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Electrochemical Impedance Study and Characteristics of Polyaniline Film Electrodes

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The ac response of polyaniline (PA) film electrodes in 0.5 M H_2SO_4 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 metal and redox sites of the polymer controlled the rate of the charge transfer process at the film electrode. The oxidation of the PA film brought about a decrease in charge transfer resistance at lower potentials than the first half-wave potential of PA. The redox capacitance of the polymer indicated the dependence on the potential and film thickness, which was expected from a finite diffusion model. A large capacitance of the order of 3—30 mF cm^{-2} in the partially oxidized state is explained in terms of the charge saturation effect associated with the finite thickness. Impedance plots at high frequencies (the kHz range) suggested the occurrence of a hydrogen adsorption reaction in the reduced state. The PA film probably swells with the electrolyte. A counter ion to maintain the electroneutrality of the polymer can go into and out of the film with negligible resistance.

The good stability of polyaniline (PA) in a conducting state in air and easy electrochemical preparation of its film in acidic aqueous media make it an attractive new electronic material.[1—4] The photocharacteristics of the PA-electrolyte junction have recently been examined because of its usefulness as a photoactive material of inexpensive solar cells with large area.[5] Fundamentally interesting properties of PA are related to its novel conductor–insulator transitions induced by electrochemical doping–undoping and by the change in pH. The charge transport through the electroactive polymer film and charge transfer reactions at the metal/polymer and polymer/electrolyte interfaces play key roles in the behavior of the polymer coated on metal surfaces. Electrochemical impedance spectroscopy[6] is suited for investigating the kinetics of the polymer film electrode because the system is only infinitesimally perturbed with respect to the steady state. This method has successfully been applied to the studies of redox property of the PA film.[7—9] The electrochemical behavior of this system of theoretical and practical importance is very complex owing to the intrinsic inhomogeneity of the polymers. To characterize the electrode processes occurring in surface polymer films, it is necessary to examine the variation of their impedance response as a function of experimental parameters, such as electrode potential, film thickness, and electrolyte concentration. In this work, we investigate the effects of oxidation state of PA and film thickness on the kinetic parameters of the electrode processes by measuring its ac response over the wide range of frequency.

Experimental

The PA films were electrochemically deposited on Pt or ITO glass (0.25 or 1 cm^2) from 0.5 M H_2SO_4 solution (M= mol dm^{-3}) containing 0.1 M aniline. The potential of the working electrode was cycled between −0.1 and 0.8 V vs. Ag/AgCl at a scan rate of 100 mV s^{-1} for 100—300 cycles. Film growth was monitored by measuring the charge passed during the polymerization, and the film thickness (L) was estimated from the relationship between the height (H) of the cyclic voltammogram peak vs. film thickness ($L/\mu\mathrm{m}=0.059$ $H/\mathrm{mA\ cm}^{-2}$), a relationship which was analyzed by Stilwell and Park.[1] Electrochemical experiments were done in a one-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 the electrochemical measurements. The ac 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 ac signal was 10 mV. The impedance response of the cell with two PA electrodes 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 done in the solutions with the electrode of two-band type,[10] on which the polymer bridged the gap between two Pt bands.

Results and Discussion

Redox Behaviors. A cyclic voltammogram of the PA film electrode has two pairs of oxidation–reduction peaks in 0.5 M H_2SO_4.[3] Polyaniline was reversibly doped at lower potentials than 0.8 V, but it degraded slowly at higher potentials because of the hydrolysis of the C=N bond formed. Some reports have identified its degradation product as *p*-benzoquinone.[2,11] The oxidation state of PA at each potential (E) can be calculated from the charge (Q) required to oxidize the fully reduced polymer. The average charge (x) on the polymer chain per aniline unit was estimated from Eq. 1 on the assumption that PA hydrolyzed completely on oxidation up to two electrons/unit (x=2), when all carbon–nitrogen bonds became double bonds.

$$x = 2Q_2/Q_1, \qquad (1)$$

where Q_1 is the charge required to oxidize the reduced form $[-C_6H_4NH-]$ up to complete decomposition and Q_2 is that up to a certain oxidation level. The repeat unit of PA could be expressed as $[-C_6H_4NHC_6H_4\overset{\cdot+}{N}H-]$ at 0.4 V because the value of x was equal to 0.5 at this potential. On account of the recombination of the adjacent cation radicals, however, the concentration of the cation radical was not always proportional to x, as suggested by the absorption spectra and conductivity of the PA film. At about 0.8 V where the x value amounted to 1, the repeat unit was presumed to be the quinonoid form $[-C_6H_4-N=C_6H_4=N-]$. This presumption is consistent with the observation of the oxidative degradation.

As the PA film was oxidized, the absorption peak at 330 nm assigned to a π–π^* transition of the aromatic structure decreased and new absorption peaks developed at 420—440 nm and at >800 nm with an isosbestic point at 470 nm.[12,13] The absorbance at 430 nm had a maximum at an x value of 0.4; thereafter it decreased gradually with further oxidation. This decrease is probably due to the transformation of the radical cations into *p*-benzoquinone diimine at x above 0.4. The abrupt decrease in both absorbances at 330 and 430 nm at x above 0.8 corresponded with the formation of the quinonoid state.[12,13] In accord with the changes in absorbance at 430 and 880 nm, the conductance of the film measured by the two-band method was proportional to the oxidation level at x below 0.2; this increase can be ascribed to the formation of a mobile radical cation in the PA matrix.[12,14] The resistance–x curve showed that both the reduced state and the quinonoid state are insulators, and the partially oxidized state is conductive in acidic solutions.[14]

Impedance Response of the Polymer Electrode. Since almost all kinetic parameters of electrode processes depend on the potential and/or film thickness in an electroactive film, 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-limited regions corresponding to each process: the charge transfer region at high frequencies, the Warburg region at medium frequencies, and the finite diffusion region at low frequencies.

Typical impedance diagrams of the PA film electrode are presented in Figs. 1 and 2. At lower potentials (in the reduced state), a vertical branch was observed in the low frequency range and a semicircle due to a parallel RC element was observed in the medium frequency range. The diameter of the semicircle, which gives the value of R, decreased with increased positive potential. At higher potentials than 0.1 V, only a vertical branch

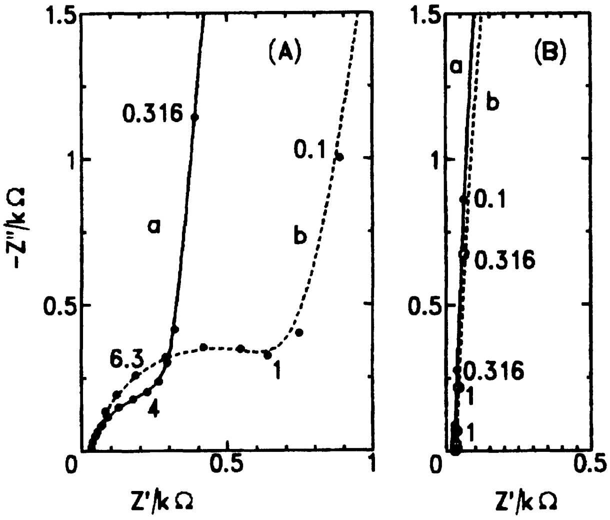

Fig. 1. Typical complex plane impedance diagrams. (A): −0.05 V, (B): 0.2 V. Film thickness/μm; curve a: 0.14, b: 0.31. Numerical values in the figure exhibit frequencies in Hz.

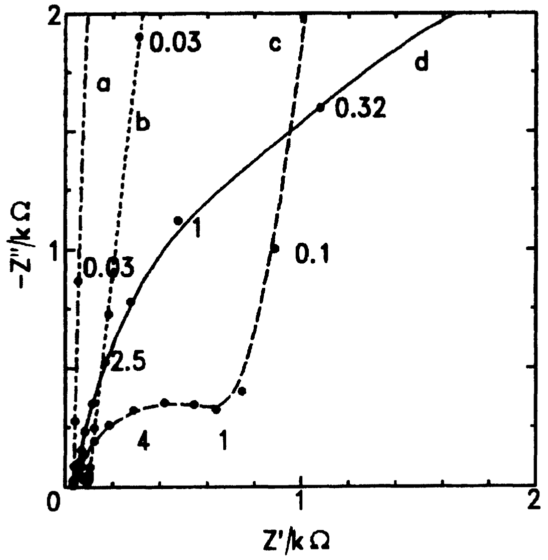

Fig. 2. Typical complex plane impedance diagrams (L=0.31 μm). Potential/V; curve a: 0.4, b: 0, c: −0.05, d: −0.1. Numerical values in the figure exhibit frequencies in Hz.

was observed over the frequency range of 10—10^{-3} Hz.

The impedance response of the film electrode was interpreted on the basis of the Randles equivalent circuit shown in Fig. 3, where R_s is the ohmic resistance, C_{dl} the double layer capacitance at the electrode interfaces, R_c the total charge transfer resistance of the Faradaic process, and Z_d the impedance due to the diffusion in a 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

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

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. 2 corresponds to Eq. 3 for semiinfinite diffusion.

$$Z_d = (1-j)\sigma\omega^{-1/2} \qquad (3)$$

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 films, i.e., $\omega L^2/D \ll 1$.

$$Z_d = (2/9)^{1/2}\sigma L D^{-1/2} - j\sigma(2D)^{1/2}(\omega L)^{-1} \qquad (4)$$

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

$$R_L = (2/9)^{1/2}\sigma L D^{-1/2}, \quad C_L = \sigma^{-1}L(2D)^{-1/2} \qquad (5)$$

Figure 4 shows the values of R_c calculated from the semicircle in the medium frequency range. The value of R_c decreased as the potential was raised. For the electrode reaction $X+e \rightarrow Y$ 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,[17] and thus the derivative dR_c/dE is negative in the range of $E<E^\circ$. If we assume that the electron injection at the metal–polymer interface controls the rate of the charge transfer process, the potential change in R_c mentioned above can be anticipated because the $E_{1/2}$ value of the first redox process is 0.17 V as shown by the cyclic voltammetry. The decrease in R_c with the potential was also similar to the change in electronic resistivity of the PA film in the low potential range where the mobile radical cation was formed. Since R_s was independent of both potential and film thickness, the resistance due to electron migration should be in series with R_c. We suppose that R_c mirrors the resistivity of the film. In any event, the potential dependence of R_c results from increased concentration of the cation radical form with increasing positive potential, which is due to the following reaction.

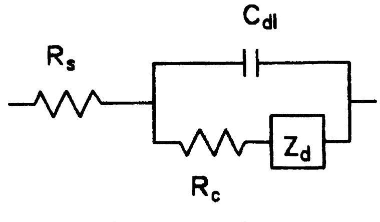

Fig. 3. The equivalent circuit for ac response of film electrode.

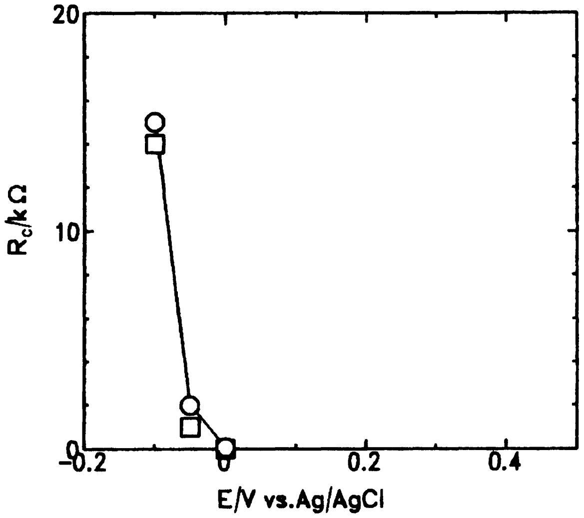

Fig. 4. Change in R_c with applied potential. Film thickness/μm; ○: 0.23, □: 0.15.

$$[-C_6H_4NH-] \rightarrow [-C_6H_4\overset{\cdot\,+}{N}H-] + e. \qquad (6)$$

At negative potentials, another semicircle was observed in the higher frequency range (the kHz range) than that of R_c. The diameter of this semicircle (7—10 Ω at −0.1 V) was independent of the film thickness in the range of L=0.08—0.31 μm. A similar semicircle was also observed on a bare Pt electrode. The impedance and admittance diagrams of the Pt electrode are shown in Fig. 5, which indicate that its electrical equivalent circuit can be regarded as a combination of resistors and capacitors as shown in Fig. 5. According to the impedance diagrams, the ratio of time constants of the series RC and parallel RC elements was between 10 and 100 (R_s=60.5 Ω). The C_{dl} values calculated from the diameter and the frequency at the vertex of the semicircle were 12.5 μF cm^{-2} at 0.3 V and 130 μF cm^{-2} at −0.1 V, which were the order of double layer capacitance at the metal/solution interfaces. The values obtained for R_h decreased as the potential was lowered. The cyclic voltammogram of Pt in H_2SO_4 indicated two hydrogen adsorption peaks at around 0 V, which were followed by H_2 evolution at potentials below −0.2 V. The PA film electrode generated H_2 at the same potentials, too. Thus, the semicircle appearing in higher frequency range for the reduced film is ascribable to the hydrogen adsorption layer or adsorption reaction 7

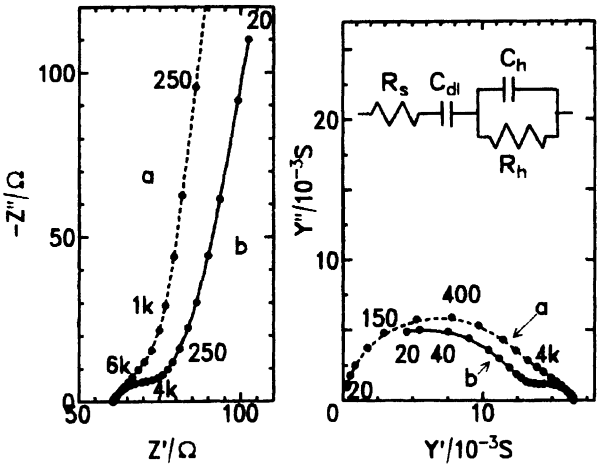

Fig. 5. Impedance and admittance diagrams of bare Pt electrode. Potential/V; curve a: 0.3, b: −0.1.

of hydrogen.

$$\mathrm{H^+ + e \rightarrow H} \qquad (7)$$

This suggestion was supported by the examination[10] of the film resistance; its variation with the pH of solutions implied that either the PA film contained the solution among fibrils or hydrogen ions migrated through the polymer by the acid-dissociating reaction 8 of the amino groups.

$$[\text{-C}_6\text{H}_4\text{NH}_2^+\text{-}] \rightarrow [\text{-C}_6\text{H}_4\text{NH-}] + \text{H}^+ \qquad (8)$$

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.[7—9] This finite slope can result from a distribution of relaxation times due to the inhomogeneity of the film (possible nonuniform film thickness).[16] The degree of deviation was examined from the viewpoint of a constant phase element behavior[6] (Eq. 9), which gives an inclined straight line in the complex impedance plane,

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

where A and ϕ are frequency-independent parameters, and $0 \leqq \phi \leqq 1$. This equation describes an ideal capacitor (A=1/capacitance) for ϕ=1 and an ideal resistor (A=resistance) for ϕ=0. Figure 6 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 0.97±0.01 in the range of L=0.08—0.31 µm. This value indicates that the impedance of the partially oxidized film is almost capacitive in the range of frequency<100 Hz. The values of ln A calculated from the intercept at ln ω=0 decreased linearly with increasing ln L; this result was in accord with the expectation from Eq. 5 because $A \approx 1$/capacitance as shown above.

Thus, applying Eq. 4 to the impedances at low frequencies (in the mHz range), we evaluated a value of C_{L} from a slope of the Z'' vs. ω^{-1} plot.

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

Figure 7 shows that C_{L} is proportional to the film thickness, which is in accord with Eq. 5. At low frequencies, diffusion across the thin film is accomplished during one-half cycle of the applied signal. Thus C_{L} is regarded as the redox capacitance of the polymer. As presented in Fig. 8, the C_{L} value increased with an increase in positive potential and went through a maximum in the vicinity of the $E_{1/2}$; this behavior was expected from the Warburg coefficient for the metal–solution system.[17] These results lead to the conclusion that the electron

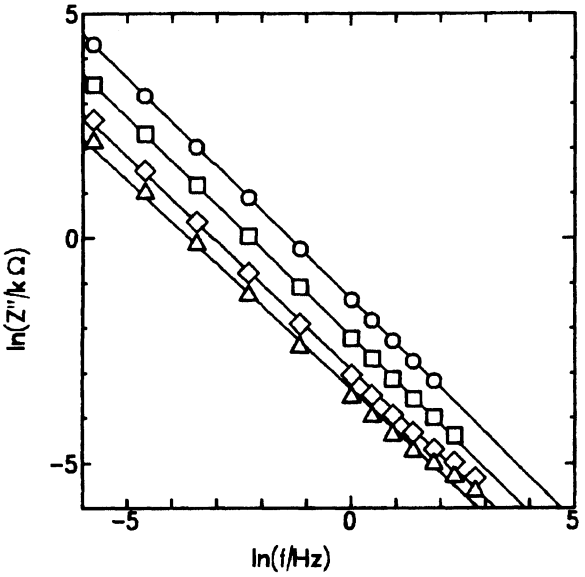

Fig. 6. Variations in imaginary part of impedance with frequency (0.4 V). Film thickness/µm; ○: 0.085, □: 0.14, ◇: 0.23, △: 0.31.

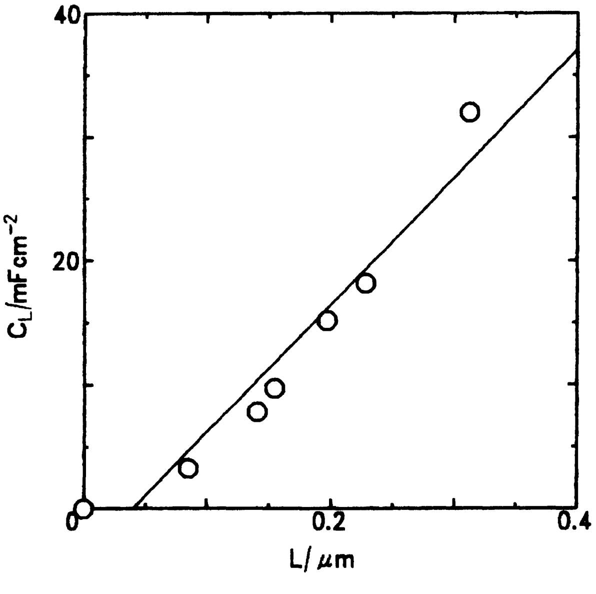

Fig. 7. Dependence of C_{L} on film thickness. Potential; 0.2 V.

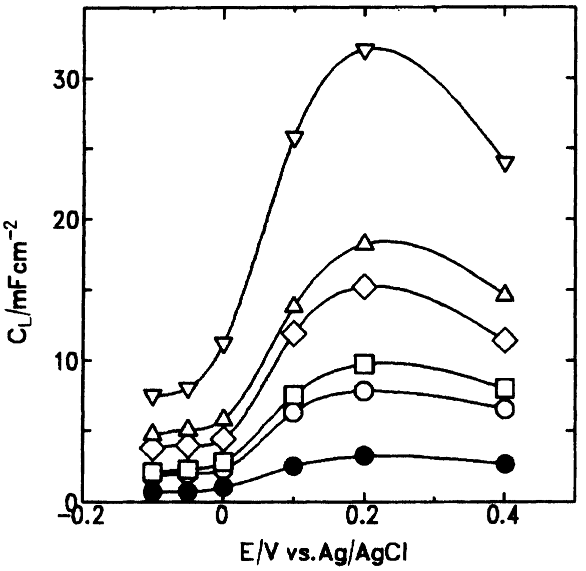

Fig. 8. Change in C_L with applied potential. Film thickness/µm; ▽: 0.31, △: 0.23, ◇: 0.2, □: 0.16, ○: 0.14, ●: 0.085.

exchange between metal and redox sites of the polymer controls the rate of charge transfer process at the PA film electrode. This conclusion implies the diffusing species in the film to be electrons. A counter ion to maintain the electroneutrality of the polymer can go into and out of the film with negligible resistance because the film swells with the electrolyte.

We could not find a reliable value of the limiting resistance R_L because of the lack of a well-defined Warburg region in the impedance plot; the lack was probably due to the small film thickness. If the impedance measured at low frequencies is expressed as a series combination of R_L and C_L (Eq. 4), C_L should be related to the Faradaic charge required to oxidize the polymer under dc conditions, as follows.[8,18]

$$C_L = dQ/dE \qquad (11)$$

Consequently, a bulk parameter C_L should show the potential variation similar to that of the voltammetric current/scan rate obtained at a slow scan rate. As presented in Fig. 8, the C_L vs. E curve indicated a maximum near the voltammetric current peak (0.2 V) obtained at a scan rate of 5 mV s^{-1}. A C_L value of 30 mF cm^{-2} at the peak potential was comparable to a capacitance of 41 mF cm^{-2} deduced from the cyclic voltammogram of the same cell (L=0.31 µm). A large capacitance C_L of the order of 3—30 mF cm^{-2} in the partially oxidized state may be explained in terms of the finite thickness and/or porous nature of the polymer film.[19] Feldberg[20] 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 the porous polymer. The model would lead, however, to too fine fibrils for the polymers, as it was criticized by Feldman et al.[21] A C_{dl} value of 240—400 µF cm^{-2} estimated in our experiment did not indicate a very large surface of the film. Thus, we consider that the large capacitance of the PA film is due to the charge saturation effect associated with the finite diffusion.[18] A possible explanation for the high current plateau after the peak can be a continuous change in redox potential with the oxidation state[19] because the site–site interaction in the polymer depends on the fraction of unoccupied redox sites.

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