Electrochemical Characteristics of Polythiophene Film Electrodes in Acetonitrile Solution

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The effect of electrode potential and film thickness on the kinetic parameters of the oxidation process of polythiophene (PT) was investigated by an a.c. impedance method and conductivity measurements. The conductivity of a PT film increased with its oxidation and reached a limiting value at higher potentials than 0.8 V despite a rise in oxidation state of PT. The oxidation of the PT film lowered the activation energy of electric conduction, which suggested the broadening of a polaron band. An increase in the oxidized form of thiophene unit brings about the decrease in charge transfer resistance at the polymer electrode in the lower potential range than the half-wave potential of PT. Both the redox capacitance of the polymer and d.c. resistance associated with the diffusion of a charge carrier indicated the dependence on the potential and film thickness which was expected from a finite diffusion model. A large capacitance of the order of 1—30 mF cm^{-2} in the oxidized state is explained in terms of the charge saturation effect due to the finite thickness and porous nature of the polymer film.

Electrical conducting polymers have received considerable attention because of their possible applications to organic batteries, sensors, electrochromic displays, and semiconductor devices.$^{1—3)}$ The good stability of polythiophene (PT) in air makes it an attractive electronic material.$^{4)}$ In order to develop more effective films for polymer–electrolyte junctions, it is necessary to have a detailed knowledge of the electrode processes at polymer films. Charge transport through the polymer films and charge transfer reactions at the metal/polymer and polymer/electrolyte interfaces play key roles in the behavior of electroactive polymers coated on metal surfaces. The kinetic methods with large perturbations induce unhomogeneous states for the electroactive polymer films.$^{5)}$ Electrochemical impedance spectroscopy$^{6)}$ has one advantage over techniques involving large perturbations: The system is only infinitesimally perturbed with respect to the steady-state. This method has been used to study the redox mechanism of poly(3-alkylthiophene).$^{7)}$ Bobacka et al. examined the double layer structure at the PT–electrolyte interface by analyzing its impedance data.$^{4)}$ In this work, we investigate the effect of electrode potential and film thickness on the kinetic parameters of the PT film electrode by measuring its a.c. response over the wide range of frequency.

Experimental

Materials. Thiophene (Kanto Chemicals, >98.0%) was distilled before use, and tetraethylammonium perchlorate recrystallized from water and dried in vacuo. All electrolyte solutions were prepared with doubly-distilled acetonitrile. The preparation of the solutions and cell fabrication were carried out in an argon-filled dry box at ambient temperatures.

Apparatus and Procedures. The PT films were electrochemically deposited on Pt or ITO glass (0.25 cm^2) at a current density of 5 mA cm^{-2} from acetonitrile solutions containing 0.1 M thiophene and 0.1 M tetraethylammonium perchlorate (M=mol dm^{-3}). Film growth was monitored by measuring the charge passed during polymerization, and the film thickness was estimated from the relationship (2.5 nm cm^2 mC^{-1}) between the charge passed vs. film thickness; the relationship was determined by Waltman et al.$^{8)}$ Electrochemical experiments were carried out in a one-compartment, three-electrode glass cell at room temperature. An Ag/AgNO$_3$ in acetonitrile and a large Pt gauze (>10 cm^2) were used as the reference and counter electrodes, respectively. Cyclic voltammograms were obtained by a Hokuto Denko HA-501 potentiostat coupled with an HB-104 function generator and recorded on a Yokogawa 3025 X–Y recorder. The a.c. impedance of the electrochemical cell was measured with an NF Electronic Instruments S-5720C frequency response analyzer coupled to an HA-501G potentiostat over the frequency range of 10^{-3}—10^3 Hz. The amplitude of the applied a.c. signal was 10 mV. The impedance response of the dry cell, Pt/polymer film/Au, was measured on an HP 4284A LCR meter over the frequency range of 20—10^6 Hz. The dry cell were made up by undoping the polymer at a given potential after the polymerization, thorough rinsing the film in pure acetonitrile, and subsequent vacuum-depositing Au on it. The in situ measurements of conductance of the PT film were carried out in the solutions with the electrodes of two-band type which were described previously.$^{9)}$ Absorption spectra were measured on a Hitachi U-3210 UV-visible spectrophotometer.

Results and Discussion

Conductivity of PT Film. It is well known that PT is electrochemically doped and undoped with anions.$^{3)}$ From the potential dependence of absorption spectrum and conductance of the film, PT was found to be in a fully reduced state at −0.5 V. Figure 1 shows the charge (Q) required to oxidize the polymer from −0.5 V to a given potential (E). The Q vs. E relation gave no sigmoid curve, whereas the cyclic voltammogram of PT showed an anodic current peak at about 0.7 V. This result is probably due to a high current

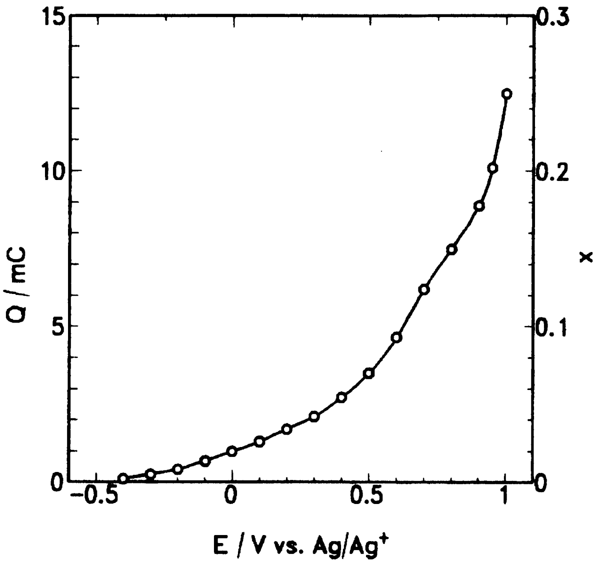

Fig. 1. The charge required to oxidize PT from −0.5 V to a given potential. Electrode area: 0.25 cm^2, film thickness: 0.53 μm. The values of the average oxidation number of thiophene unit are shown too.

plateau after the oxidation peak, which has been ascribed to a large capacitance effect characteristic of the conducting polymers.[10] In order to express the oxidation state of PT, we used the average oxidation number (x) of thiophene unit on the basis of its fully reduced form [$-C_4H_2S-$]. The value of x was estimated from Eq. 1 on the assumption that the efficiency of the polymerization was 100%.

$$x = 2Q/(Q_m - Q_r) \quad (1)$$

where Q_m is the charge for electrochemical preparation of the polymer and Q_r the charge required to reduce the as grown polymer at −0.5 V.

$$n\ C_4H_4S \xrightarrow{Q_m} [-C_4^{m+}H_2S-]_n + 2n\ H^+ + n(2+m)e \quad (2)$$

$$[-C_4^{m+}H_2S-]_n + mn\ e \xrightarrow{Q_r} [-C_4H_2S-]_n \quad (3)$$

where n is the total number of thiophene unit in the polymer and m the oxidation number of the as grown polymer. The obtained value of x is shown in Fig. 1 too. An x value of 0.25 at 1.0 V indicates that 25% of the total thiophene units undergoes one electron oxidation at this potential. The oxidation of PT at higher potentials than 1 V resulted in an irreversible transformation of its cyclic voltammogram.

Figure 2 shows the conductance of the PT film measured by the in situ method. The film conductance increased with oxidation of the polymer and reached a limiting value at higher potentials than 0.8 V despite an increase in x; the same change has been noted for poly(3-methylthiophene).[11] The similar dependence on the potential was found in absorption spectra of the PT film. The polymer in the reduced state had a absorption peak at 470—480 nm, whose edge gave a value of 2.04 eV for the formation energy of exciton. Upon oxidation, the polymer indicated a new absorption peak at 750—800 nm with an isosbestic point at 590 nm. These spectral behaviors are in good agreement with the ones reported in the literature.[12,13] The absorption peak growing in a long wavelength region can be ascribed to the creation of polaron (mobile cation radical) levels within the forbidden band.[13] The variations of absorptances at 480 and 750 nm with the potential are presented in Fig. 3, which indicates that the peak at 750 nm developed at the expense of the peak at 480 nm. Both absorptances approached limiting values in the high potential range. The activation energies (E_a)

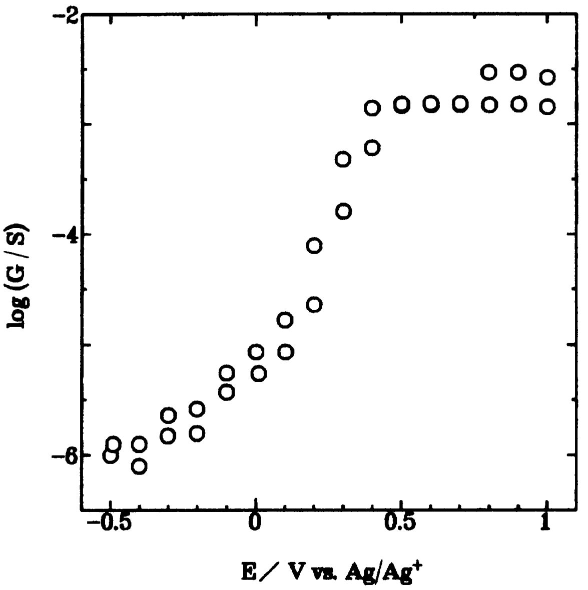

Fig. 2. Conductance of PT film measured in solutions by the in situ method.

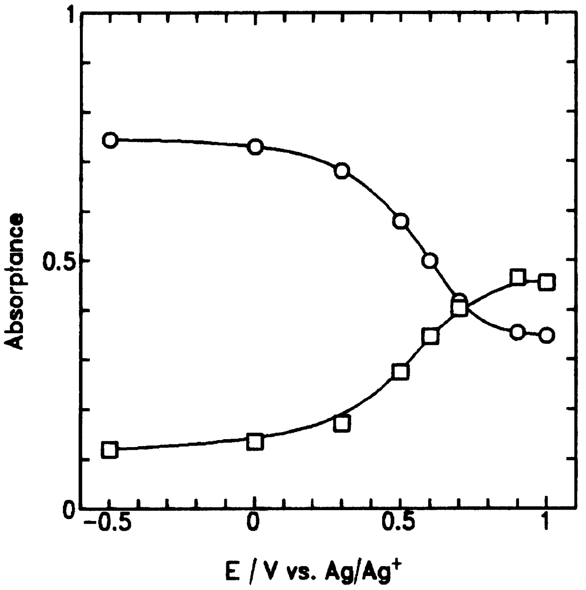

Fig. 3. Variations in absorptance of PT film with applied potential. Wavelength; ○: 480 nm, □: 750 nm.

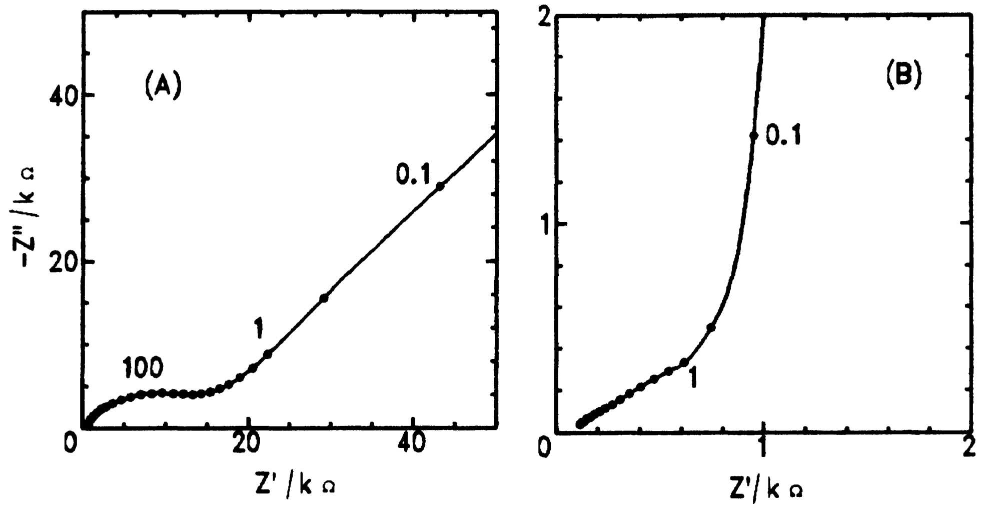

Fig. 4. Typical complex plane impedance diagrams (L=0.62 µm). Potential/V; (A): −0.5, (B): 0.3. Numerical values in the figure exhibit frequencies in Hz.

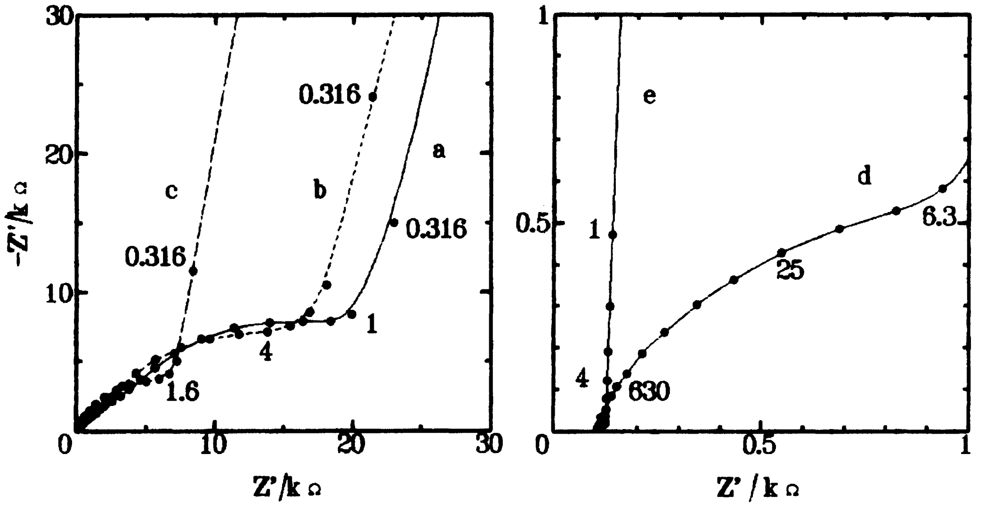

Fig. 5. Typical complex plane impedance diagrams (L=0.06 µm). Potential/V; curve a: −0.4, b: −0.2, c: 0, d: 0.2, e: 0.6. Numerical values in the figure exhibit frequencies in Hz.

of electric conduction for differently oxidized polymers was also examined by using the dry cell. Table 1 shows the E_a values of the dried films, which are much smaller than the formation energy of exciton. An increase in oxidation state of PT decreased the activation energy of electric conduction. The above results suggest the formation of a bipolaron band due to the recombination of polarons in a fully oxidized state.[12]

Table 1. Activation Energy of Electric Conduction, and Film Resistance and Capacitance for the Dried PT Film

Doping potential/V	E_a/eV	R/kΩ	C/nF
−0.5	0.4	30	1.4
−0.3	0.3	8.0	2.0
0.3	0.08	0.16	1.3
0.6	0.04	0.032	—
As grown polymer[a]	0.02	0.01	—

a) Polymerization potential=1.6 V.

Impedance Response of Polymer Electrode. Since almost all kinetic quantities of electrode processes depend on the potential and/or film thickness (L) in electroactive films, the effect of these experimental parameters was investigated over the whole range of frequency of interest. Typical complex plane impedance diagrams for the PT film electrode are presented in Figs. 4 and 5. A film of L=0.62 µm showed both a linear 45° branch (the diffusion-controlled region) and vertical branch (the capacitive region) in the complex impedance diagram, while a thin film of L=0.06 µm rarely showed the former branch. At lower potentials, a semicircle or an arc due to a parallel RC element was observed in the high frequency range. The diameter of the semicircle giving the value of R decreased with increased positive potential, and no semicircle was observed at higher potential than 0.3 V.

The impedance response of the film electrode was interpreted on the basis of the modified Randles equivalent circuit[14] shown in Fig. 6, where R_s is the electrolyte resistance, C_{dl} the double layer capacitance at the electrode interfaces, R_c the charge transfer resistance of the Faradaic process, Z_d the impedance due to diffusion in the film, and Z_m the one due to electronic migration in the bulk film. From an electrical point of view, the diffusion impedance in a film can 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. 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., a linear (45°) branch in the impedance diagram (the diffusion-controlled region). Another linear branch appears in the diagram at low frequencies and for thin film, i.e., $\omega L^2/D \ll 1$.

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

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

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

When there are large differences in the relaxation times of various electrode processes, the impedance diagram shows the different frequency-limited regions corresponding to each process. The region of the charge transfer process appears generally in higher frequencies than that of the diffusion process.

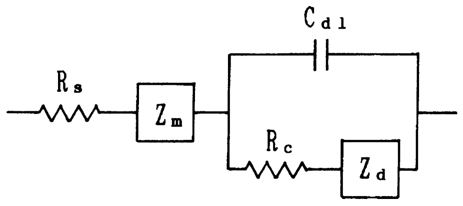

Fig. 6. The equivalent circuit for a.c. response of film electrode.

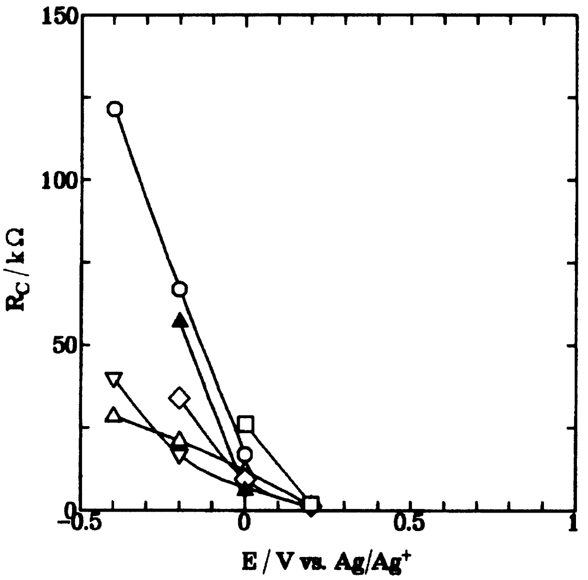

Fig. 7. Change in R_C with potential. Film thickness/μm; ○: 1.0, ▲: 0.58, □: 0.35, ◇: 0.16, △: 0.10, ▽: 0.06.

Figure 7 shows the value of R_c determined from the semicircle in high frequency (1—10^3 Hz). The value of R_c decreased as the potential was raised. For the electrode reaction X+e→Y at a metal–solution interface, R_c goes through a minimum at the standard potential ($E°$) owing to the potential changes in concentrations of X and Y,[14] and thus the derivative dR_c/dE is negative in the range of $E < E°$. If this relation also holds for the polymer electrode, we anticipate the potential change of R_c mentioned above because the half-wave potential of PT was about 0.60—0.65 V according to the cyclic voltammetry. Accordingly, we presume that the potential dependence of R_c shown in Fig. 7 results from an increase in concentration of the oxidized form with increased positive potential, which is due to the following reaction.

$$\mathrm{P} \longrightarrow \mathrm{P}^{+\bullet} + \mathrm{e}. \tag{8}$$

Where P is the reduced form of the thiophene unit and $\mathrm{P}^{+\bullet}$ its oxidized form. At lower potentials ($E<0$ V) and for thick sample, another arc was observed in the higher frequency range than that of R_c although the division into two arcs accompanied a considerable obscureness. The resistance estimated from the arc in higher frequency, which was regarded as the one due to electronic migration in the bulk film, decreased with increasing potential.

We also examined the a.c. response of the PT film by using an ion-blocking electrode (the dry cell). Since both the impedance and admittance diagrams of the dried film showed a semicircle or part of one, the electrical equivalent circuit for the film was taken as a combination (1) or (2) of resistors and a capacitor shown in Fig. 8.[14] Table 1 also shows the values of R_1 changing

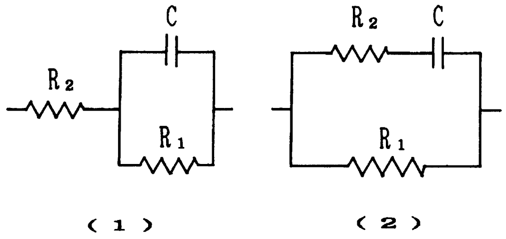

Fig. 8. Electrical equivalent circuits for dry cell.

with the doping potential and of C presented in Fig. 8; the values were determined from the diameter and frequency at the vertex of the semicircle. The values of C indicated no variation in the permittivity of PT with its oxidation state. The value of R_{l} regarded as the resistance of the film decreased largely with an increase in oxidation state of PT, which agreed with the result of the in situ conductance measurement. The charge transport through the polymer is ensured by the interchain electron transfer.[15] Therefore, the film conductivity vs. E curve could be expected to show a maximum if the rate of electron exchange reaction between the reduced and oxidized sites has the potential dependence similar to that of R_{c} for the metal–solution system. The film conductance vs. potential relations measured, however, indicated no maximum.

Fig. 9 shows the values of R_{L} estimated from the magnitude in resistance of the diffusion-controlled region. The quantity R_{L}, called the limiting resistance, represents the d.c. resistance associated with the diffusion of a charge carrier. The values of R_{L} were roughly proportional to the film thickness, which was in accord with the expectation from Eq. 7. The values increased largely as the potential was lowered, although the appearance of the 45° branch was limited in the high potential range. For the metal–solution system, the Warburg coefficient σ has a minimum value at $E°$ as can be seen from Eq. 9.[14]

$$\sigma = RT(nF)^{-2}(2D)^{-1/2}[C_{\mathrm{X}}^{-1} + C_{\mathrm{Y}}^{-1}] \tag{9}$$

where C_{X} and C_{Y} are the concentrations of X and Y, respectively, and the other symbols have their usual meanings. Thus we can anticipate the potential change of R_{L} mentioned above if D is independent of the potential.

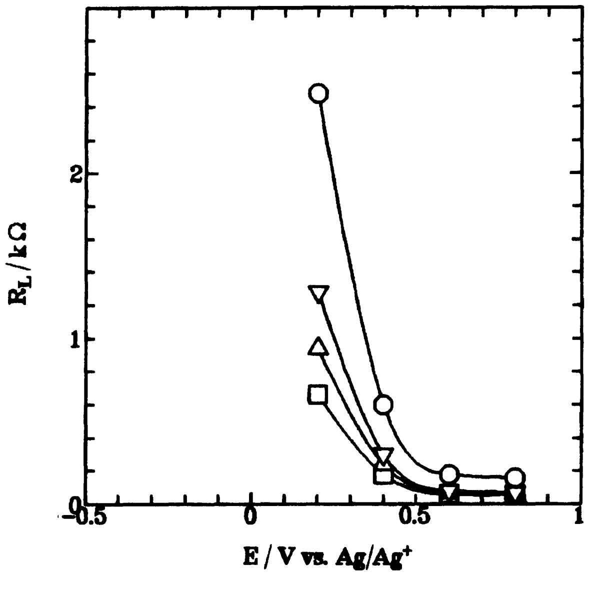

Fig. 9. Change in R_{L} with potential. Film thickness/μm; ○: 2.8, ▽: 1.0, △: 0.58, □: 0.30.

Since the imaginary part (Z'') of the impedance measured changed with ω^{-1} at very low frequencies (in the mHz range), as expected from Eq. 6, we evaluated a value of C_{L} from a slope of the Z'' vs. ω^{-1} plot.

$$\mathrm{d}Z''/\mathrm{d}\omega^{-1} = 1/C_{\mathrm{L}} \tag{10}$$

Figure 10 shows that C_{L} is proportional to the film thickness too, which is in accord with Eq. 7. As presented in Fig. 11, the C_{L} value increased with a positive shift of the potential and went through a maximum at 0.6—0.7 V, which was expected from σ for the metal–solution system. Mermilliod et al. have observed a maximum near $E°$ in the C_{L} vs. E curve for polypyrrole.[10]

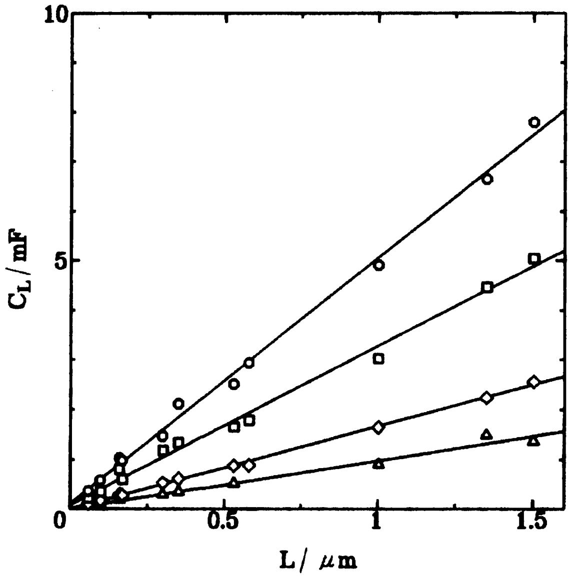

Fig. 10. Dependence of C_{L} on film thickness. Potential/V; ○: 0.6, □: 0.4, ◇: 0.2, △: 0.

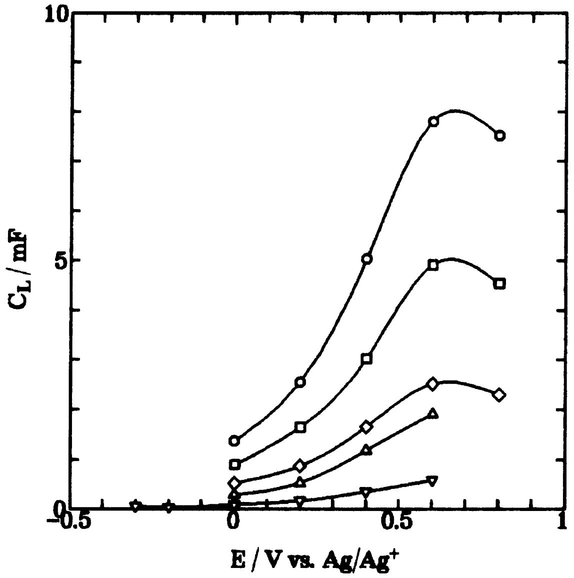

Fig. 11. Change in C_{L} with potential. Film thickness/μm; ○: 1.5, □: 1.0, ◇: 0.53, △: 0.30, ▽: 0.10.

The above results on R_L and C_L lead to the conclusion that the charge transfer process at the PT film electrode occurs at the metal–polymer interface. A counterion to maintain electroneutrality can go into and out of the polymer film with small resistance because the film swells with the electrolyte. Since the impedance measured at very low frequencies was expressed as a series combination of R_L and C_L, C_L could be related to the Faradaic charge required to oxidize the polymer under d.c. conditions, as follows.[17)]

$$C_L = \mathrm{d}Q/\mathrm{d}E. \tag{11}$$

Consequently, a bulk parameter C_L, called the redox capacitance of the polymer, should show the potential variation similar to that of the voltammetric current/scan rate obtained at a slow scan rate. As presented in Fig. 11, the C_L vs. E curve indicated a maximum in the vicinity of a voltammetric current peak (0.65 V) obtained at a scan rate of 5 $\mathrm{mV\,s^{-1}}$. A C_L value of 8 $\mathrm{mF\,cm^{-2}}$ at the peak potential was comparable to a capacitance of 11 $\mathrm{mF\,cm^{-2}}$ deduced from the cyclic voltammogram of the same cell (L=0.3 μm). A large capacitance of the order of 1—30 $\mathrm{mF\,cm^{-2}}$ in the oxidized states may be explained in terms of the finite thickness and porous nature of the polymer film.[10)] A high current plateau after the oxidation peak at polymer electrodes has been attributed by Feldberg[18)] to the charging of a double layer at the wide surface of the porous polymer. A C_{dl} value of 40—200 $\mu\mathrm{F\,cm^{-2}}$ estimated in the present experiment, however, did not imply a very large surface of the PT film. We consider that the large capacitance is due to the charge saturation effect associated with the finite diffusion.[10)]

Using Eq. 7 with the measured values of R_L and C_L, we calculated the values of D to be: $(1.4\pm0.6)\times10^{-9}$ $\mathrm{cm^2\,s^{-1}}$ at 0.2 V, $(3\pm2)\times10^{-9}$ $\mathrm{cm^2\,s^{-1}}$ at 0.4 V, $(5\pm3)\times10^{-9}$ $\mathrm{cm^2\,s^{-1}}$ at 0.6 V. The D values are comparable to those obtained for polypyrrole[19)] rather than for poly(3-methylthiophene).[7)] The values of D slightly tended to increase with the oxidation of PT, whereas they were independent of the film thickness. If the mobile species is electron or cation radical, the variation in oxidation state of the polymer possibly causes a variation in D because the site–site interaction in the polymer depends on the fraction of an unoccupied redox site. The uncertainty in the value of D due to a finite slope of the so-called vertical branch, however, is too high to draw conclusions on the interaction. The finite slope of complex impedance plot in the low frequency range can result from the nonuniform film thickness.[15)] To get a better understanding of the polymer film electrodes, one must investigate the inhomogeneity of the polymer film.

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