

Influence of the Doped Counteranions on the Penetration of H⁺ Cations Through Poly(*N*-methylpyrrole)

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SYNOPSIS

The reduction of H⁺ cations on the Pt electrode coated with poly(*N*-methylpyrrole) (PNMP) film was studied in an acidic aqueous solution. The reduction depends strongly on the counteranions originally doped in PNMP during polymerization. H⁺ cations can penetrate the neutral or overoxidized film from PNMP(TsO⁻), in which the H⁺ diffusion coefficient is estimated as 10⁻⁵ cm² s⁻¹ by the potential step chronoamperometry method. But the neutral or overoxidized film from PNMP(NO₃⁻) is closed for H⁺ penetration. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

A conducting polymer can be potentially useful in batteries,¹ in displays,² or as electrocatalysts³ or protective films.⁴ For batteries, displays, and electrocatalysts, ions should be able to enter and leave the polymer freely, while for corrosion protection, the polymer should be closed for ion penetration. It is useful for these applications to study the oxidation/reduction reaction of the redox-active species in electrolytes on the electrode coated with the conducting polymer. The reactions could be divided into two types according to the role of the polymer in the reaction. First, the polymer may act as a mediator for electron transfer between the electrode and the reactants in the electrolyte, i.e., the reactions take place in the interface between the solution and the polymer.^{5,6} In the second type of reaction, the reactants penetrate the polymer film without reacting with it. The reactions may take place on the interface between the polymer and the metallic substrate. An example is the reduction of H⁺ cations on the metallic electrode coated with polymer film, studied by Bard et al.⁷ and Schultze et al.^{6,8} The mechanism of the reaction has been clarified in that it takes place on the metallic substrate and the polymer only acts as a partition between the electrode

and the solution.^{8,9} Therefore, the membrane properties of the polymer will exert a decisive influence on the reaction. The properties of the polymer depend strongly on the doped counteranions,¹⁰⁻¹³ but no report has referred to the influence of the counteranions in the polymer on this type of reaction.

We employed the anions of TsO⁻, Cl⁻, and NO₃⁻ as the counteranions in PNMP. The influence of these anions on the H⁺ reduction on the Pt electrode coated with PNMP was studied in this article.

EXPERIMENTAL

The PNMP film was formed by anodic polymerization of 0.1 M *N*-methylpyrrole in the aqueous solution of 0.2 M of various supporting electrolytes under a constant current of 0.5 mA/cm². The supporting electrolytes used were sodium chloride, sodium tosylate (TsONa), and sodium nitrate. The pH value of the solutions was adjusted to pH 3 by adding a corresponding acid solution. A Pt disc with a surface area of 7 mm² was used as the working electrode.

Cyclic voltammetry (CV) measurement was carried out using an EG&G PAR Model 174A polarographic analyzer, Model 175 Universal programmer, and a saturated calomel reference electrode (SCE). A potential scan rate of 20 mV/s was used unless otherwise stated. Potential step chronoamperometry was performed at -0.6 V vs. SCE after PNMP was polarized at -0.1 V vs. SCE for 5 min. The pH value

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of the solutions was measured using a KENT EIL 7045/6 pH meter. The overoxidization of PNMP was carried out in a 0.1M NaOH aqueous solution at 0.8 V vs. SCE for 10 min.

RESULTS AND DISCUSSION

H⁺ Reduction on the Pt Electrode Coated with Neutral PNMP Film

It is well known that the Pt electrode could catalyze the reduction of H⁺ in an acidic aqueous solution. In the cyclic voltammogram of the Pt electrode in 0.2M TsONa of pH 2, the reduction of H⁺ cations begins at the potential of ca. -0.3 V vs. SCE and the peak potential of the reduction is -0.52 V vs. SCE, as shown in Figure 1. The cathodic peak current at the first cycle is 0.55 mA. The cathodic peak is significantly stronger than is the anodic peak, probably because some hydrogen molecule produced in the reduction escaped before reoxidation.

Figure 2 shows the cyclic voltammogram of the electrode of Pt coated with PNMP (TsO⁻) in a 0.2M TsONa aqueous solution of pH 3. Two redox processes could be distinguished from the cyclic voltammogram. The reduction of PNMP (TsO⁻) to its neutral state occurs from 0.6 to -0.2 V vs. SCE.⁹ The strong reduction peak from -0.4 to -0.8 V should be the reduction of H⁺ in the acidic solution, compared with Figure 1. Obviously, the reversibility of the H⁺ redox process on the electrode coated with the neutral PNMP film is much better than that on the naked Pt electrode. The neutral PNMP film is an insulator with the conductivity of 10⁻¹¹ S cm⁻¹.⁶ So, the reduction of H⁺ may occur on the surface of the Pt substrate. In the following, the electro-

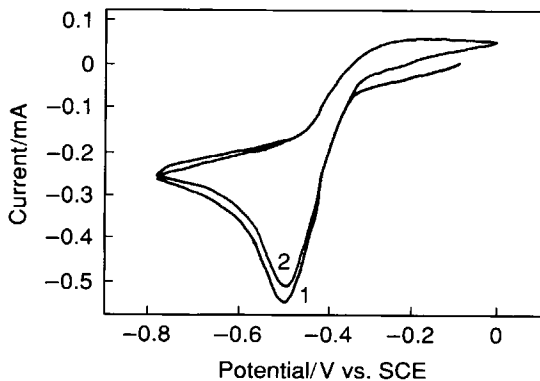


Figure 1 Cyclic voltammogram of uncoated Pt electrode in 0.2M TsONa of pH 2: (1) first reduction scan; (2) second reduction scan.

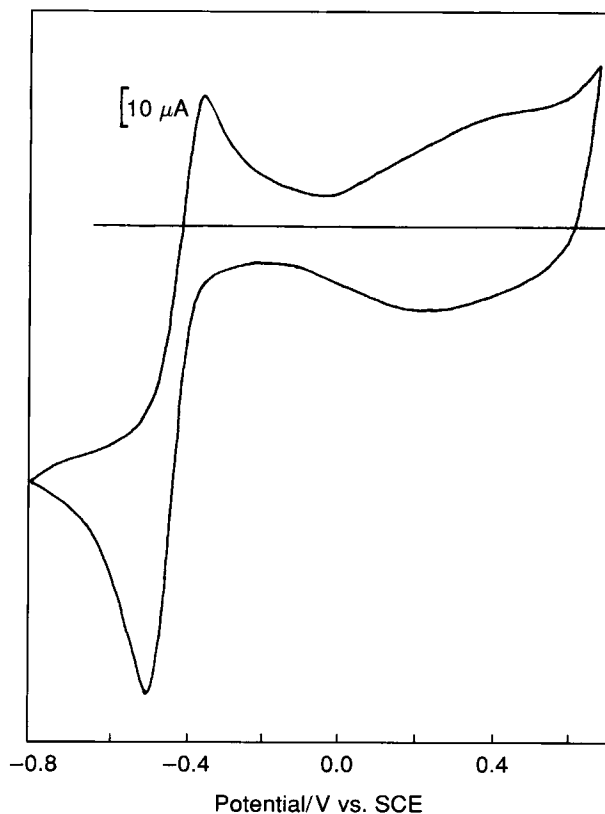


Figure 2 Cyclic voltammogram of Pt electrode coated with PNMP(TsO⁻) film in 0.2M TsONa of pH 3.

chemical process between 0.0 and -0.8 V was studied, since only the H⁺ reduction was concerned here.

The Pt electrode coated with the neutral PNMP (TsO⁻) [reduced from PNMP (TsO⁻)] film with the thickness of 40 mC cm⁻² was investigated in a 0.2M TsONa aqueous solution of pH 2 [see Fig. 3(a)]. The cathodic peak current at the first cycle is 0.45 mA, which is weaker than that of the uncoated Pt electrode, probably due to the less active area for H⁺ reduction on the coated electrode. When the thickness of the film increases to 100 mC cm⁻¹, the H⁺ reduction remains unchanged with the peak current of 0.45 mA [see Fig. 3(b)], indicating that the active surface area for H⁺ reduction and the supply of H⁺ cation is not affected by the thickness of the film. It can be seen from Figures 1 and 3 that the reversibility of the oxidation in the cyclic voltammograms is enhanced with the coating of the neutral PNMP (TsO⁻) film as mentioned above. Also, a quasi-reversible CV plot is obtained for the electrode coated with the thicker PNMP film [Fig. 3(b)]. Perhaps, the PNMP film could keep the hydrogen produced in the reduction from escaping; then, the oxidation becomes more reversible.

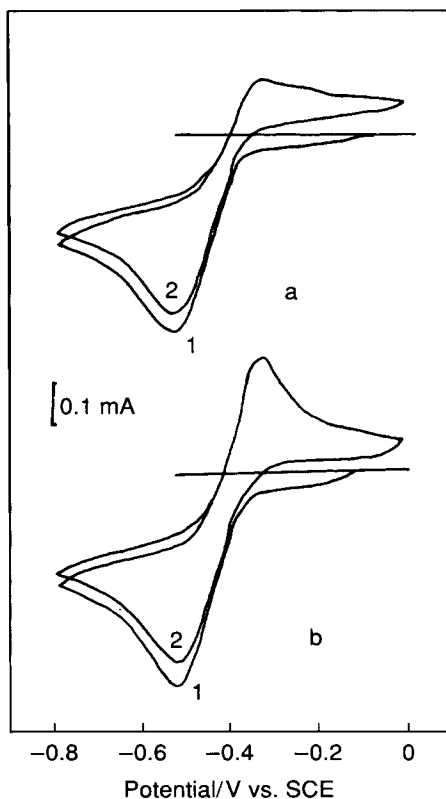


Figure 3 Cyclic voltammetric curve of Pt electrode coated with PNMP(TsO⁻) film of (a) 40 and (b) 100 mC cm⁻² in 0.2M TsONa of pH 2: (1) the first reduction scan; (2) the second reduction scan.

The Pt electrode coated with the neutral PNMP(Cl⁻) film was also investigated in 0.2M TsONa aqueous solution of pH 2. The peak current at the first cycle is 0.37 mA for the film with the

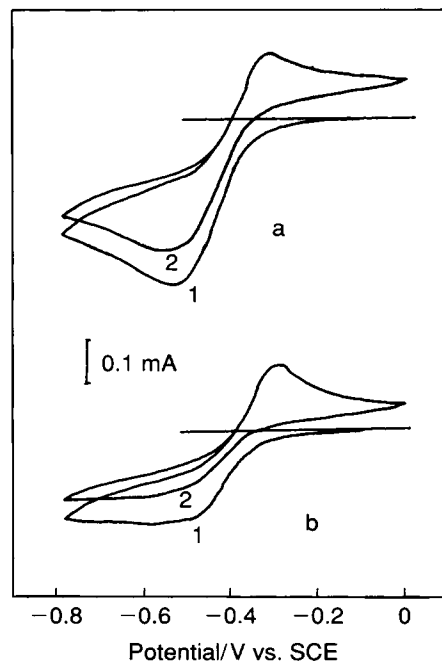


Figure 4 Cyclic voltammetric curve of Pt electrode coated with PNMP(Cl⁻) film of (a) 40 and (b) 100 mC cm⁻² in 0.2M TsONa of pH 2: (1) first reduction scan; (2) second reduction scan.

thickness of 40 mC cm⁻² (see Fig. 4), which is lower than that on the Pt electrode coated with the PNMP(TsO⁻) film of the same thickness. When the thickness of the film increases to 100 mC cm⁻², the cathodic peak current at the first cycle is 0.20 mA. These results indicate that the channels for H⁺ penetration in neutral PNMP(Cl⁻) may be less or smaller than those in neutral PNMP(TsO⁻). In this

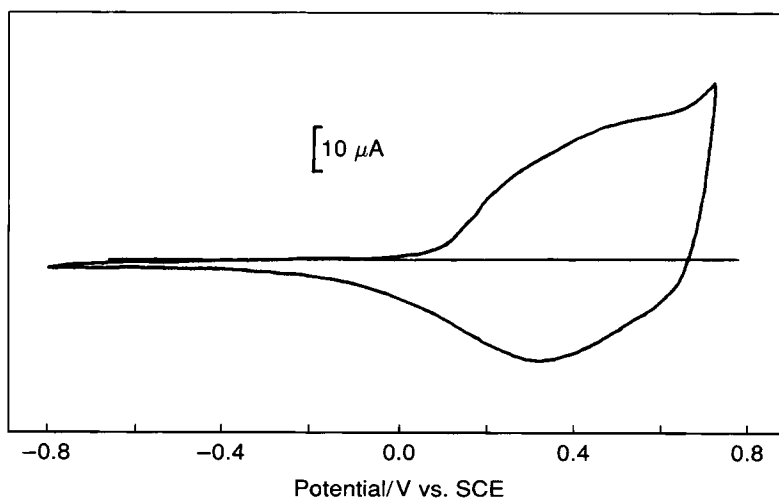


Figure 5 Cyclic voltammetric curve of Pt electrode coated with PNMP(NO₃⁻) film in 0.2M NaNO₃ of pH 3.

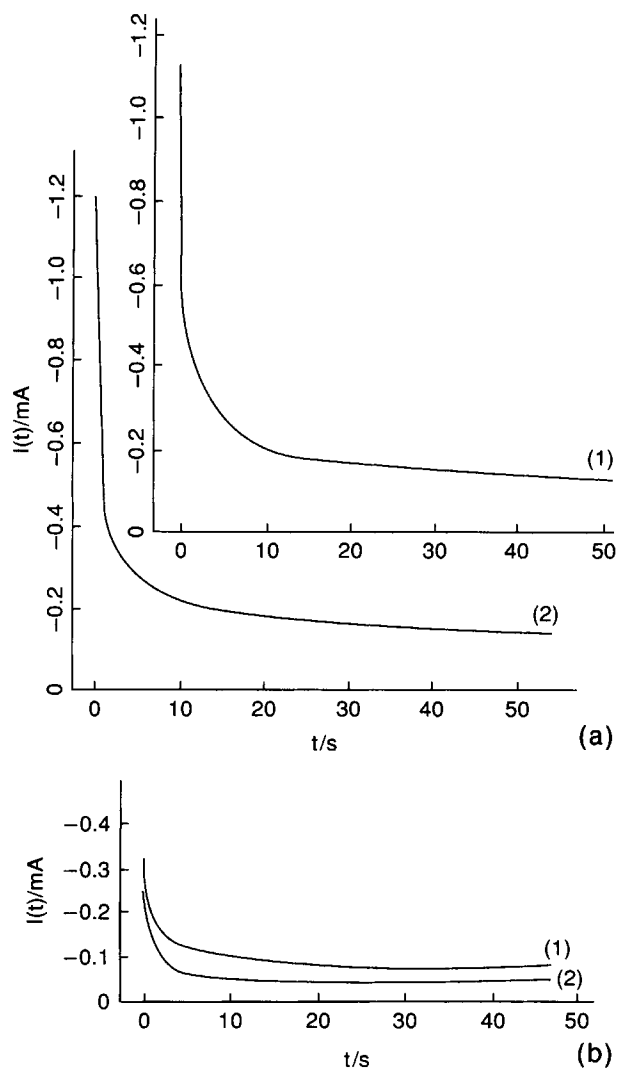


Figure 6 Current decay curve in response to potential step at -0.6 V vs. SCE of Pt electrode coated with (a) PNMP(TsO⁻) film and (b) PNMP(Cl⁻) film with the thickness of (1) 100 and (2) 200 mC cm⁻² in 0.2M TsONA solution of pH 1.86.

case, the thicker film might hinder the penetration of H⁺ cations.

When the polymerization of *N*-methylpyrrole is carried out in NaNO₃ solution, the PNMP film doped by the NO₃⁻ anion is obtained. The Pt electrode coated with the PNMP(NO₃⁻) film was also investigated by cyclic voltammetry in a 0.2M TsONA aqueous solution of pH 2. The H⁺ reduction in the potential range from -0.2 to -0.8 V is not observed. Maksymiuk and Doblhofer⁹ thought that the process of H⁺ cations penetrating the polymer was accompanied by that of anions entering into the polymer from the electrolyte. So, one may think that it is

because TsO⁻ is too large to enter neutral PNMP(NO₃⁻). But when the Pt electrode with PNMP(NO₃⁻) is investigated in a NaNO₃ or NaCl acidic aqueous solution, the reduction of H⁺ cations was not yet observed, as shown in Figure 5. This seems that the neutral film from PNMP(NO₃⁻) is closed for H⁺ cation penetration.

It has been found that there exists a free volume in the conducting polymer through which gas or ion or solvent can pass.^{11,14-16} The above results imply that there exist H⁺ ion channels in neutral PNMP(TsO⁻) and PNMP(Cl⁻). For neutral PNMP(TsO⁻), H⁺ cations can penetrate the polymer and the process is little related to the thickness of the film. For neutral PNMP(Cl⁻), H⁺ penetration depends greatly on the thickness of the film. For neutral PNMP(NO₃⁻), the penetration of H⁺ cations does not take place. Obviously, the penetration of the H⁺ cation through the neutral polymer depends strongly on the doped counteranions. The different influence of the counteranions has also been observed when the conducting polymer is used as a gas or solvent separation.^{11,14}

The counteranions in the conducting polymer can exchange with the anions in an electrolyte through the electrochemical process.¹⁷ PNMP(NO₃⁻) can be gained by dedoping and redoping of PNMP(TsO⁻) in NaNO₃ solution. The Pt electrode coated with such-gained PNMP(NO₃⁻) film is investigated. In acidic solution, the H⁺ reduction takes place the

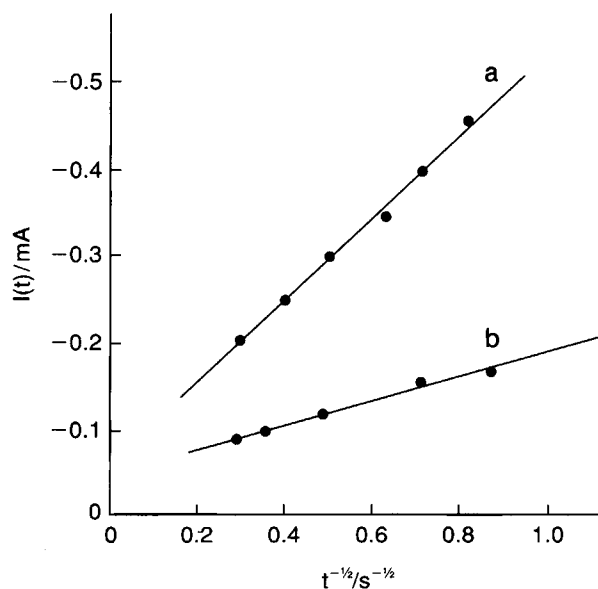


Figure 7 Current (i_t) dependence of time ($t^{-1/2}$) in potential step chronoamperometry of Pt electrode coated with neutral (a) PNMP(TsO⁻) film and (b) PNMP(Cl⁻) film.

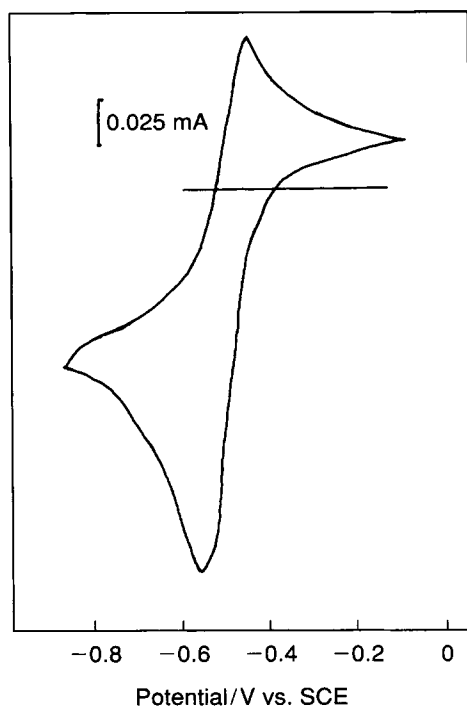


Figure 8 Cyclic voltammogram of Pt electrode coated with overoxidized PNMP(TsO⁻) film with thickness of 100 mC cm⁻² in 0.2M TsONa solution of pH 1.86.

same as that on the Pt electrode coated with the PNMP(TsO⁻) film. On the other hand, the PNMP(Cl⁻) film is obtained by the treatment of the PNMP(NO₃⁻) film in NaCl solution. The H⁺ reduction is not observed yet on the Pt electrode coated with such-obtained PNMP(Cl⁻) film. These results imply that the channel structure of neutral PNMP films is determined by the nature of the original counteranions, i.e., by the electropolymerization condition.

Potential step chronoamperometry was carried out on the Pt electrode coated with the neutral PNMP film in a 0.2M TsONa electrolyte of pH 1.86 at -0.6 V vs. SCE. For the neutral PNMP(TsO⁻) film, the beginning current is -1.12 mA for the film with the thickness of 100 mC cm⁻² and -1.20 mA for the film with the thickness of 200 mC cm⁻² [see Fig. 6(a)]. At last, both currents reach stable values; the stable current is -0.12 mA for the film with the thickness of 100 mC cm⁻² and -0.13 mA for the film with the thickness of 200 mC cm⁻². For the neutral PNMP(Cl⁻) film, the beginning current is -0.32 mA for the film with the thickness of 100 mC cm⁻² and -0.26 mA for the film with the thickness of 200 mC cm⁻² [see Fig. 6(b)]. The stable current is 0.06 mA for the film with the thickness of 100 mC cm⁻² and 0.03 mA for the film with the thickness of 200 mC

cm⁻². These results imply that the concentration of H⁺ cations on the surface of the Pt electrode decreases with increase of the thickness both at the beginning and at the stable state. The stable current depends little on the thickness for the neutral PNMP(TsO⁻) film, while it depends strongly on the thickness for the neutral PNMP(Cl⁻) film. These results are in accordance with the results of the CV measurement.

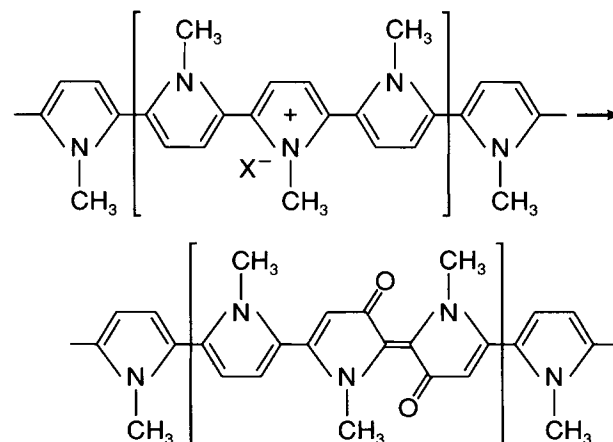
The diffusion coefficient D_0 can be estimated from the current decay curve. The relation between the current $i(t)$ and the time (t) is described as the Cottrell equation¹⁸:

$$i(t) = \frac{FAD_0^{1/2}C}{\sqrt{\pi t}}$$

where A is the area of the Pt electrode; F , the Faraday constant, and C , the volume concentration of H⁺ cations in the electrolyte. From the slope of the straight line of $i(t)$ to $t^{-1/2}$ (see Fig. 7), the D_0 of H⁺ cations penetrating neutral PNMP(TsO⁻) and PNMP(Cl⁻) is estimated as 7×10^{-5} and 7×10^{-6} cm² s⁻¹, respectively. The D_0 of the anions passing the PPy film was attained as 10^{-9} cm² s⁻¹.¹⁹ Obviously, the penetration of H⁺ cations through the film is much faster than that of the anions.

H⁺ Reduction on the Pt Electrode Coated with Overoxidized PNMP Film

The overoxidized PNMP film is obtained by polarizing the PNMP film in a 0.1M NaOH aqueous solution at +0.8 V vs. SCE. After overoxidation, the color of the film changes from brown to gold. For polypyrrole, the overoxidation takes place with the release of the counteranions and carbonylation of the β -C atom in the pyrrole ring.²⁰ The same process may occur to PNMP as below:



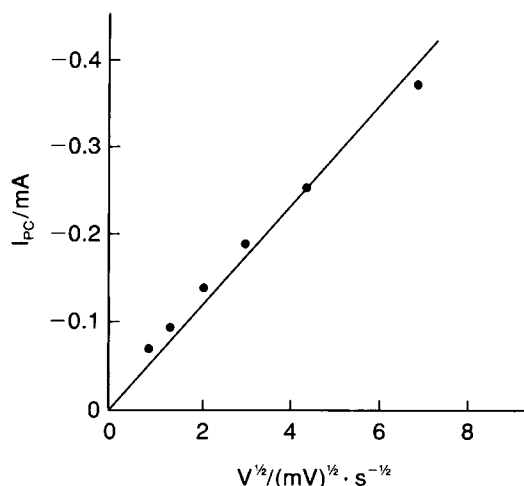


Figure 9 Potential scan rate (v) dependence of the cathodic peak current (i_{pc}) in cyclic voltammetry of the Pt electrode coated with overoxidized PNMP(TsO⁻) film.

After overoxidation, the conjugation is broken and the polymer changes from the conducting state to the insulating state. This process is irreversible, and the overoxidized polymer cannot be reduced again.

Cyclic voltammetry of the Pt electrode coated with the overoxidized PNMP(TsO⁻) is performed in a 0.2M TsONa aqueous solution of pH 1.86, as shown in Figure 8. The H⁺ reduction takes place similarly to that of the neutral film. It is certain that the reduction cannot take place on the interface between the polymer and the electrolyte, but can on the interface between the polymer and the Pt electrode. The peak current (I_{pc}) increases with the potential scan rate (v) and it is proportional to $v^{1/2}$ (see Fig. 9). This indicates that the process is controlled by diffusion.

When the Pt electrode is coated with the overoxidized polymer from PNMP(NO₃⁻), the H⁺ reduction does not yet occur. This indicates that the overoxidized film from PNMP(NO₃⁻) is also closed to H⁺ cation penetration.

It has been found that overoxidized polypyrrole can exclude anions to form porous and ion-selective membranes.²¹ The above results imply that there also exists H⁺ ion channels in the overoxidized PNMP(TsO⁻) film.

Potential step chronoamperometry was carried out to investigate the reduction of the H⁺ cation on the Pt electrode coated with the overoxidized PNMP film from PNMP(TsO⁻). The beginning current for the film of 100 mC cm⁻² is higher than that for the film of 200 mC cm⁻² and both currents almost reach the

same stable values at last. The diffusion coefficient of H⁺ cations through the overoxidized film is estimated as 10⁻⁵ cm² s⁻¹ with the same method as above.

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