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Characterization of Charge Transfer and Charge Transport in Polypyrrole Film Electrodes

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The a.c. response of polypyrrole film electrodes in 0.2 M KNO_3 was investigated at different applied potentials and film thicknesses. The results of impedance analysis on the basis of the Randles equivalent circuit indicated that the electron exchange between a metal and the polymer controlled the rate of charge-transfer process at the film electrode. Accordingly, the oxidation of the polymer proceeds from the back of the film to its surface. The resistance due to electric migration in the film strongly depended on the concentration of the supporting electrolyte; this dependence suggests that the migration is ionic. This effect may be due to a change in the solvent swelling of the polymer. The oxidation of the polymer brought about each decrease in the charge-transfer resistance at a metal–polymer interface and the limiting resistance associated with the diffusion of charge carriers. The low-frequency pseudocapacitance of the polymer increased with increasing oxidation level and film thickness, which was expected from a finite diffusion model.

Electrical conducting polymers have received considerable attention because of their possible applications to organic batteries, sensors, electrochromic devices, and semiconductor devices.$^{1,2)}$ Fundamentally interesting properties of the polymers are related to their novel conductor–insulator transitions induced by electrochemical doping–undoping. Easy electrolytic preparation of polypyrrole film in aqueous media and facile chemical derivatization of the polymer make it an attractive new electronic material.$^{3)}$

Electrochemical behavior of polypyrrole of theoretical and practical importance is very complex owing to intrinsic inhomogeneity of the polymer.$^{4)}$ The charge transport through the polymer film and the charge transfer at metal/polymer and polymer/solution interfaces play key roles in the redox kinetics of the polymer coated on a metal. The charge/mass-transport processes are directly related to fundamental properties, such as film conductivity and ionic permeability. Electrochemical impedance spectroscopy$^{5)}$ has widely been applied to kinetic study of the polymer film electrodes$^{6—8)}$ because this technique can in principle give a wealth of information on the systems. There have, however, been serious differences among the interpretations of the data obtained, because the nature and dynamics of mobile species remain obscure in the conducting polymers in contact with an electrolyte solution.$^{4)}$ To elucidate the charge movement through the polymer films from metal to solution, it is necessary to examine the variation of their impedance responses as a function of experimental variables, such as electrode potential, film thickness, and electrolyte concentration; so far such examinations have little been done.

In this work, we investigate the effects of these experimental variables on the kinetic parameters of electrode processes of polypyrrole by measuring its a.c. response over the wide range of frequency.

Experimental

Polypyrrole films were electrochemically deposited on Pt or ITO glass (0.12 or 1 cm^2) at a current density of 0.1 mA cm^{-2} from 0.2 M KNO_3 solution ($M=mol\,dm^{-3}$) containing 0.2 M pyrrole. The film thickness (L) was estimated from a relationship (3.3 $\mu m\ cm^2\ C^{-1}$) between the charge passed during polymerization and the film thickness; the relationship was analyzed by Amemiya et al.$^{1)}$ 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. All electrolyte solutions were prepared with doubly-distilled water and purged with nitrogen gas before and during electrochemical measurements. The a.c. impedance of the electrochemical cell was measured with an NF Electronic Instruments S-5720C frequency response analyzer coupled to a Hokuto Denko HA-501G potentiostat over the frequency range of 10^{-3}—10^3 Hz. The amplitude of the applied a.c. signal was 10 mV (peak to peak). The impedance response of the cell having two polypyrrole films oxidized under the same conditions was also measured on an HP 4284A LCR meter over the frequency range of 20—10^6 Hz. The in situ measurements of conductivity of the film were carried out in the solutions with the electrode of two-band type,$^{9)}$ on which the polymer bridged the gap between two Pt bands.

Results and Discussion

Redox Behaviors. It is well-known that polypyrrole is electrochemically doped and undoped with anions.[3] We calculated the oxidation level of the polymer at each potential (E) from the charge (Q) required to oxidize the fully reduced polymer and its mass.

$$[-C_4H_2NH-]_n + xnA^- \xrightarrow{Q} [-C_4^{x+}H_2NH-]_n(A^-)_{xn} + xne \quad (1)$$

where n is the total number of pyrrole units in the polymer and x the average charge on the polymer chain per unit. The x vs. E relation gave no apparent sigmoid curve, whereas the cyclic voltammogram of polypyrrole showed an anodic current peak at about −0.25 V. This result is probably due to a high current plateau after the oxidation peak, which has been ascribed to a large capacitance effect characteristic of the conducting polymers.[2] An x value of 0.3 obtained for the as grown polymer was somewhat smaller than that determined in acetonitrile by Feldman et al.[10]

The polymer in the reduced state exhibited an absorption peak at 390 nm and, on oxidation, developed a new absorption peak at 750—800 nm with an isosbestic point at 470 nm (in the range of 0.3—−0.6 V). The absorption peak growing in a long wavelength region has been ascribed to the creation of mobile radical cation (polaron) or dication (bipolaron) levels within the forbidden band.[11] The variations in absorbance at 390 and 800 nm with the oxidation level are presented in Fig. 1, which indicates that the peak at 800 nm developed at the expense of the one at 390 nm. Both absorbances reached limiting values in a highly oxidized state.[12]

The x dependence similar to the absorption spectra was found in the conductance of the polypyrrole film. Figure 1 also shows the conductance measured by the two-band method. The film conductance increased exponentially with x, but then reached a limiting value at x above 0.2. An increase in film conductance with early oxidation is attributable to the formation of polarons in the polymer matrix (Eq. 2).

$$-P-P-P-P-P- \xrightarrow{-e} -\overset{+}{P}-P-P-P-\dot{P}- \quad (2)$$

$$-\overset{+}{P}-P-P-P-\dot{P}- \xrightarrow{-e} -\overset{+}{P}-P-P-P-\overset{+}{P}-, \quad (3)$$

where P denotes the pyrrole unit. From esr experiments, Waller et al.[4] indicated that the polaron concentration passed through a maximum at $x=0.17$ because of the evolution of the bipolarons with increasing x (Eq. 3). These results have suggested that the electric conduction in polypyrrole cannot be solely attributed to the polaron, and the bipolaron is involved particularly in high oxidation state, too.[4]

Impedance Response of Polymer Electrode. Since almost all kinetic parameters of electrode processes in an electroactive film depend on the potential and/or film thickness, the effects of these experimental variables were closely examined over the whole range of frequencies of interest. When there are large differences in the relaxation times of various electrode processes, complex plane impedance diagrams show the different frequency regions corresponding to each electrode process. The increasing order of the relaxation times is generally: those of the ohmic resistance < of the charge transfer process < of diffusion process.

Typical impedance diagrams of the polymer electrode are presented in Figs. 2 and 3. At lower potentials, a vertical region was observed in the low frequency range and a semicircle due to a parallel RC element was ob-

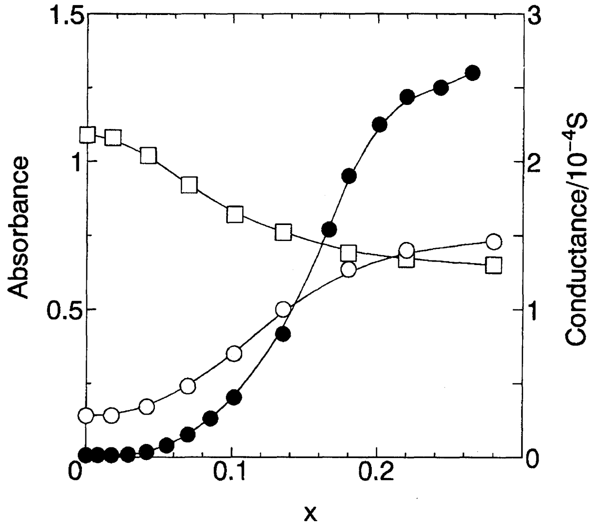

Fig. 1. Variations in absorbance and conductance of PP film with oxidation level. ○: absorbance at 800 nm, □: absorbance at 390 nm, ●: conductance. Electrolyte: 0.2 M KNO$_3$.

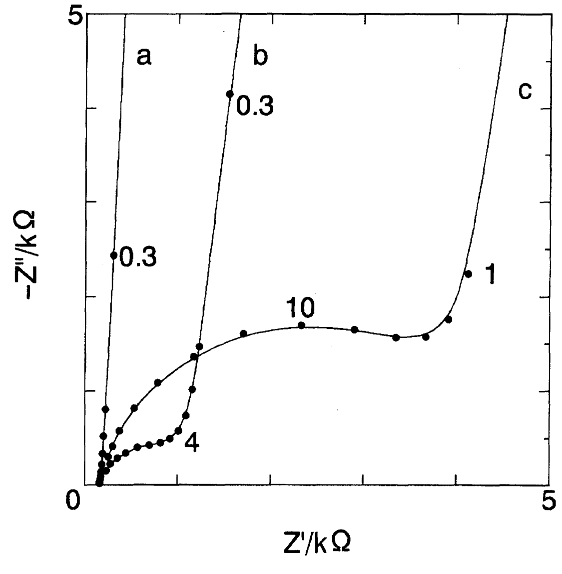

Fig. 2. Typical complex plane impedance diagrams (L=0.083 μm). Potential/V; curve a: 0, b: −0.5, c: −0.6. Numerical values in the figure exhibit frequencies in Hz.

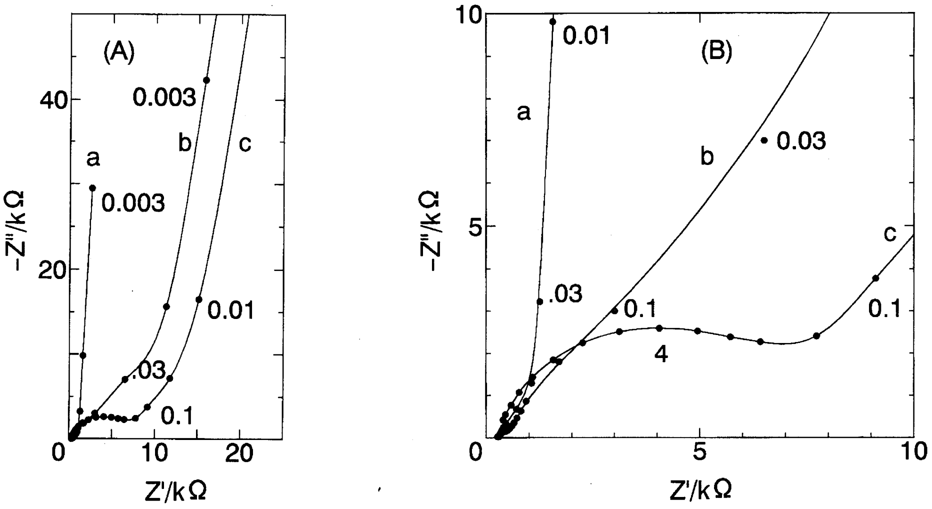

Fig. 3. Typical complex plane impedance diagrams (L=0.67 µm). (A): Potential/V; curve a: −0.2, b: −0.45, c: −0.6. (B): The high frequency part of the diagram. Numerical values in the figure exhibit frequencies in Hz.

served in the high frequency range. A thick film moreover showed a linear 45° region in the medium frequency range. The diameter of the semicircle decreased with a positive shift of the potential. At higher potentials than −0.2 V, only a vertical region was observed over the frequency range of 10^2—10^{-3} Hz.

The impedance responses of the polymer electrode were interpreted on the basis of the Randles equivalent circuit shown in Fig. 4, where R_s is an electrolyte resistance, C_e the double layer capacitance at the film electrode, R_c the charge-transfer resistance at the film interfaces, R_m the resistance due to electric migration in the film, and Z_d the impedance due to diffusion in the film.

Figure 5 shows the diameters of the semicircles indicating the contribution due to capacitive charging of the interfaces; the diameters increased largely as the potential was lowered. The resistance of the charge-transfer reaction ($X+e \rightarrow Y$) at a metal–solution system goes through a minimum at its formal potential owing to the potential changes in concentrations of the redox species X and Y.[13] If we suppose that the polymer is a composite of the reduced and oxidized sites, a decrease in its oxidation level increases the diameter of the semicircle through R_c in the potential range below −0.3 V because the half-wave potential ($E_{1/2}$) of polypyrrole is −0.31 V as shown by its cyclic voltammetry. We notice, however, that the value of $E_{1/2}$ given as the average of anodic and cathodic peak potentials corresponds to a potential of x=0.133. The appearance of the voltammetric peak at x below 0.5 implies that the polymer becomes less oxidizable in higher oxidation state owing to the interaction between charged sites on the polymer chain. Since there is no independent redox species in conducting polymers, we can't define their formal potential.

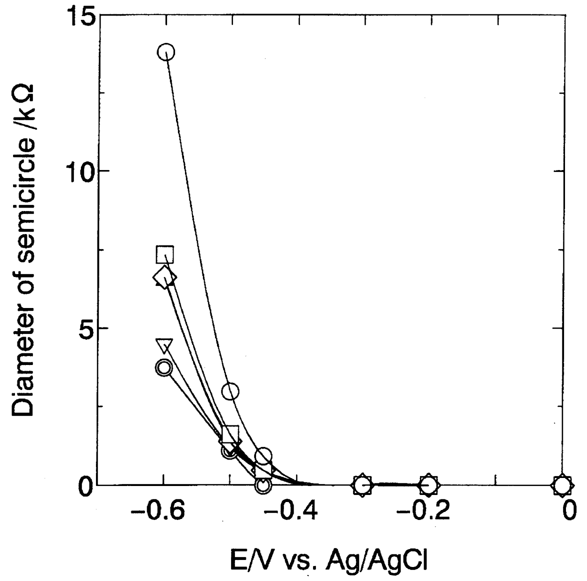

Fig. 5. Change in diameter of semicircle with applied potential. Film thickness/µm; ○: 1.33, □: 0.67, ◇: 0.33, △: 0.17, ▽: 0.083, ◎: 0.042.

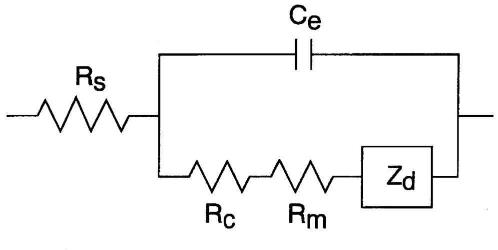

Fig. 4. The equivalent circuit for a.c. response of film electrode.

Although the film conductance measured by the two-band method increased with x, the ohmic resistance obtained from the high frequency intercept of impedance plots with the real axis was unvaried with both potential and film thickness. On the other hand, the semicircle enlarged with increasing film thickness. These

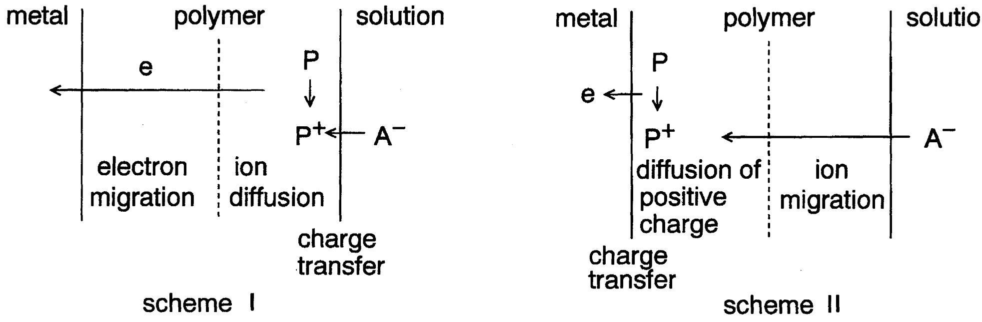

Fig. 6. Schemes for charge transfer and charge transport in film electrodes. Scheme I: a case of the electronic conductivity of the film ≫ its ionic conductivity. Scheme II: a case of the ionic conductivity ≫ the electronic conductivity.

results suggest that the diameter of the semicircle also include R_m, because R_c should be independent of film thickness. We have the probable schemes shown in Fig. 6 for the charge transfer and charge transport at the film electrode. Scheme I is a case of the electronic conductivity ≫ ionic conductivity of the film, where the oxidation of the polymer proceeds from the surface of the film to its inner. Scheme II is a case of the ionic conductivity ≫ electronic conductivity, where the oxidation proceeds from the back to the surface. If the electric migration in the film is electronic, R_m increases largely with reduction of the polymer, as expected from the film conductance measured by the two-band method. If the migration is ionic, R_m can decrease with increased concentration of supporting electrolytes. We found that the impedance response of polypyrrole strongly depended on the electrolyte concentration. For a reduced film (L=0.33 μm), the values of diameter of the semicircle were 25 kΩ at a concentration of 0.01 M, 2.9 kΩ at 0.1 M, and 0.8 kΩ at 1 M. This dependence suggests that the migration is ionic or/and R_c includes the charge-transfer resistance due to ion injection at the polymer/solution interface. The former view is supported by an enlargement of the semicircle with increasing film thickness. Inzelt et al.[14] interpreted the similar effect in a redox polymer as the variations in frequencies of the chain and segmental motions of the polymer. We consider, however, this effect as a change in solvent swelling of the film, which can cause a change in the rate of ion migration. These results lead to the conclusion that the electrode reaction (the formation of charged sites) at polypyrrole film electrodes takes place at the metal–polymer interface. A counterion to maintain the electroneutrality of the polymer goes into and out of the film with negligible resistance, which suggests that the film swells with the solution.

Figure 7 shows the resistive magnitude of the liner 45° region. Their estimates are not very exact except for thick films because of the indefinite 45° region. The values increased as the potential was lowered. The experimental data at medium and low frequencies can be satisfactorily explained in terms of the diffusional transport of a charge carrier within the film. For an electroactive polymer film in contact with a solution containing no redox couple, Z_d can electrically be equivalent to the impedance of a finite transmission line.[15,16] The general expression for this impedance at an angular frequency ω is

$$Z_d = (1-j)\sigma\omega^{-1/2}\coth(j\omega L^2/D)^{1/2}, \tag{4}$$

where j is the imaginary unit, σ the Warburg coefficient, and D the diffusion coefficient of a charge carrier in the film. When $\omega L^2/D \gg 1$, Eq. 4 corresponds to Eq. 5 for semiinfinite diffusion.

$$Z_d = (1-j)\sigma\omega^{-1/2}. \tag{5}$$

This limiting behavior is equivalent to that of the Warburg impedance, i.e., the linear 45° region in the impedance diagram (the diffusion-controlled region). Another linear region appears in the diagram at low frequencies and for thin films, i.e., $\omega L^2/D \ll 1$.

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

This vertical region corresponds electrically to a series combination of frequency-independent resistance R_L and capacitance C_L.

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

The values of R_L, which is associated with finite diffusion, are identified with the resistive magnitude of the linear 45° region. The values were roughly proportional to the film thickness. This relation was in accord with the expectation from Eq. 7. Figure 7 also shows the values of σ calculated from the slope of $|Z_d|$ vs. $\omega^{-1/2}$ plots (Eq. 5) in the diffusion-controlled region. The σ vs. E curve indicated the potential dependence similar to that of the R_L vs. E curve, as expected from Eq. 7. For the diffusional transport within the conducting polymer,[15] the Warburg coefficient is given by

$$\sigma = RT(F)^{-2}(2D)^{-1/2}C_P^{-1} \tag{8}$$

where C_P is the concentration of a diffusing species (charged site or counterion), and the other symbols have their usual meanings. In the polypyrrole film, C_p increases with increasing positive potential because it is proportional to the oxidation level of the polymer. Thus the derivative $d\sigma/dE$ can be negative for the polymer electrode.

The real impedance response at low frequencies showed a deviation from the ideal vertical line; the impedance plots in the low frequency range were not exactly vertical to the real axis. It is a rather common problem in the studies of polymer films.[17,18] This finite slope can result from a distribution of relaxation times due to inhomogeneity of the film, e.g., possible nonuniform film thickness.[17] The degree of deviation was examined from the viewpoint of a constant phase element behavior,[5] which gives an inclined straight line in the complex impedance plane (Eq. 9).

$$Z_{\mathrm{cpe}} = A(j\omega)^{-\phi} = A\omega^{-\phi}[\cos \pi\phi/2 - j\sin \pi\phi/2], \quad (9)$$

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 $\phi=0$. Figure 8 shows the variations in the imaginary part (Z'') of the measured impedance with the frequency. The slopes of the straight lines gave a ϕ value of 0.96±0.01 at 0 and −0.2 V. This value indicates that the impedance of the partially oxidized film is almost capacitive in the range of frequency below 100 Hz. The values of $\ln A$ calculated from the intercept at $\ln\omega=0$ decreased linearly with increasing $\ln L$ over the range of L=0.042—1.33 μm; this result was in accord with the expectation from Eq. 7 because $A \approx 1/$capacitance as shown above.

Thus, applying Eq. 6 to the impedance at low frequencies (in the mHz range), we evaluated a value of C_L from a slope of the Z'' vs. ω^{-1} plot.

$$dZ''/d\omega^{-1} = 1/C_L \quad (10)$$

At low frequencies, the diffusion across a thin film is accomplished during one-half cycle of the applied signal. As presented in Fig. 9, the pseudocapacitance C_L was proportional to the film thickness over the potential range measured. Figure 10 shows that C_L increases with oxidation of the polymer and reaches a limiting value at higher oxidation levels. From Eqs. 7 and 8, we could merely expect an increase in C_L with increasing oxidation level if the density of the film remained unchanged. The values of redox capacitance calculated

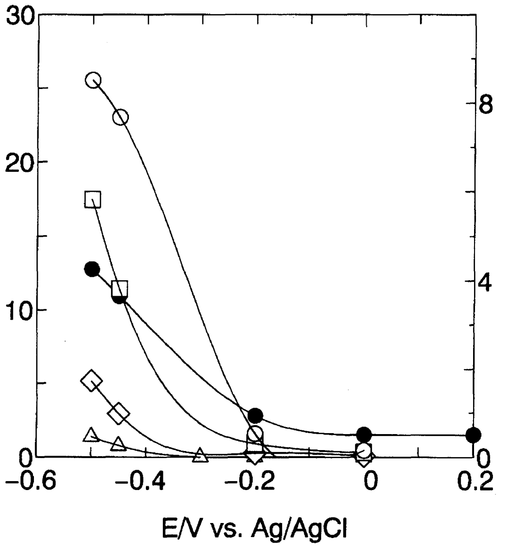

Fig. 7. Change in R_L with applied potential. Film thickness/μm; ○: 1.33, □: 0.67, ◇: 0.33, △: 0.17. ●: the value of σ (L=0.67 μm).

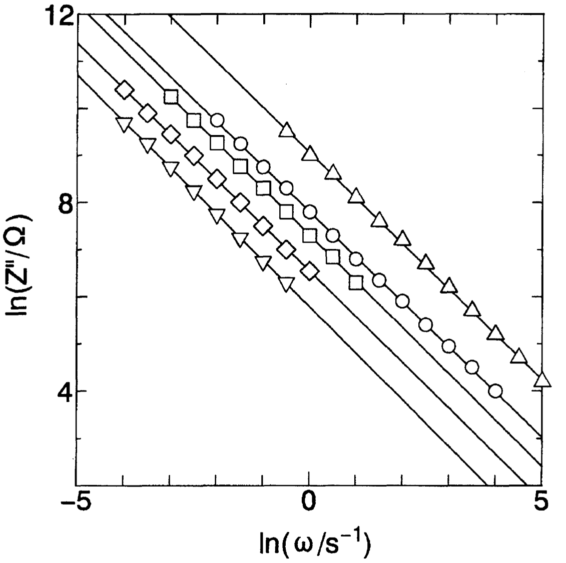

Fig. 8. Variations in imaginary part of impedance with frequency. Potential; 0 V. Film thickness/μm; △: 0.042, ○: 0.17, □: 0.33, ◇: 0.67, ▽: 1.33.

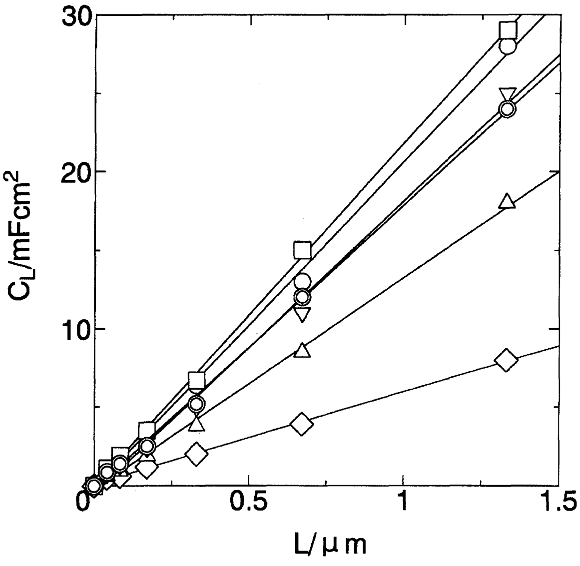

Fig. 9. Dependence of C_L on film thickness. Potential/V; ○: 0, □: −0.2, ▽: −0.45, ◎: −0.5, △: −0.6, ◇: −0.7.

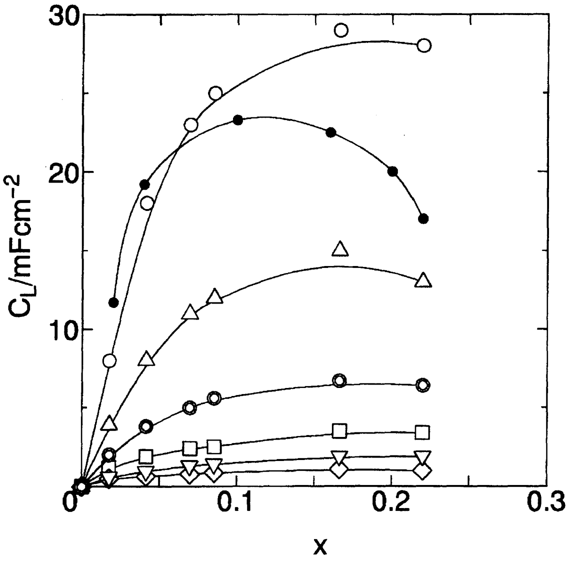

Fig. 10. Change in C_L with oxidation level of polymer. Film thickness/μm; ○: 1.33, △: 0.67, ◎: 0.33, □: 0.17, ▽: 0.083, ◇: 0.042. ●: the value of redox capacitance (L=0.33 μm).

from dQ/dE are indicated in Fig. 10, too. The values were 3—4 times larger than C_L and had a maximum at a medium oxidation level because of a maximum occurring on the dQ/dE vs. E curve. Since C_p vs. E curves have no maximum for polypyrrole, it is incorrect that C_L is identified with the redox capacitance (i.e. voltammetric current/scan rate) as often seen in previous publications.[2,9)]

A large capacitance C_L of the order of 1.9—29 mF cm^{-2} (L=0.083—1.33μm) observed in the partially oxidized state is explained in terms of the finite thickness and/or porous nature of the polymer film.[2)] Feldberg[19)] suggested that a high current plateau after the oxidation peak at polymer electrodes was due to the charging of a double layer at the wide surface of porous polymers. The model would lead, however, to too fine fibrils for the polymers, as it was shown by Feldman et al.[10)] A C_e value of 40—100 μF cm^{-2} (at −0.5 and −0.6 V) estimated in this work indicated no very large surface of the film, because it very probably included an internal double layer capacitance within the swollen polymer. Thus, we conclude that the frequency-independent capacitance arising in the low frequency range is due to the diffusional transport through the film with a finite thickness.

Using Eq. 7 with the measured values of R_L and C_L, we calculated the values of D to be: $(2\pm1)\times10^{-10}$ cm^{2}s^{-1} at −0.5 V, $(3\pm2)\times10^{-10}$ cm^{2}s^{-1} at −0.45 V, $(5\pm3)\times10^{-10}$ cm^{2}s^{-1} at −0.3 V, $(15\pm5)\times10^{-10}$ cm^{2}s^{-1} at −0.2 V. The D values are comparable to those obtained in acetonitrile for polypyrrole (10^{-9}—10^{-11} cm^{2}s^{-1}).[8,20)] The values of D slightly tended to increase with oxidation of the polymer, whereas they were unvaried with the film thickness. If a diffusing species is the positively charged site, a variation in oxidation state of the polymer causes a variation in D because the site–site interaction in the polymer depends on the fraction of the charged sites.

Conclusion

The main conclusions of the paper are summarized as follow:

(1) The diameter of semicircle of the impedance plot decreases with increasing positive potential; this change results from both decreases in R_m and R_c with increased concentration of the oxidized site.

(2) The formation of the charged sites takes place at the metal–polymer interface because the film probably swells with the solution. Accordingly, the oxidation proceeds from the back of the film to its surface.

(3) The values of R_L are proportional to the film thickness and increase largely as the potential is lowered. The C_L values increase with oxidation of the polymer and reach a limiting value at higher oxidation levels. These behaviors agree with those expected from the diffusional transport of a charge carrier through the film with a finite thickness.

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