Increased Redox-Reaction Rate of Quinhydrone at N-Substituted Polypyrrole Film Electrodes

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A poly[1-methyl-3-(pyrrol-1-ylmethyl)pyridinium] perchlorate-coated glassy carbon electrode noticeably decreased the charge-transfer resistance (R_t) of quinhydrone relative to a naked glassy carbon electrode. The redox species was not concentrated into a polymer film; this result differs markedly from the very good absorption of anthraquinonesulfonates and indigosulfonates by a polymer film. The dependence of R_t and the interfacial capacitance on the film thickness implies that the charge-transfer process occurs at the film-solution interface, because the polymer film is appreciably electronically conductive at positive potentials. Because of a change in the film conductivities with the potential, the polymer-coated electrode increased the anodic peak current of quinhydrone by three times, but decreased its cathodic peak current by two fifths, relative to that of a naked electrode. Although the decrease in R_t at a polymer-film electrode is somewhat ascribed to an increasing area, which is due to a porous film surface, the electrocatalytic effect of the polymer film can be attributed to an increasing standard rate constant of the charge-transfer process; this increase may be due to the adsorption of quinhydrone on the polymer surface.

Electroactive polymers such as polyaniline, polypyrrole, and polythiophene have high conductivities in their oxidized forms, and are reversibly switched between conducting and insulating states.[1] The electroactive polymers deposited on electrodes perform an important function in transporting electrons and ions through a polymer film. A polymer-modified electrode can provide very dence reaction sites compared with a naked electrode, and can mediate electron transfer to a solution species. Thus, electronically conducting polymers have received considerable attention because of their possible applications to organic batteries, sensors, electrochromic devices, and electrocatalysis.[2]

The oxidation-reduction of a conducting polymer electrode allows ionic species to go into/out of the polymer in order to maintain its electroneutrality.[3] We have planned to use this method to control the release/binding of a particular ion from/to a polymer film. For that purpose the following electrochemical reactions, which cause a substantial change in the interaction between the ionic species and the polymer, can be utilized: changes in the oxidation state of the polymer and in the ionic charge of the redox species incorporated into the film.

The anion-exchange properties of the oxidized form of polypyrrole have often been used to immobilize catalytic species on electrode surfaces.[4,5] However, the binding capacity of polypyrrole disappears when it is reduced. There has recently been considerable interest in preparing functionalized polypyrrole films.[6] If the conductive polypyrrole backbone facilitates rapid electron transport to all areas of the film, the functionalized polypyrroles are attractive in the mediation of electron transfer and the electrocatalysis

of slow electrochemical reactions. Mao and Pickup[7] have prepared a polypyrrole film with anion-exchange properties by polymerizing quaternized 3-(pyrrol-1-ylmethyl) pyridine and showed that this polycationic film can incorporate large amounts of hexacyanoferrate(II). The high concentration of permanent cationic sites in the film is expected to increase its permeability to ions.[7] This increase should lead to more rapid ion transport through the film, which is a physical property required for chemically modified electrodes. We[8] have recently examined the incorporation of organic anions into a polycationic film. It greatly increased the voltammetric peak currents of anthraquinonesulfonate and indigosulfonate ions. This electrocatalytic effect of the polymer film was attributed to an effective extraction of the anions from very dilute solutions. Besides electrostatic binding of the anions to the polymer, a hydrophobic interaction between them contributed significantly to effective extraction. This result implies that uncharged molecules in aqueous media can also to some extent be incorporated into the polymer film. For an effective control of the binding of organic ions, there is a need to assess the relative importance of hydrophobic and electrostatic interactions.[9]

In this paper we consider the influence of a poly[1-methyl-3-(pyrrol-1-ylmethyl)pyridinium]·perchlorate film on the redox kinetics of the p-benzoquinone/hydroquinone couple by electrochemical impedance spectroscopy as well as the causes of an observed electrocatalytic effect.

Experimental

Materials.   3-(Pyrrol-1-ylmethyl)pyridine was obtained from Aldrich and used without further purification. Acetonitrile (Kanto

Chemical, GR) was distilled over calcium hydride immediately before use, and tetrabutylammonium perchlorate (Kanto Chemical, GR) was recrystallized from ethanol and dried in vacuo at 70 °C. Quinhydrone, hydroquinone, and sodium sulfate were purified by recrystallization from water. All other chemicals were analytical-grade commercial materials and used as received.

Preparation. 1-Methyl-3-(pyrrol-1-ylmethyl)pyridinium iodide was prepared from 3-(pyrrol-1-ylmethyl)pyridine and methyl iodide according to a literature procedure,[7] followed by substitution of I^- with ClO_4^-. The prepared compound was characterized by ^1H NMR, IR spectroscopy, and elemental analysis.[8] Poly[1-methyl-3-(pyrrol-1-ylmethyl)pyridinium] perchlorate (poly-MPP) films were electrolytically deposited on glassy carbon (GC, area=0.07 cm^2) at a current density of 0.8 mA cm^{-2} from acetonitrile solutions containing 0.05 M (1 M=1 mol dm^{-3}) MPP and 0.1 M tetrabutylammonium perchlorate. The elemental analysis and IR spectrum of an obtained sample confirmed that the polymer was formed via the oxidative polymerization of pyrrole. The polymer films were grown to a total charge of 0.72 C cm^{-2} for many measurements. According to an empirical equation relating the charge passed during polymerization to the film thickness,[7] this total charge corresponds to a film thickness of 4.8 μm. After having been immersed in an aqueous solution of 0.2 M Na$_2$SO$_4$–0.01 M H$_2$SO$_4$ for 2 h, the polymer film electrodes were used for electrochemical experiments.

Procedures and Apparatus. All of the electrolyte solutions for electrochemical measurements were prepared with doubly-distilled water and purged with nitrogen gas before and during the measurements. Electrochemical experiments were carried out in a two-compartment, three-electrode glass cell at room temperature. A large Pt gauze (20 cm^2) and an Ag/AgCl/3.4 M KCl electrode were used as counter and reference electrodes, respectively. All of the electrode potentials are referred to the Ag/AgCl electrode. 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. impedances of the polymer film electrode were measured on an NF Electronic Instruments S-5720C frequency-response analyzer coupled to a Hokuto Denko HA-501G potentiostat. The impedances were measured at five discrete frequencies per decade over the range of 10^3—10^{-3} Hz at an amplitude of 10 mV (peak to peak). The electronic conductivity of the polymer film in contact with an electrolyte solution was measured with an interdigitated array electrode[10] covered with a sufficiently thicker film than a band spacing of 5 μm, the electrode which, by itself, forms a metal/film/metal cell. The oxidation level of the polymer film was potentiostatically controlled with the counter and reference electrodes.

Results and Discussion

N-substituted polypyrroles possess a more positive redox potential and a lower degree of doping level compared with that of polypyrrole.[11] In aqueous media, a poly-MPP film was irreversibly oxidized at around 0.8 V on the first anodic scan, which led to a virtual disappearance of the electroactivity. Therefore, the film going through a cycle virtually produced no faradiac currents in the potential range where the p-benzoquinone/hydroquinone couple showed a pair of redox waves (its redox potential=0.36 V at pH 2.3). Figure 1 exhibits cyclic voltammograms of poly-MPP-coated and naked GC electrodes in a 0.2 M Na$_2$SO$_4$–0.01 M H$_2$SO$_4$solution containing 1 mM quinhydrone, indicating that the polymer film
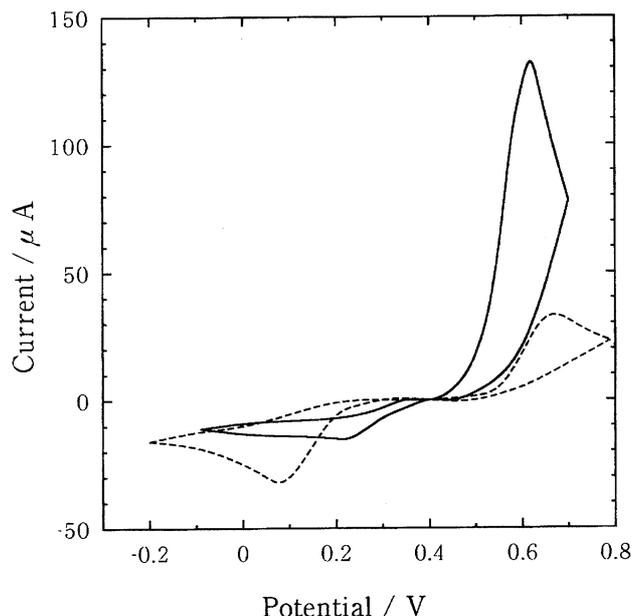

Fig. 1.   Cyclic voltammograms of poly-MPP-coated GC electrode (——) and naked GC electrode (···) in a 0.2 M Na$_2$SO$_4$–0.01 M H$_2$SO$_4$ solution containing 1 mM quinhydrone. Scan rate = 100 mV s^{-1}.

on GC significantly influences the rate of the electrode reaction of the redox couple. Two points are noteworthy: First, anodic and cathodic peak currents became unequal. Second, the separation of anodic and cathodic peak potentials ($\Delta E_p = E_{pa} - E_{pc}$) decreased. The values of ΔE_p were 300—400 mV at a polymer-coated electrode for a potential scan-rate range of 50—200 mV s^{-1}, whereas they were 500—600 mV at a naked GC electrode. The positive shift in E_{pc} was large compared with a less-positive shift in E_{pa}, as shown in Fig. 2; on the other hand, the equilibrium potential remained unaffected. The peak currents of quinhydrone increased linearly with the square root of the scan rates over the range of 5—200 mV s^{-1} at both the polymer-coated and naked GC electrodes. Figure 3 shows the linear dependence of the peak currents on the concentration of quinhydrone in a 0.2 M Na$_2$SO$_4$–0.01 M H$_2$SO$_4$ solution. The polymer-coated electrode noticeably increased the anodic peak current, but decreased the cathodic peak current to two fifths, relative to a naked electrode. The ratio of the anodic-to-cathodic peak currents at the polymer-coated electrode was about five in the scan rate range of 5—200 mV s^{-1}.

In order to gain further data for the redox kinetics of the polymer-film electrode, the frequency response of its impedance was examined. Complex-plane impedance diagrams show frequency-limited regions characteristic of elemental electrode processes, if there are large differences in their relaxation times. Figure 4 represents typical impedance diagrams of poly-MPP-coated and naked GC electrodes in 0.2 M Na$_2$SO$_4$–0.01 M H$_2$SO$_4$ solutions. A semicircle due to a parallel resistance-capacitance element was observed only in the presence of quinhydrone in the solutions. Figure 5 shows the diameter (R) of the semicircle and the capacitance

T. Komura et al.

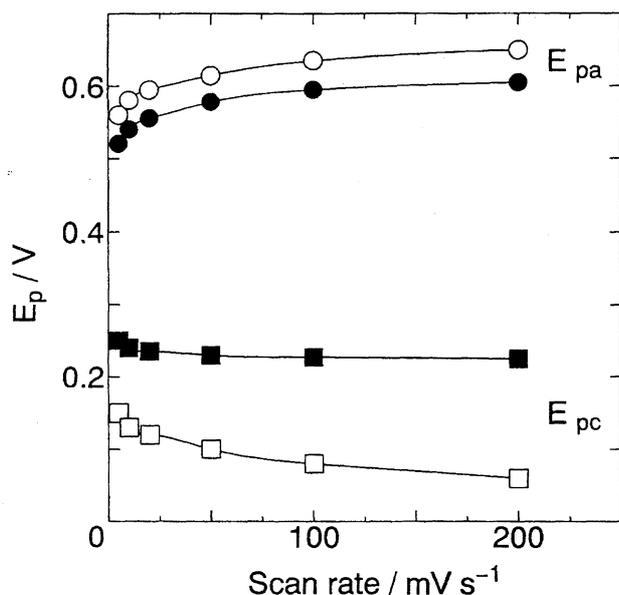Bull. Chem. Soc. Jpn., 70, No. 5 (1997) 1063

Fig. 2. Peak potentials of quinhydrone at poly-MPP-coated GC electrode (●, ■) and naked GC electrode (O, □). Circles, anodic peak; squares, cathodic peak.
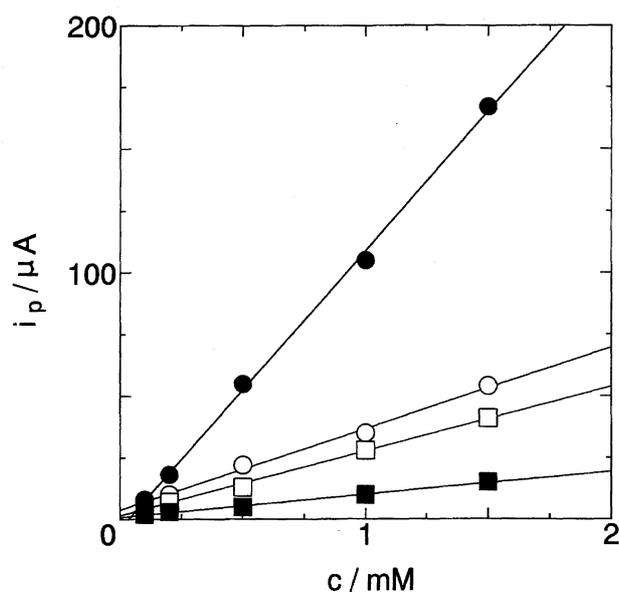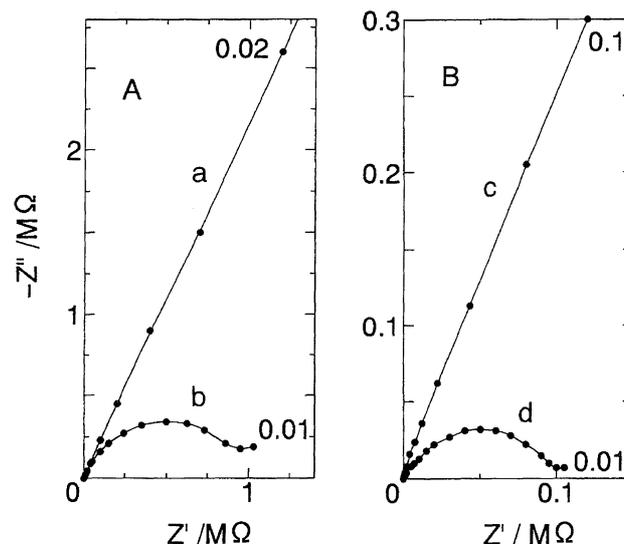

Fig. 4. Typical complex plane impedance diagrams of naked GC electrode (A) and poly-MPP-coated GC electrode (B) in the absence (a, c) and the presence (b, d) of quinhydrone in a 0.2 M Na_2SO_4–0.01 M H_2SO_4 solution. Applied potential: 0.36 V. Numerical values in the figure exhibit frequencies in Hz.
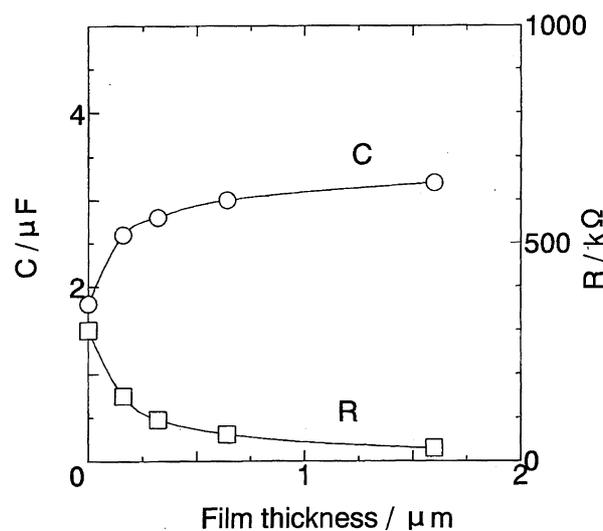

Fig. 3. Dependence of peak currents at poly-MPP-coated GC electrode (●, ■) and naked GC electrode (O, □) on the concentration of quinhydrone in a 0.2 M Na_2SO_4–0.01 M H_2SO_4 solution. Circles, anodic peak; squares, cathodic peak. Scan rate = 100 mV s⁻¹.

Fig. 5. Changes in the diameter of semicircle (□) and capacitance (O) with film thickness. Applied potential: 0.36 V.

(C) calculated from the relationship $\omega_{max} = (RC)^{-1}$, where ω_{max} is the angular frequency at the vertex of a semicircle. The capacitance, which was independent of the quinhydrone concentrations, increased slightly (from 2.6 to 3.2 μF) as the film thickened from 0.15 to 1.6 μm; this change indicates that the measured capacitance is not one of the bulk film, but an interfacial double-layer capacitance. If we measured the impedance of the bulk film, the capacitance should decrease with increased film thickness according to the relation $C = \varepsilon A/d$, where ε is the permittivity of the film, A is

the electrode surface area, and d is the film thickness. The semicircle is, therefore, due to the parallel combination of a charge-transfer resistance and a double-layer capacitance. A large diameter of the semicircle observed is ascribed to a slow charge-transfer rate of quinhydrone; this was also verified by the large ΔE_p values, as mentioned above.

Figure 6 shows changes in the charge-transfer resistance (R_t) with the concentration (c) of quinhydrone in solution. The values of R_t were inversely proportional to the quinhydrone concentration at both poly-MPP-coated and naked GC electrodes. From a comparison of their R_t values, it was found that the polymer-coated electrode gave a fairly small R_t compared with that of the naked electrode. This
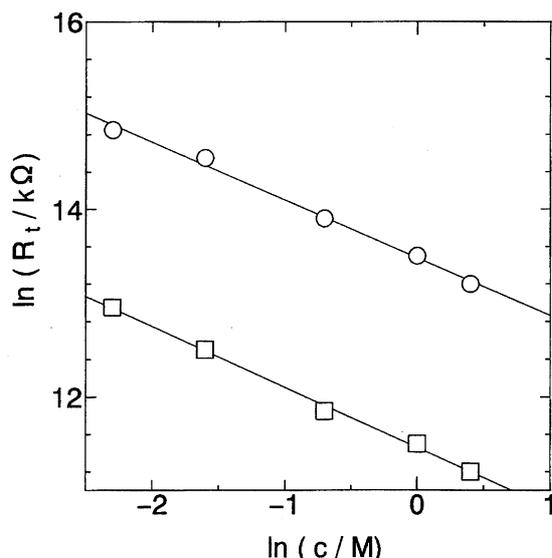
1064 *Bull. Chem. Soc. Jpn., 70, No. 5 (1997)*

Redox Rate of Quinhydrone at Polypyrrole

Fig. 6.   Changes in charge-transfer resistances at naked GC electrode (O) and poly-MPP-coated GC electrode (□) with the quinhydrone concentration in a 0.2 M Na_2SO_4–0.01 M H_2SO_4 solution. Applied potential: 0.36 V.

decrease in R_t causes ΔE_p to decrease. The relation between R_t and the composition of the redox couple was examined in a 0.2 M Na_2SO_4–0.01 M H_2SO_4 solution. The impedances of the electrodes were measured at the equilibrium potentials reached at each composition (the total concentration of the redox couple=1 mM). Figure 7 shows that the values of R_t reached a minimum at nearly equal concentrations of p-benzoquinone and hydroquinone. This concentration dependence of R_t can be easily understood from the exchange current (i_o) for the charge-transfer reaction of a redox couple,[12)
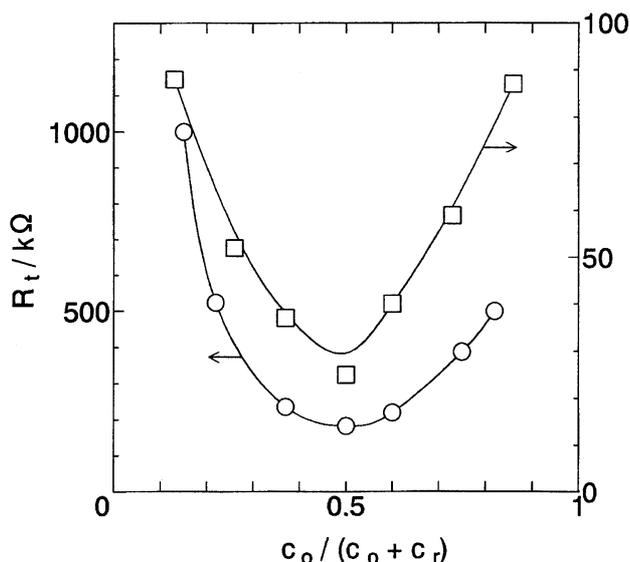

Fig. 7.   Relationship between R_t and the composition of redox couple in a 0.2 M Na_2SO_4–0.01 M H_2SO_4 solution. Circles, naked GC electrode; squares, poly-MPP-coated GC electrode. Impedances were measured at each equilibrium potential. The total concentration of redox couple is 1 mM.

$$R_t^{-1} = nF(RT)^{-1}i_o = (nF)^2(RT)^{-1}Ak^\circ\ c_r^a\ c_o^{1-a}, \qquad (1)$$

where n is the number of electrons transferred in the heterogeneous reaction, k° is the apparent standard rate constant (including the proton concentration for electrode reactions where protons participate), α is the transfer coefficient, c_r is the concentration of the reduced species in solution, and c_o is that of the oxidized species; all other symbols have their usual meanings. Equation 1 predicts that R_t reachs a minimum at $c_o/(c_r+c_o)=1-\alpha$. The linear relations seen in $[-\ln R_t - \ln c_o]$ vs. $\ln(c_r/c_o)$ plots of experimental data gave α values of 0.57 to the polymer-coated electrode and 0.35 to the naked electrode. The difference in α can account for a larger shift in E_{pc} than that in E_{pa}. Since $c_r=c_o=c/2$ for quinhydrone, Eq. 1 is reduced to

$$R_t^{-1} = (nF)^2(2RT)^{-1}Ak^\circ c. \qquad (2)$$

Therefore, assuming that the surface area of the polymer-coated electrodes was equal to that of a naked electrode, we evaluated the k° values at pH 2.3 to be $(2.0\pm0.4)\times10^{-5}$ cm s^{-1} for polymer-coated electrodes and $(2.7\pm0.3)\times10^{-6}$ cm s^{-1} for a naked electrode from the slopes of $\ln R_t$ vs. $\ln c$ plots shown in Fig. 6.

A change in R_t with the pH of solutions was examined at a given concentration of quinhydrone. The impedances of a polymer-coated electrode were measured at the equilibrium potentials reached at different acidic pH's, which corresponded exactly with the redox potentials of electrode reaction 3,

$$Q + 2H^+ + 2\,e \rightarrow H_2Q, \qquad (3)$$

where Q is p-benzoquinone and H_2Q is hydroquinone. Figure 8 indicates that the logarithm of R_t increases linearly with an increase in pH. This result corresponds well with the change expected from Eq. 2, because the apparent standard rate constant decreases with increasing pH for electrode re-
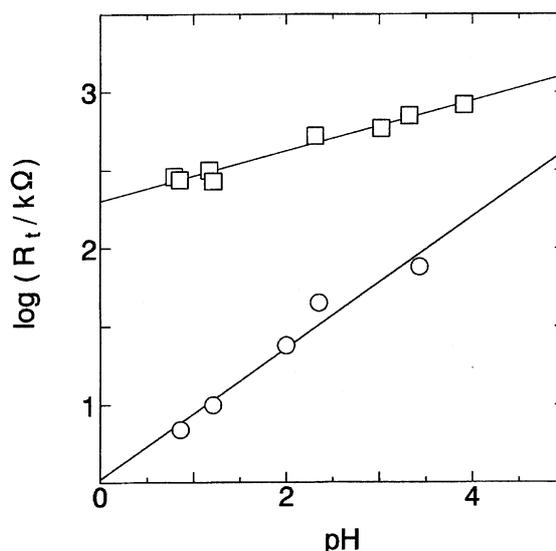

Fig. 8.   Charge-transfer resistances at poly-MPP-coated GC electrode (O) and naked GC electrode (□) as a function of the pH of a Na_2SO_4 solution containing 1 mM quinhydrone.

action 3. As shown in Fig. 8, the ratio of R_t for the polymer-coated and naked GC electrodes was lower in acidic solutions than in neutral solutions. A possible cause of this difference is a difference in the transfer coefficients at the polymer and GC surfaces, because the value of the transfer coefficient varies the dependence of the apparent standard rate constant on the proton concentrations.

As shown in Figs. 6 and 8, the polymer-coated electrode decreased R_t to 1/7—1/8 in weakly acidic solutions relative to a naked electrode. This decrease in R_t is most probably caused by the concentration of the redox species into the film, an increase in the area used for the charge-transfer process, or adsorption of the redox species on the polymer surface. We tried to evaluate the amount of the redox species incorporated in a poly-MPP film by cyclic voltammetry. After having been equilibrated with a 0.2 M Na_2SO_4–0.01 M H_2SO_4 solution containing 1 mM quinhydrone, a poly-MPP-coated electrode was transferred to a pure supporting electrolyte solution, and its linear sweep voltammogram was measured. Its peak currents were, however, too small to give the exact concentration of quinhydrone in the film; the anodic peak current was less than 3% of that measured in the soaking solution. This result is in contrast to the surprisingly good absorption of anthraquinonesulfonates and indigosulfonates by the polymer film; their partition coefficients were estimated to be $(5—20) \times 10^3$ in 0.1 M NaCl.[8]

The dependence of R_t and the double-layer capacitance on the film thickness can provide information on the location where the charge-transfer process occurs. As shown in Fig. 5, R_t decreased slightly with increased film thickness; this change is contrary to the behavior of the double-layer capacitance. The slight changes in R_t and the capacitance with the film thickness can both be ascribed to a gradual increase in the reaction area, which is due to a more porous surface of a thicker film. This means that the heterogeneous electron-transfer process may occur at the film-solution interface.

In order that electrode reaction 3 can occur at the film surface, it is necessary for the polymer film to be electronically conductive near to the redox potentials of quinhydrone. The following voltammetric behavior of the polymer-coated electrode may reflect the effect of the conductivity of the film. As the film thickened, the anodic peak currents increased, and the cathodic peak currents decreased, as shown in Fig. 9. At the same time, the cathodic peak potentials shifted in the positive direction, whereas the anodic peak potentials showed a small negative shift (Fig. 2). This behavior can be explained by assuming that the electronic conductivities of poly-MPP films increase with increased electrode potential, because it approachs the redox potential (around 0.8 V) of a polymer whose polypyrrole backbone should be nonconducting in the completely reduced state.[1,13] Thus, the conductance of a poly-MPP film in contact with the electrolyte solution was examined with an interdigitated array electrode, which, by itself, formed a metal/film/metal cell. The symmetrical cell has been used to isolate electronic transport, since any ion transport across the interface is blocked. Figure 10 shows impedance plots obtained with the cell; the plots show the
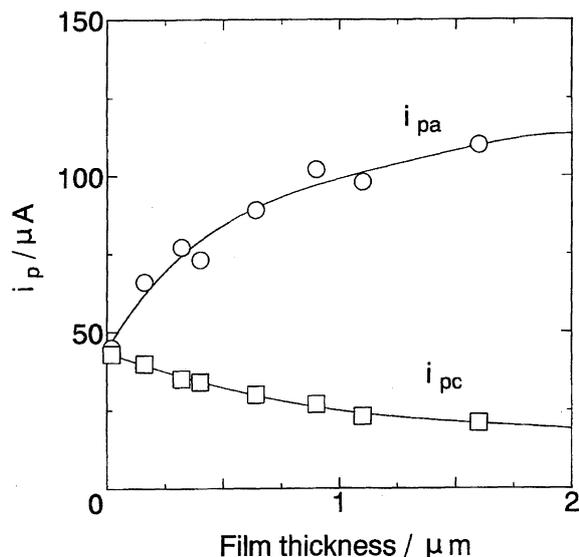

Fig. 9. Dependence of anodic peak current (O) and cathodic peak current (□) on film thickness. Cyclic voltammograms were measured at a scan rate of 200 $mV\,s^{-1}$ in a 0.2 M Na_2SO_4–0.01 M H_2SO_4 solution containing 1 mM quinhydrone.

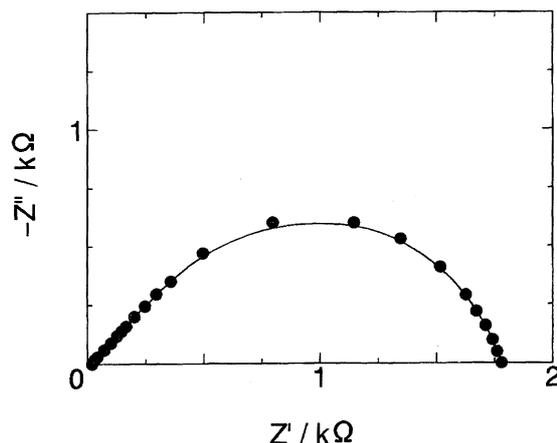

Fig. 10. Typical impedance plots for a metal/film/metal cell where the film is in contact with a 0.2 M Na_2SO_4–0.01 M H_2SO_4 solution. After the polymer film had been equilibrated at 0.39 V, the impedances of the cell were measured.

finite Warburg behavior with a d.c. resistance. As derived by Buck,[14] the width of a finite Warburg arc (R_w) can be expressed as

$$R_w = RTF^{-2}d(ADc)^{-1}, \qquad (4)$$

where D is the diffusion coefficient of an electronic charge carrier, and c is its concentration. Figure 11 shows a change in R_w with the electrode potential, indicating that the electronic conductance of the film gradually increases with increased electrode potential. The change in the film conductivities may be due to an increasing concentration of electrons, because it is fairly presumed that the diffusion coefficient is independent of the oxidation level of the polymer. Thus, the poly-MPP film seems to mediate more electrons between GC and a solution species as the electrode potential
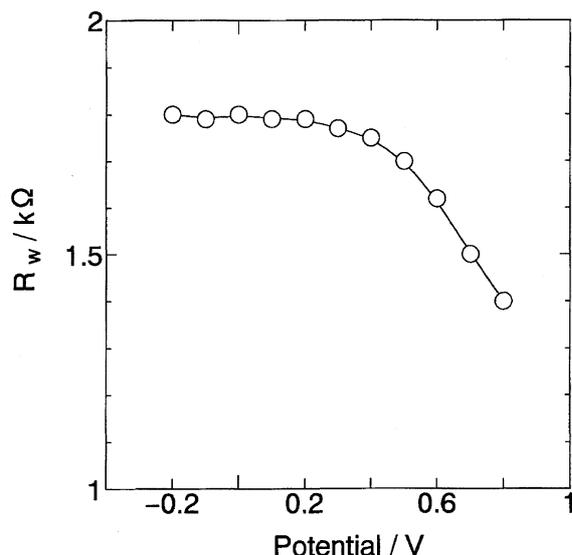
Fig. 11. Change in R_w with electrode potential.

approachs the redox potential of the polymer. This inference is also supported by a voltammetric result, that the electrocatalytic effect of the polymer film was reduced to half at higher pH's where the redox potentials of quinhydrone shifted to a less-positive direction. Since it is fairly presumed that the redox potential of poly-MPP is independent of the pH, the redox potentials of quinhydrone should go away from that of the polymer as the pH is increased. This movement of the electrode potentials may result in the smaller conductivities of the film at higher pH's. Electron transport through polypyrrole and poly-MPP films in acetonitrile has been adequately described by using both electronic and redox conduction models, which are related by the Nernst–Einstein equation.[13]

We tried to estimate the roughness factor of the film surface from the impedance responses measured in a pure supporting electrolyte. Owing to the porosity and inhomogeneity of the electrode surfaces, the real impedance response of the electrodes gave an inclined straight line in the complex impedance plane (curves a and c in Fig. 4), which differed from the ideal vertical line due to a pure capacitance in series with a resistance. The inclined straight line was analyzed on the basis of a constant-phase element[15] whose impedance has the form

$$Z_{cpe} = B(j\omega)^{-\phi}, \tag{5}$$

where j is the imaginary unit, ω is the angular frequency, and B and ϕ ($0 \leq \phi \leq 1$) are frequency-independent parameters. The slopes of the complex-plane impedance plots gave ϕ values of 0.89 for the polymer-coated electrode and 0.94 for the naked GC electrode (polished with 1 µm alumina slurry). The fractional exponent (ϕ) has been related to the surface roughness of electrodes in terms of the fractal geometry.[16,17] From the determined ϕ values, the so-called fractal dimension, which is a purely geometric quantity, was estimated to be 2.12 for the polymer-coated electrode and 2.06 for the naked electrode. The difference between the roughness factors of the two electrodes is too small to ex-

plain the difference in charge-transfer resistances. From the above discussion, we tentatively suggest that a flexible polymer adsorbs quinhydrone, particularly hydroquinone by ion–dipole and dipole–dipole interactions. The adsorption of the redox species is likely to cause its surface concentration to be heightened, or the activation energy of charge transfer to be lowered; this may increase the standard rate constant of the charge-transfer process. Some voltammetric results, however, were inconsistent with the relation expected from the theory of electrode adsorption;[18] the ratio of anodic to cathodic peak currents was independent of the potential scan rate over the range of 2—200 mV s^{-1}. It is next necessary to understand the precise mechanism of the increase in the standard rate constant.

Conclusion

The poly-MPP-coated electrode noticeably decreased R_t of quinhydrone relative to that of a naked GC electrode. Differing markedly from anthraquinonesulfonates and indigosulfonates, the redox species was not concentrated into the polymer film. The dependence of R_t and the interfacial capacitances on the film thickness implied that the heterogeneous electron-transfer process occurred at the film-solution interface, because the polymer film was appreciably electronically conductive at positive potentials. Although the decrease in R_t at the polymer film electrode is somewhat ascribed to an increase in the reaction area, which is due to a porous film surface, the increasing surface roughness does not have much effect. The electrocatalytic effect of the polymer film can be attributed to an increase in the standard rate constant of the charge-transfer process, which may be due to the adsorption of quinhydrone on the polymer surface. Explicating the precise mechanism of the increase is a theme that should be of great interest to all of us.

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