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Electrocatalytic behaviour of a poly(*N*-methylaniline) filmed electrode to hydroquinone

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Poly(*N*-methylaniline) (PNMA) was prepared on a bare platinum electrode by electrooxidation of *N*-methylaniline in $1.0\,\mathrm{mol\,dm^{-3}}$ HCl. The PNMA film was more stable to anodic treatment than the polyaniline film. The electric conductivity of the PNMA film was potential dependent. High conductivity appeared only within the potential region where PNMA itself was redox-active. The PNMA filmed electrode showed redox response to dissolved hydroquinone whose redox current was evident within the potential region. Furthermore, the PNMA film behaved as an electrocatalyst for the electrode reaction of hydroquinone. The kinetics of the electrocatalytic reaction were investigated mainly using a rotating disc electrode. The experimental results obtained were analysed by the theory of Albery and Hillman, and the rate constant of the electron cross-exchange transfer between hydroquinone and the redox-active sites in the film (k) was determined and found to be $6.4 \times 10^3\ \mathrm{M^{-1}\,s^{-1}}$ at 20° C.

1. Introduction

Polyaniline (PANI) has occupied a prominent position in electric conducting polymers because of its unique and useful properties. Among these properties, interest has been focused on selective redox response to dissolved species and electrocatalytic behaviour of the PANI film. The selective response is based on the potential dependence of the electric conductivity of the PANI film. The conductivity is drastically changed by the electrode potential, and high conductivity appears only within the potential region where PANI itself is redox-active [1]. Within the region, the electrode reactions of the dissolved species take place on the PANI filmed electrode. Furthermore, the films are expected to catalyse electrode reactions, since it is thermodynamically possible that the dissolved species are oxidized or reduced by the oxidized or reduced sites in the film.

The electrocatalytic behaviour on the PANI filmed electrode has already been established with respect to the electrode reactions of several inorganics such as ferrous ion [2], iodide ion and hexacyanoferrate ion [3]. However, the behaviour for organics is not yet well understood, and little is known about the kinetics and mechanism of the electrode processes despite their importance. If the electrocatalytic behaviour is observed for the electrode reactions of organics as well as inorganics, the PANI filmed electrode will be a useful electrocatalyst for organic electrolytic syntheses. Unfortunately, however, the redox activity of the PANI film is damaged during the electrolysis by oxidative deterioration [4], and the film loses its electrocatalytic property [5].

We are now investigating poly(*N*-methylaniline) (PNMA) instead of PANI because it is expected to have two advantages over PANI. First, PNMA is more stable to the oxidative electrolytic conditions than PANI. The methyl groups combined with the nitrogen atoms in the PNMA polymer chain suppress the hydrolytic segmentation of the chain due to the electronic inductive effect. Secondly, the methyl groups enhance the affinity between PNMA and dissolved organics, and give rise to a higher catalytic property than PANI.

The present paper shows that the PNMA film is found to act as an electrocatalyst for the oxidation of hydroquinone. The kinetics and mechanism of the electrocatalytic reaction are also elucidated, and the rate constant of the electron cross-exchange transfer between hydroquinone and the redox-active sites in the film is determined and found to be $6.4 \times 10^3\ \mathrm{M^{-1}\,s^{-1}}$ at 20° C using Albery and Hillman's theory. This large value suggests that the redox sites in the PNMA film have high electrocatalytic activity.

2. Experimental details

2.1. *Materials*

N-methylaniline (Nakarai Tesque Co., Ltd) was used after distilling under reduced pressure. Hydroquinones were of the highest grade (from Tokyo Chemical Industry Co., Ltd) and were used after recrystallization from ethanol. These organics were kept in the dark and used within a week. Water was purified with an Aquarius GS-20 system (Tokyo Kagaku Sangyo Co., Ltd) and used within a few hours. An aqueous solution was prepared from the distilled water. The PNMA filmed electrode was

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prepared by the electro-oxidation of *N*-methylaniline in 0.1 M (1 M ≡ 1 mol dm^{-3}) H_2SO_4. Further details are described in the previous paper [6]. The film thickness of PNMA was determined from either scanning electron micrographs (Model S-2300, Hitachi Ltd) or the redox charge of the PNMA film itself [7].

2.2. *Cyclic voltammetry*

A platinum wire electrode was used as the test electrode throughout. The cylindrical electrode was a 1 mm platinum wire, sealed in a glass tube, with a small glass globe at the lower end (total electrode area: 0.510 cm^2). A saturated calomel electrode (SCE) was used as the reference electrode and a platinum plate with an electrode area of about 8 cm^2 was used as the counter electrode. Prior to use, the platinum wire electrode was treated with aqua regia for 30 s and then polarized by repeated potential cycling between −0.2 and 1.25 V vs SCE in 0.1 M H_2SO_4 until a voltammogram showed the features associated with hydrogen adsorption/desorption and oxide formation/removal [8].

All cyclic voltammograms were measured with a Hokuto Denko HA-301 potentiostat connected to a Hokuto Denko HB-104 function generator and to a Rikadenki RW-21 *x–y* recorder. All the measurements were performed in a one compartment cell. The SCE was connected to the cell by means of a salt bridge filled with saturated KCl solution. The solution level in the calomel compartment was lower than the level in the working cell, so that contamination by chloride ions was prevented.

2.3. *Rotating disc electrode voltammetry*

The rotating disc electrode (RDE) had a surface area of 0.292 cm^2. The pretreatment of the electrode was by polishing with alumina powder with an average diameter of 74 μm. The RDE voltammograms were measured with a Nikko Keisoku RDE measuring system connected to the same potentiostat, function generator and *x–y* recorder as described in Section 2.2.

All experiments were carried out at room temperature (20° C).

3. Results and discussion

3.1. *Potential dependence of the conductivity of PNMA*

The same procedure as described in the previous paper [9] was applied to determine the electric resistivity (R) of PNMA at various potentials. A special comb-shaped microelectrode represented in Fig. 1 was employed. The microelectrode was made by evaporating thin platinum films onto a glass substrate. The combined terminal A and B was used as the working electrode. A plantinum plate (area: ca. 8 cm^2) and an SCE was used as the counter and reference electrode. The PNMA film was electrodeposited on the working electrode until the film covered the comb-shaped part of the electrode. The terminals A and B were separated and the electrode was transferred into 0.1 M H_2SO_4. When the terminal A was held at various potentials, the current–voltage characteristics between the terminals A and B were measured during a 10 mV voltage excursion. The resistivity (R) of the PNMA film was determined by the current–voltage characteristics obtained. The lowest resistivity (R_0) was found at 0.42 V vs SCE. Figure 2(b) shows the potential dependence of conductivity of PNMA, R_0/R. The conductivity is significantly changed by the potential. High conductivity appears only within the potential region where PNMA itself is

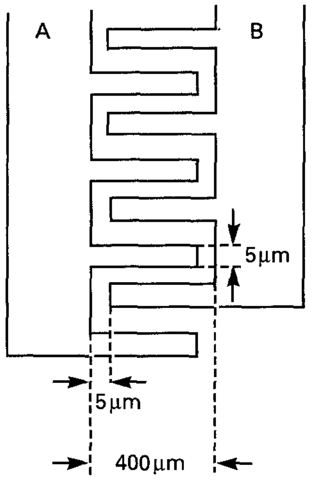

Fig. 1. A schematic design of a Pt film comb-shaped electrode.

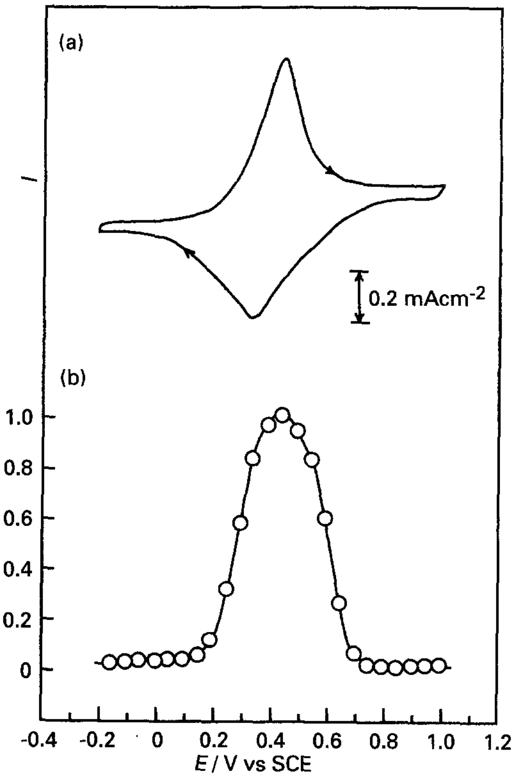

Fig. 2. (a) Cyclic voltammogram showing the redox activity of the PNMA film itself in 0.1 M H_2SO_4 at 20 mV s^{-1}. (b) Potential dependence of the conductivity of the PNMA film in 0.1 M H_2SO_4, where R denotes the electric resistance of the film. The minimum resistance (R_o) is obtained at 0.42 V.

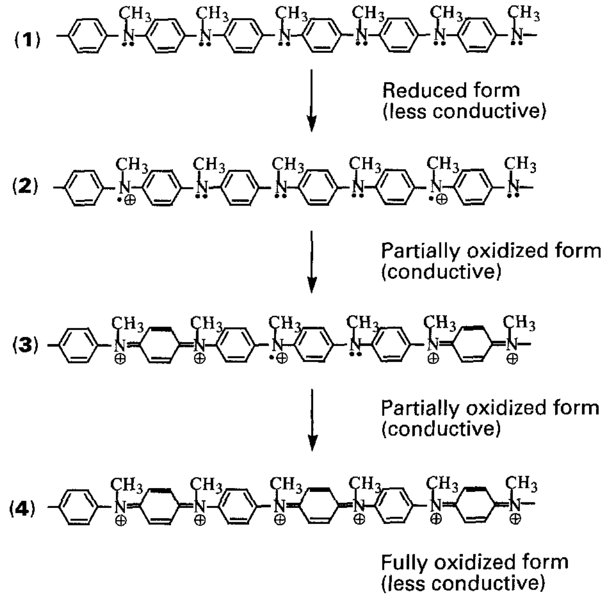

Fig. 3. Proposed electrooxidation process of PNMA.

redox active (Fig. 2(a)). The potential region is 0.1 V narrower than that for PANI [10].

The redox current of PNMA corresponds to the formation/removal of the cation radical (polaron) sites in the PNMA polymer chain. Several oxidation states of PNMA can be expressed as shown in Fig. 3. The fully reduced state, **(1)** is less conductive because of few cation sites as charge carriers. The partially oxidized states such as **(2)** and **(3)** are probably sufficiently cation-rich to enable PNMA to be conductive. However, when too many cation sites are generated in the polymer chain, their electrostatic repulsion causes a Peierls' distortion, and the distortion favours formation of an energy gap [11]. Therefore, the fully oxidized state, **(4)**, loses the conductivity.

Similar potential dependence, as illustrated in Fig. 2(b) was observed for several other poly(*N*-alkylaniline)s. The potential region showing high conductivity depended on the chain length of the *N*-substituting alkyl groups. The longer the chain length, the more positively the region shifted. For example, the region of poly(*N*-butylaniline) ranged from 0.35 to 0.70 V, and was 0.1 V more positive than that for PNMA. This shift is probably caused by the greater inductive effect of the butyl group.

3.2. *Stability of the PNMA film to oxidative deterioration*

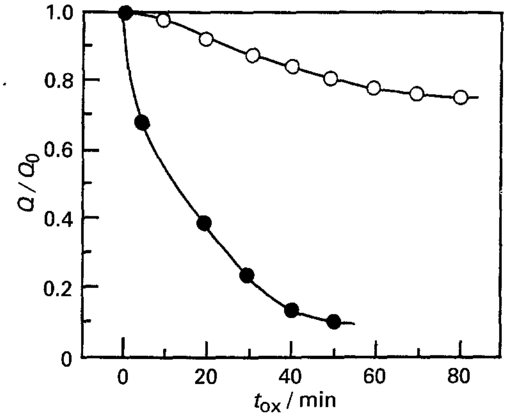

Fig. 4. Effect of anodic treatment on the redox activity of the PNMA (○) and PANI (●) films. Q: redox charge. Q_0: redox charge before the treatment. The anodic treatment was carried out by polarizing each polymer film at 1.0 V vs SCE in 0.1 M H_2SO_4.

The stability of the PNMA film to anodic treatment was examined by monitoring the redox charge. The PNMA film was polarized at 1.0 v vs SCE and each cyclic voltammogram was measured at different polarization times (t_{ox}). The redox charge (Q) was determined by integrating the voltammogram. Figure 4 shows the relationship between t_{ox} and Q/Q_0, where Q_0 denotes the initial redox charge without the anodic treatment. The relationship for the PANI film is also shown in the same figure for comparison. The durability of the PNMA film against the anodic treatment is much greater than that of the PANI film. The redox activity of the PNMA film still remains at $t_{ox} = 80$ min, while that of the PANI film almost disappears.

It is widely accepted that the PANI film deteriorates and loses its redox activity when polarized at potentials greater than 0.7 V vs SCE [4]. The polarization generates quinoid-imine-cation structures in the polymer chain. The structure is easily hydrolysed and the polymer chain breaks. For the PNMA film, however, the hydrolysis is probably prevented as the quinoid-imine-cation structures are stabilized by the inductive effect of the methyl groups. Consequently, the PNMA film is stable to the anodic treatment.

3.3. *Electrocatalytic response on the PNMA filmed electrode*

Figure 5 shows the cyclic voltammograms of dissolved hydroquinone measured with the PNMA filmed electrode and a bare platinum electrode for comparison. For the PNMA filmed electrode, the redox wave of

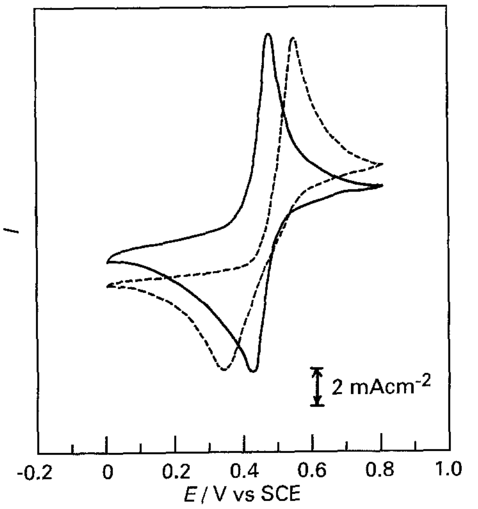

Fig. 5. Cyclic voltammograms of 10 mM hydroquinone in 0.1 M H_2SO_4 at 20 mV s^{-1}. (- - - -): a bare Pt electrode. (————): the PNMA filmed electrode. Film thickness: 0.43 μm.

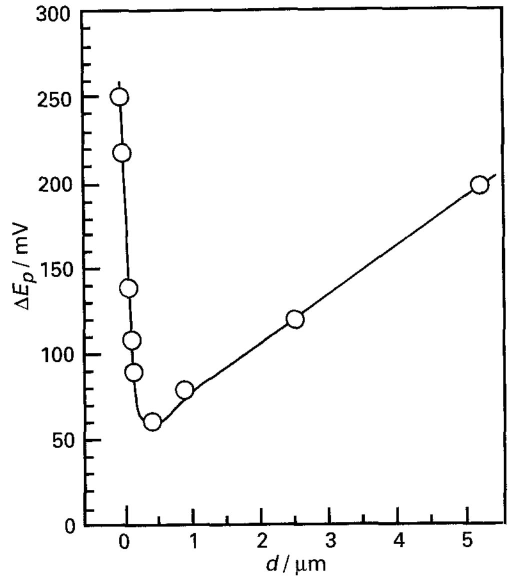

Fig. 6. Relationship between the peak separation in the cyclic voltammogram of hydroquinone (ΔE_p) and the thickness of the PNMA film (d).

hydroquinone is evident since the redox potential is within the potential region where the PNMA film has high conductivity (Fig. 2(b)). It is noteworthy that the peak potential separation of the cyclic voltammogram, ΔE_p, obviously decreases with coating of the PNMA film: 210 mV for the bare platinum electrode; 58 mV for the PNMA filmed electrode. This behaviour suggests that the PNMA film acts as an electrocatalyst.

In the electrocatalytic reaction, three probable places where the electron transfer from hydroquinone should occur are proposed: the redox-active sites of the film surface at the solution/film interface, the redox-active sites inside the film and the surface of the electrode substrate. To examine which place plays an important role in the electron transfer, the cyclic voltammograms of hydroquinone were taken with several PNMA filmed electrodes with different film thicknesses (d) and with a PNMA filmed indium–tin oxide (ITO) electrode.

The plots of ΔE_p against d obtained from the voltammograms measured with the former electrodes are shown in Fig. 6. In $d < 0.4\,\mu m$, ΔE_p sharply decreases with d. This strongly suggests that the electron transfer between hydroquinone and the redox-active site of PNMA takes place, not only on the surface of the film, but also inside the film. The number of redox-active sites increases with d and then ΔE_p is lowered. If the electron transfer occurred only at the redox-active sites of the film surface, ΔE_p would not depend on d. If $d > 0.4\,\mu m$, ΔE_p gradually rises again. The rise is probably caused by the iR drop of the film. The iR drop begins to affect ΔE_p when d exceeds $0.4\,\mu m$, although the number of redox-active sites increases with d. As a result, in the range $0.1\,\mu m < d < 5\,\mu m$, ΔE_p is less than 210 mV and the PNMA film functions as an electrocatalyst.

It has been reported that the cyclic voltammogram of hydroquinone is irreversible and little redox current is observed when it is taken with the ITO electrode [11]. A voltammogram of this is shown in Fig. 7(a). At the PNMA filmed ITO electrode (film thickness: $0.4\,\mu m$), however, the redox wave of hydroquinone is evident (Fig. 7(b)), showing that the electron transfer takes place, not on the electrode substrate, but on the PNMA film or that the rate of the electron transfer on the electrode substrate is negligibly lower than that on the film.

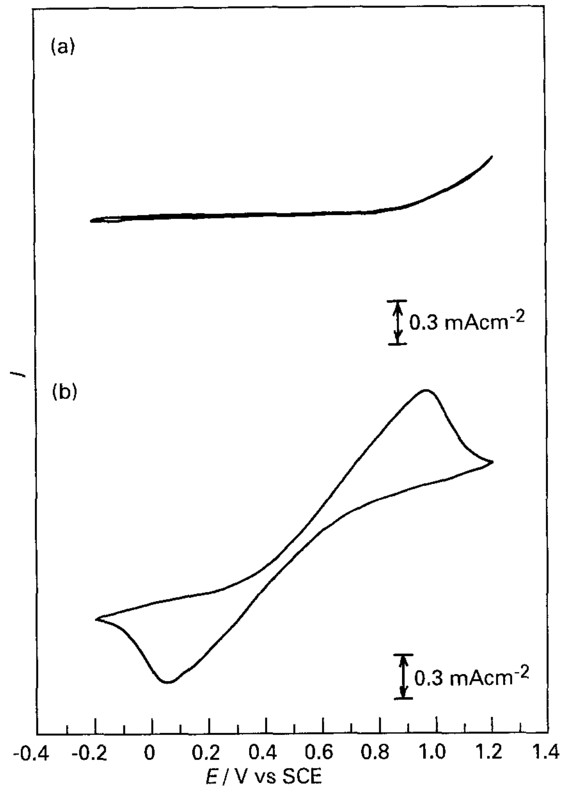

Fig. 7. Cyclic voltammograms of 10 mM hydroquinone in 0.1 M H_2SO_4 taken with a bare ITO electrode (a) and with a PNMA filmed electrode ($d = 0.61\,\mu m$). Scan rate: 20 mV s^{-1}.

3.4. *Mechanism and kinetics of the electrocatalytic reaction on the PNMA filmed electrode*

The mechanism and kinetics of the electrocatalytic reaction of hydroquinone are analyzed on the basis of the Albery and Hillman's theory [12] which deals with all electrode processes. Although several theoretical approaches were reported for the mechanism and kinetics of electrode reactions on modified electrodes [13–19], they did not deal with all electrode processes. Using Albery and Hillman's model [12], the mechanism of our electrocatalytic reaction is schematically illustrated in Fig. 8. Hydroquinone (HQ) present in the solution is converted to *o*-benzoquinone (BQ) by electron transfer from the oxidized form of PNMA (Ox^P) which is then recycled to the reduced form of PNMA (Red^P) by electron transfer from the electrode substrate.

Albery and Hillman introduced the overall electrochemical rate constant k'_{ME}/cm s^{-1} to compare k'_{ME} with normal electrochemical rate constants for unmodified electrodes. All the electrode processes can be described quantitatively by k'_{ME}. As pointed out by

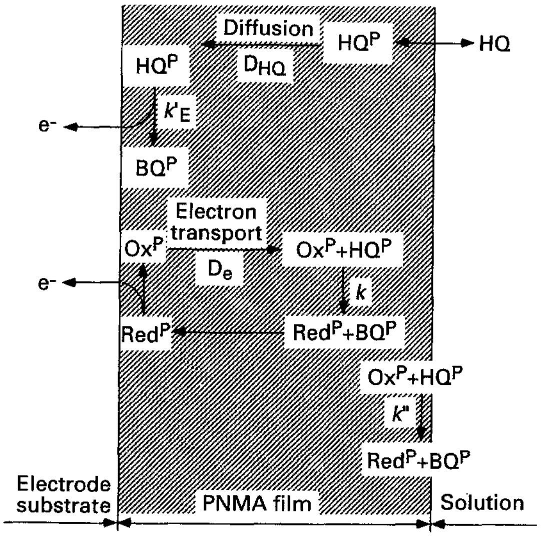

Fig. 8. Schematic depiction of all probable processes for electrochemical response of the PNMA filmed electrode to hydroquinone. HQ: dissolved hydroquinone in the solution. BQ: dissolved *p*-benzoquinone in the solution. HQ^P : hydroquinone present in the PNMA film. BQ^P: *p*-benzoquinone present in the film. Ox^P: oxidized form of PNMA. Red^P: reduced form of PNMA. k'_E, k and k'': corresponding rate constant. D_{HQ} and D_e: corresponding diffusion coefficient.

several authors [20–22], k'_{ME} can in most cases be determined from the intercept of a Koutecky–Levich plot (i_L^{-1} against $\omega^{-1/2}$ plot) for a rotating disc electrode (RDE) [23]: i_L is the limiting current and ω is the angular frequency of rotation. The Koutecky–Levich equation in this case is

$$\frac{1}{i_L}=\frac{1}{2FAk'_{ME}[HQ]}+\frac{1}{1.24FAD_{HQ}^{2/3}\nu^{-1/6}\omega^{1/2}[HQ]} \tag{1}$$

where F is the Faraday number, A the electrode area, D_{HQ} the diffusion coefficient of HQ in the solution, ν the kinematic viscosity of the solution and [HQ] the concentration of HQ in the solution. To determine k'_{ME}, the RDE voltammograms for the oxidation of hydroquinone were measured with a PNMA filmed disc electrode ($d = 0.4\,\mu$m). The Koutecky–Levich plots obtained from the RDE voltammograms are shown in Fig. 9. All plots give a straight line with slope inversely proportional to [HQ] and have finite intercepts depending on the concentration. As expected from Equation 1, a plot of the intercept against $[HQ]^{-1}$ should give a straight line with slope $(2FAk'_{ME})^{-1}$. Such plots are presented in Fig. 10 and are indeed linear. From the slope, k'_{ME} is determined and found to be $0.015\,\mathrm{cm\,s^{-1}}$.

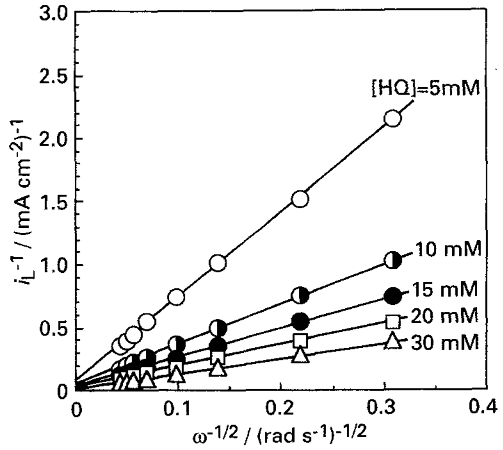

Fig. 9. Koutecky–Levich (i_L^{-1} against $\omega^{-1/2}$) plots for the oxidation of hydroquinone obtained from the RDE voltammograms measured with the PNMA filmed disc electrode. Five measured solutions were 0.1 M H_2SO_4 solutions having different concentrations of hydroquinone ([HQ]): [HQ] = 5, 10, 15, 20 and 30 mM.

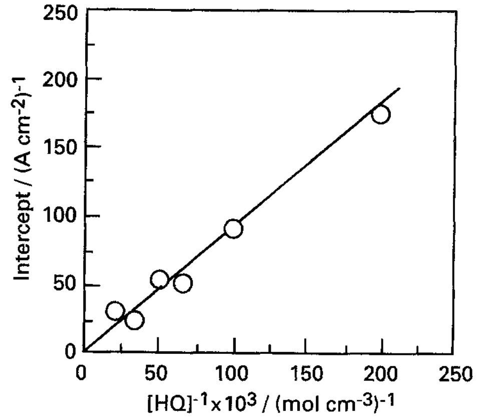

Fig. 10. Dependence of the intercepts of the plots in Fig. 9 on $[HQ]^{-1}$.

Albery and Hillman analyse all the electrode processes and formulate k'_{ME} in all probable cases. Among these cases, the 'L*k* case' is regarded as the most appropriate case for our electrocatalytic reaction. The case is characterized by the following: (i) HQ reacts with Ox^P throughout the PNMA film, with the rate constant k; (ii) both the concentration of Ox^P, $[Ox^P]$, and that of HQ inside the film, $[HQ^P]$, are constant throughout the film; (iii) the electrode reaction of HQ at the electrode substrate is negligible. The relationship between ΔE_p and d (Fig. 6) and the voltammogram of HQ measured with the PNMA filmed electrode (Fig. 7) support (i) and (iii), respectively. To obtain indirect evidence that $[HQ^P]$ is constant throughout the film, cyclic voltammograms of the PNMA filmed electrodes with different d were taken in 0.1 M H_2SO_4. The cathodic charge of the PNMA film (Q_c) was found by the integration of the voltammograms and $[Ox^P]$ was calculated from Q_c using Equation 2.

$$[Ox^P] = Q_c/FAd \tag{2}$$

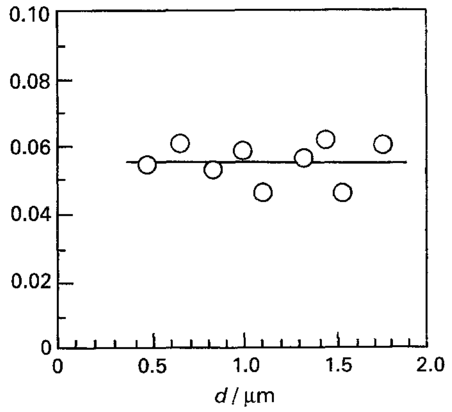

Fig. 11. Effect of d on $[HQ^P]$.

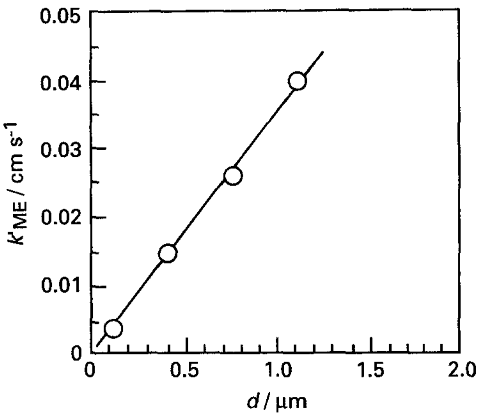

Fig. 12. A plot of d against k'_{ME}.

Figure 11 shows that the relationship between $[Ox^P]$ and d with $[Ox^P]$ is constant regardless of d: $[Ox^P] = 0.055\,\mathrm{M}$. This strongly supports (ii).

In the 'Lk case', HQ reacts with Ox^P throughout the PNMA film with the rate constant k (Equation 3).

$$HQ^P + Ox^P \xrightarrow{k} BQ^P + Red^P$$
$$\text{(throughout the PNMA film)} \qquad (3)$$

The reaction rate of Equation 3 determines the rate of the overall electrocatalytic reaction, and k'_{ME} is

$$k'_{ME} = kKd[Ox^P] \qquad (4)$$

where K expresses the partition coefficient: $K = [HQ^P]/[HQ]$. To determine k, the same RDE experiment as described previously was carried out with four PNMA filmed electrodes with values of d of 0.12, 0.40, 0.76 and 1.12 μm. A plot of k'_{ME} against d is shown in Fig. 12 and is linear. The slope of $3.54 \times 10^2\,\mathrm{s}^{-1}$ gives $k = 6.4 \times 10^3\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, assuming $K = 1$. This value is in agreement with that expected by Albery and Hillman, except that $[Ox^P]$ is much smaller than their value, $[Ox^P] = 10\,\mathrm{M}$. This suggests that the redox sites in the PNMA film had high electrocatalytic activity.

4. Conclusions

PNMA film behaves as an electrocatalyst for the electrooxidation of hydroquinone, as does the PANI film. The advantage of the PNMA film over the PANI film is its stability to anodic treatment. The PNMA film is more stable to anodic treatment than the PANI film: the PNMA film still has sufficient redox activity when held at 1.0 V vs SCE for 80 min. The PANI film deteriorates and loses its redox activity under the same conditions.

In the electrocatalytic reaction of hydroquinone at the PNMA filmed electrode, the electron cross-exchange transfer between the redox active sites in the PNMA film and hydroquinone controls the overall electrochemical rate. The rate constant was determined and found to be $6.4 \times 10^3\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ using Albery and Hillman's theory. The value suggests that the redox sites in the PNMA film had high electrocatalytic activity.

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