_o^{-1}(C-C_p)^{\alpha-1}C_p^{-\alpha}, \qquad (3)$$

where k_o is the standard rate constant, α is the transfer coefficient, and the other symbols have their usual meanings. Due to the change in the polaron concentration with the potential, R_c goes through a minimum at the formal potential, at which C_p is equal to $C/2$. It is expected for polypyrrole that R_c increases with decreasing oxidation level in the potential range below -0.2 V, because the half-wave potential ($E_{1/2}$) of polypyrrole is -0.21 V, as shown by its cyclic voltammetry. The result shown in Fig. 4 is in accord with this expectation. We notice, however, that this $E_{1/2}$ value, given as the average of anodic and cathodic peak potentials, corresponds to an oxidation level of $x=0.14$ (Fig. 4). If $E_{1/2}$ is identified with the formal potential, this value of x means that one can only extract 0.25—0.3 electrons/pyrrole unit from the polymer; an x value of 0.3 has been determined for the as grown polymer.[8)] The appearance of the voltammetric oxidation peak at x below 0.5 implies that the polymer becomes less oxidizable in its higher oxidation state, due to the repulsive interaction between charged sites on the π-conjugated polymer chain. Because there is no independent redox species in conducting polymers, we call attention to the indefinability of their formal potential.

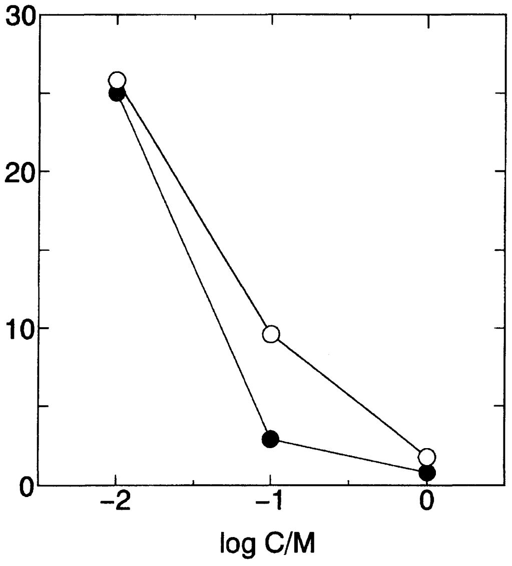

Fig. 5. Charge-transfer resistances at different concentrations of KNO_3 in solutions. ○: twin electrodes (-0.6 V), ●: electrochemical system (-0.5 V).

Figure 5 shows the values of R_c at different concentrations of KNO_3 in the solutions. The values decreased with increasing concentration of the supporting electrolyte. Although there is a question as to the constancy of the oxidation potential, k_o is independent of the electrolyte concentration in the solution. Because polypyrrole has no polar groups, and basically no ion-exchangeable groups, its higher-order structure and the degree of solvent swelling may remain unchanged during the permeation of electrolytes. We suggest that the activity of polarons varies with the concentration of an indifferent electrolyte solution (C_o), even if the potential difference between a metal and the solution (E) is kept constant. For systems in which C_p is much higher than the concentration of co-ions (cations) in the polymer phase, the doping isotherm, such as Eq. 4, has been derived by Vorotyntsev et al.[11)]

$$\ln C_p{}^2/(C-C_p) = F(RT)^{-1}(E-E^\circ) + \ln C_o, \qquad (4)$$

where E° includes the standard chemical potentials of counterions in the solution and polymer phases. This expression predicts that an increased concentration of the electrolyte solution makes the polaron concentration increase and the formal potential shift to a negative potential. The formal potential also varies with the electrolytes. The permeation of an electrolyte through the film, however, makes doping isotherms complicated. On the basis of the electronic equilibrium at the metal/polymer interface, and ionic equilibrium at the polymer/solution interface, the following doping isotherm can be derived:

$$\ln C_p/(C-C_p) = F(RT)^{-1}(E-E^\circ) - \ln C_f/C_o, \qquad (5)$$

where C_f is the concentration of anions in the polymer. In the limiting case of $C_p \ll$ the concentration of co-ions in the polymer phase, the second term on the right-hand side of Eq. 5 becomes constant (i.e., the distribution equilibrium of an electrolyte is reached). Then, the polaron concentration varies with the electrolyte (as well as the formal potential), though it is independent of the concentration of an electrolyte solution.

On the other hand, the permeation of an indifferent electrolyte through the polymer can modify the extent of polaron–polaron interaction. A broad current peak observed in the cyclic voltammograms of conducting polymers[2)] may be ascribed to a large repulsive interaction between the polymer charges at higher oxidation levels, because such interaction results in a continuous shifting in the oxidation potential with increased concentration of the polarons. An increasing concentration of ions in the polymer leads to a smaller interaction between the polymer charges because of a larger electrostatic shielding due to the ions, which results in an increased rate of oxidation of the polymer.

Figure 6 shows both the peak currents and peak potentials of the cyclic voltammograms at different concentrations of KNO_3 in the solutions. An increase in the concentration of the electrolyte solution raised the peak current and moved the peak potential to a more negative potential. Moreover, $E_{1/2}$ of polypyrrole varied from electrolyte to electrolyte as follows (at 0.1 M):

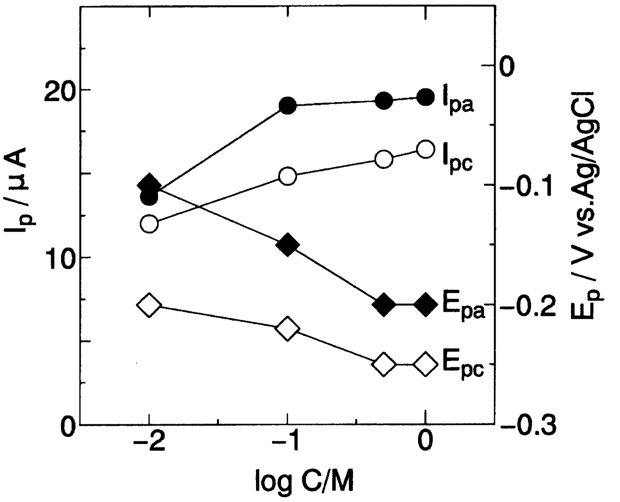

Fig. 6. Peak currents and peak potentials of cyclic voltammograms at different concentrations of electrolyte solution. Scan rate: 500 mV s^{-1} for I_p, 50 mV s^{-1} for E_p.

−0.20 V for KNO_3, −0.39 V for disodium 1,5-naphthalenedisulfonate, −0.46 V for Orange G, and −0.49 V for sodium *p*-dodecylbenzenesulfonate.

We thus interpreted the change in R_c with the electrolyte concentration in terms of the varying activity of the polarons. At lower potentials than $E_{1/2}$, C_p is taken to be smaller than αC because the values of α can be about 0.5.[12] Then, Eq. 3 predicts that R_c of the partially oxidized state decreases as the activity of polarons increases with increasing concentration of the electrolyte solution.

Diffusion Process. The impedance response of the polypyrrole electrode at medium and low frequencies is satisfactorily interpreted in terms of the diffusional transport of a charge carrier within the film, as shown in our previous paper.[8] The general expression for the impedance due to finite diffusion (Z_d) has been derived by some investigators.[13,14] At relatively high frequencies and for thick films, it is reduced to a well-known expression[13] concerning semiinfinite diffusion. This limiting behavior generates a linear 45° region in the impedance diagram. At low frequencies and for thin films, another linear region appears in the diagram,

$$Z_d = (2/9)^{1/2}\sigma L D^{-1/2} - j\sigma(2D)^{1/2}(\omega L)^{-1}, \qquad (6)$$

where ω is the angular frequency, j the imaginary unit, σ the Warburg coefficient, L the film thickness, and D the diffusion coefficient of a charge carrier in the film. This vertical region corresponds electrically to a series combination of frequency-independent resistance (R_L) and capacitance (C_L):

$$R_L = (2/9)^{1/2}\sigma L D^{-1/2}, \quad C_L = \sigma^{-1} L(2D)^{-1/2}. \qquad (7)$$

The values of R_L associated with the finite thickness of the film are estimated from the experimentally obtained width of the linear 45° region. The estimates of R_L were inexact, except for thick films, because of the indefinite 45° region. Figure 7 shows the values of R_L at different concentrations of KNO_3 in the solution. The values decreased along with increasing concentration of the supporting electrolyte. This change in R_L would be due to a variation in the Warburg coefficient with the electrolyte concentration of the solution. For diffusional transport within conducting polymers, the Warburg coefficient is given by the following equation:[13]

$$\sigma = RT(F)^{-2}(2D)^{-1/2}C_d{}^{-1}, \qquad (8)$$

where C_d is the concentration of a diffusing species (the polaron or counterion). The large mobility of ions in the polymer film means that the movement of electrons is a rate-determining step in the diffusion process, because the charge transport through the polymer-covered electrode needs the concurrent transport of both electrons and counterions in order to maintain the electroneutrality of the polymer. Therefore, since one takes the polaron for the diffusing species, an increase in the polaron activity with increasing ion concentration inside the film can result in a smaller Warburg coefficient (Eq. 8), and, thus, a smaller diffusion resistance (Eq. 7). We propose that the electrode reaction at polypyrrole electrodes takes place as represented by the scheme in Fig. 8. The oxidation of the polymer proceeds from the back of the film to its surface.

At low frequencies, the charge transport across a thin film is accomplished during one-half cycle of the applied signal. Thus, a pseudocapacitance proportional to the film thickness appears in the low-frequency range, and the imaginary part (Z'') of the impedance changes linearly with ω^{-1}. Figure 9 shows the capacitance evaluated from the slope of the Z'' vs. ω^{-1} plot measured.

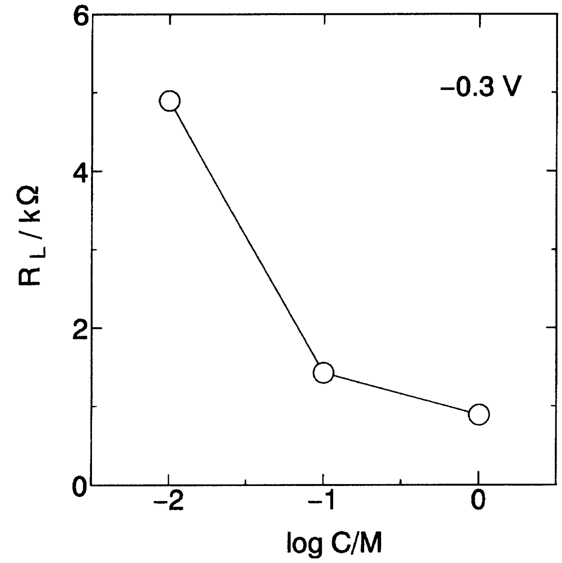

Fig. 7. Decrease in R_L with increasing concentration of electrolyte solution.

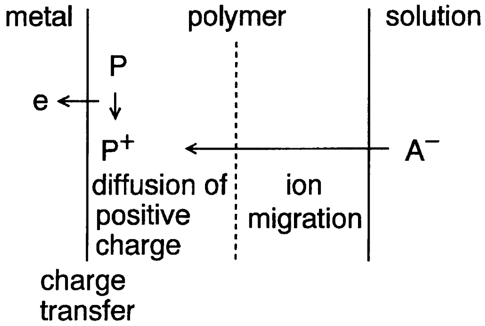

Fig. 8. Schematic illustration of charge transfer and charge transport at polymer-covered electrode.

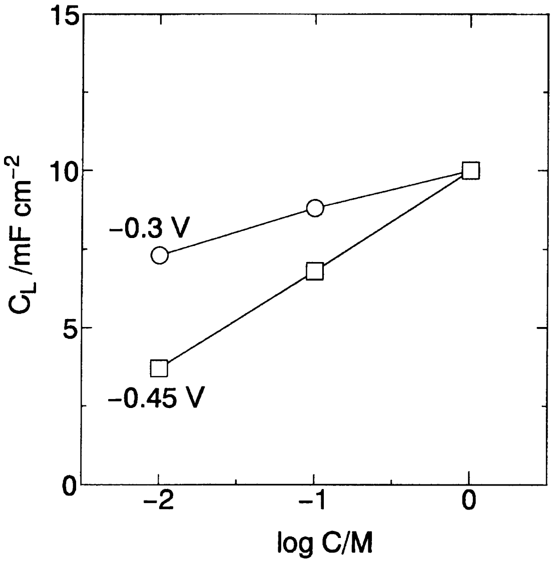

Fig. 9. Pseudocapacitance appearing in low frequency range at different concentrations of electrolyte solutions.

$$dZ''/d\omega^{-1} = C^{-1}. \qquad (9)$$

The real impedance response, however, showed a deviation from the ideal vertical line corresponding to Eq. 6; the impedance plots in the low-frequency range gave inclined straight lines (Fig. 1). The finite slope can result from a distribution of the relaxation times due to an inhomogeneity in the film.$^{4)}$ The degree of deviation was previously$^{8)}$ examined from the viewpoint of a constant-phase element behavior,$^{5)}$ which gives an inclined straight line in the complex impedance plane (Z_{cpe}),

$$Z_{\mathrm{cpe}} = A(j\omega)^{-\phi} = A\omega^{-\phi}[\cos\phi\pi/2 - j\sin\phi\pi/2], \qquad (10)$$

where A and ϕ are frequency-independent parameters, and $0 \leqq \phi \leqq 1$. This equation describes an ideal capacitor ($A = 1$/capacitance) for $\phi = 1$ and an ideal resistor (A=resistance) for $\phi = 0$. The fractional exponent (ϕ) has been related to the surface roughness of electrodes in terms of fractal geometry.$^{15)}$ Such an analysis indicated that the slopes of the experimentally obtained straight lines gave a ϕ value of 0.96±0.01 in the partially oxidized state. We thus identified the capacitance calculated from Eq. 9 with C_{L}. Figure 9 shows that C_{L} increases along with an increase in the concentration of the electrolyte solution, which is opposed to the behavior of R_{L}. This change in C_{L} is in accord with the expectation from Eqs. 7 and 8. The above results corroborate that the variations in the charge-transport parameters with the electrolyte concentration can be ascribed to an increase in the polaron activity with increasing ion concentration inside the polymer film.

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