Electrochemical Behavior of Electrodes Modified with π-Conjugated Polymers in 0.5 M H_2SO_4 (aq) and 1 M KOH (aq) Electrolytes

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Plantinum electrodes modified with 10 kinds of π-conjugated polymers have been prepared. These polymers include poly(pyridine-2,5-diyl) PPy, poly(2,2′-bipyridine-5,5′-diyl) PBpy, poly(3-octylthiophene-2,5-diyl) P3OcTh, and poly(6-hexylpyridine-2,5-diyl) P6HexPy. Films of PPy and PBpy behave as good H^+-transporting materials in 0.5 M H_2SO_4 (aq). Plots of log i vs. V for electrodes modified with the polymers give linear lines in a current density region of $10^{-5.5}$—10^{-2} A cm^{-2}. The slope of the line, $\beta = \mathrm{d}V/\mathrm{d}(\log i)$, depends on the kind of the polymer. Hydrophilic PPy and PBpy give a β value of 3.2×10^{-2} V, while hydrophobic P3OcTh and P6HexPy with long alkyl chains give a larger β value of 4.5×10^{-2} V. Diffusion coefficients of H^+ in films of PPy, PBpy, and poly(quinoline-2,6-diyl) P(2,6-Q) are estimated to be larger than 10^{-7} cm^2 s^{-1} from limiting currents at room temperature. The i–V curve of a P(2,6-Q)-modified Pt electrode shows a strong pH-dependence reflecting a chemical change of the polymer with pH. The PPy-, PBpy-, and P3OcTh-modified Pt electrodes exhibit acceleration effects for evolution of O_2 from 1 M KOH (aq).

Modification of electrodes with polymers and application of the polymer-modified electrodes in devices and in electrolytic synthesis have been the subject of many recent papers.[1—3] Although a variety of π-conjugated electrically conducting polymers have been prepared[4] and their electrochemical behavior (especially doping behavior) has been investigated,[5—8] electrolysis of water by electrodes modified with the π-conjugated polymers has received less attention. Here we report i–V relationships for electrodes modified with 10 kinds of π-conjugated polymers in electrochemical evolution of H_2 and O_2 from aqueous media.

Experimental

The polymer-modified electrodes were prepared by casting a polymer solution on a metal disk and drying the cast film under vacuum. Toluene was used for casting of poly(6-hexylpyridine-2,5-diyl) P6HexPy[9] and poly(3-octylthiophene-2,5-diyl)P30cTh,[10,11] whereas formic acid was used for casting of poly(pyridine-2,5-diyl) PPy,[9] poly(2,2′-bipyridine-5,5′-diyl) PBpy,[9] poly(quinoline-2,6-diyl) P(2,6-Q),[12] poly(2,3-di(p-tolyl)quinoxaline-5,8-diyl) PQx-(diTol),[13] and its diethyl analogue (PQx(diEt)).[13,14] Cast films of poly(2-methylanthraquinone-1,4-diyl) P(2Me-1,4-AQ),[15,16] poly(3-hexylthiophene-2,5-diyl-ethynylene) PAE-2,[17] and poly[3-(4-hydroxy-3,5-di-t-butyl)thiophene-2,5-diyl] PTh(OH)[18] were obtained from chloroform solutions. The removal of all solvent after drying under vacuum was confirmed by IR spectroscopy. The polymers were prepared according to the literature.[9—18]

The polymer-modified metal electrodes had a diameter of 6.6 mm. In the case of an indium-tin-oxide (ITO) electrode, the polymer-modification was carried out on a rectangular electrode with a dimension of 1 mm×19.5 mm. The polymer-modified metal and ITO electrodes were immersed in an aqueous solution in a Schlenk type flask purged with N_2, and the measurement was carried out under N_2 bubbling at room temperature (25±3 °C). Electrochemical data were obtained with a Hokuto Denko HAB-151 potentiostat/galvanostat and a Riken Denshi F-35 X-Y recorder.

Pt was purchased from Tokuriki Co., Ltd.; Ag (99.98% purity), W (99.95% purity) and Cu (99.9% purity) were purchased from The Nilaco Corp. The ITO (surface resistivity = 10 Ω) was kindly donated by YKK Corp. Pt (for H_2 experiments) was washed in concd HNO_3, formic acid, acetone, and hexane in this order in an ultrasonic cleaner. Pt (for O_2 experiments) was washed analogously after polishing with emery paper (roughness; #4000) and wrapping paper (3M Corp.; roughness: #8000). Other metals were polished analogously.

Scanning electron micrographs (SEM) were obtained with a JEOL T220 scanning electron microscope. The pH value was measured with a Toa HM-40V pH meter. The contact angle of water on the polymer film was measured with a Kyowa Kaimen Kagaku CA-A type contact angle meter by using deionized and filtered water.

Results and Discussion

Polymers. The following π-conjugated polymers (cf. Experimental) have been used for the present studies (Chart 1). These polymers are prepared by organometallic polycondensation and have well-defined bonding between the monomer units.[19] P3OcTh and PTh(OH) include electron-excessive thiophene rings[20] and are preferentially oxidized to give a p-doped state,[19] whereas other polymers consist of electron-deficient units[20] and are susceptible to reduction to give n-doped states.[19] Pt electrodes modified with these polymers give the following results.

H_2 Evolution Reaction in 0.5 M H_2SO_4 on Pt Modified Electrodes. Figure 1 shows cathodic i–V curves obtained

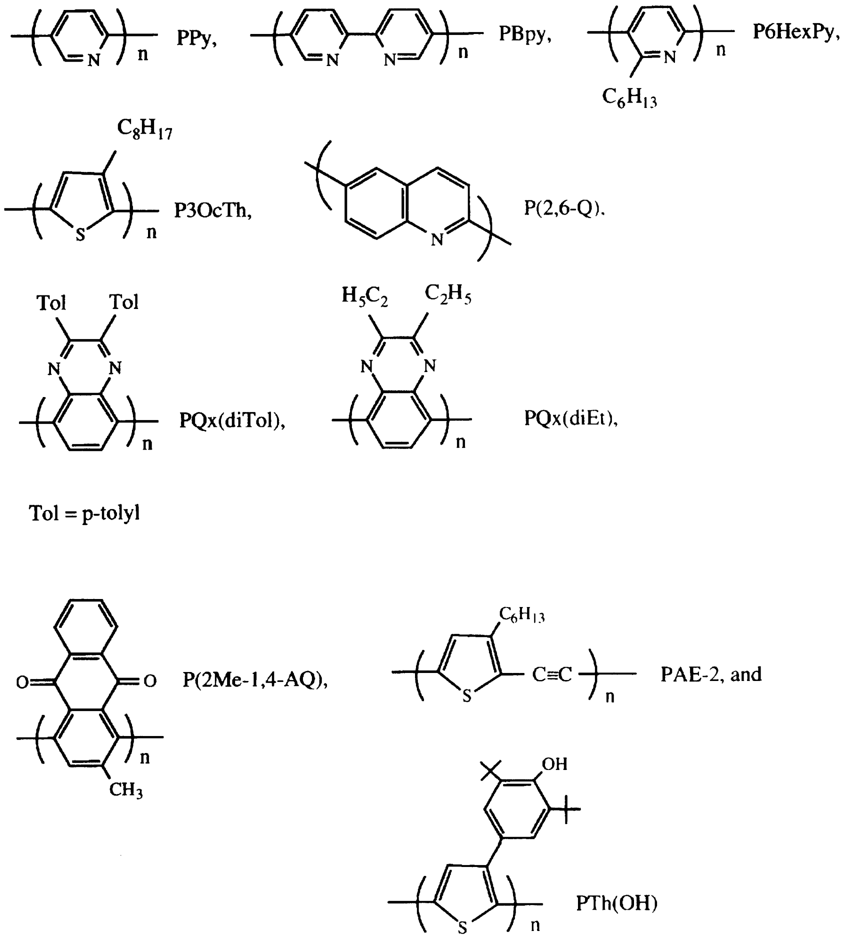


Chart 1.

with bare Pt electrode (curve a) and PPy-, PBpy- P3OcTh-, and P6HexPy-modified Pt electrodes (curves b—e) in an aqueous solution of 0.5 M H_2SO_4 (1 M=1 mol dm^{-3}); the *i–V* curves are all reproducible. As shown in Fig. 1, the polymers without hydrophobic alkyl groups (PPy and PBpy) give *i–V* curves (b and c) similar to that of the bare Pt electrode (a). On the other hand, the polymers with the hydrophobic long alkyl group (P3OcTh and P6HexPy) give much different *i–V* curves (d and e).

Plots of log *i* vs. *V* for the electrodes give straight lines in certain regions, as shown in Fig. 2. Use of other polymers also give such lines, and Table 1 summarizes slopes of the lines (β in Eq. 1) and current ranges where the lines are straight.

$$V = \alpha - \beta \log |i| . \tag{1}$$

The β value of the bare Pt electrode agrees with the reported Tafel's parameter b.[21—24]

As shown in Figs. 1 and 2, the PPy- and PBpy-modified electrodes give almost the same *i–V* curves as that of base Pt electrode. To the contrary, the P3OcTh- and P6HexPy-modified electrodes requires more negative potential for the H_2 evolution. An excess negative potential ΔE required for the cathodic reaction can be defined by the following equation

$$\Delta E = E(\text{Pt}) - E(\text{polymer modified electrode}). \tag{2}$$

and ΔE values at $i=10^{-5}$ A cm^{-2} observed with various polymer-modified electrode are also shown in Table 1.

We first expected that reduction of H^+ would take place on the surface of the polymer film by using an electron carried through the π-conjugated polymer film and the β and ΔE values would be correlated to the chemical and physical properties of the electrically conducting π-conjugated polymers. However, the negative potential for the H_2 evolution (e.g., from −0.2 to −0.6 V vs. SCE; Fig. 1) is not enough to generate any negative carriers in the π-conjugated polymer.[9,10] Although all of the polymers shown above can be converted to n-type conducting materials by reduction (or n-doping), the reduction requires potentials of about -2.2 ± 0.3 V vs. SCE.[9—19] The reduction of H^+ seems to take place on the surface of the basal Pt electrode by using H^+ carried through the polymer film, and the β and ΔE values seem to be mainly determined by the H^+-transporting ability of the polymer film.

The occurrence of the electrochemical reaction on the surface of the Pt electrode is confirmed by comparing a CV curve of the polymer-modified electrode with that of the bare Pt electrode. For example, both the PBpy-modified and P3OcTh-modified Pt electrodes give essentially the same CV

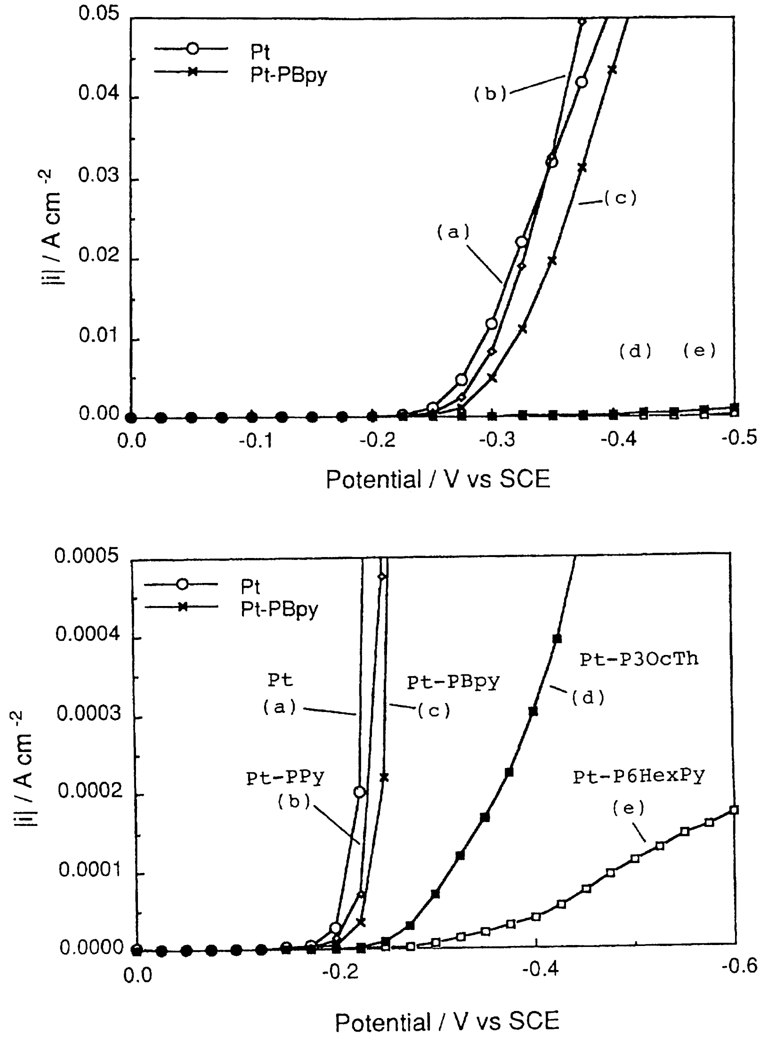


Fig. 1. i–V relationship for evolution of H_2 from an aqueous solution of 0.5 M H_2SO_4. In the lower figure, the scale of the coordinate is magnified by 10^2. Electrode: (a) bare Pt, (b) PPy-modified Pt, (c) PBpy-modified Pt, (d) P3OcTh-modified Pt, and (e) P6HexPy-modified Pt. Amount of the polymer per 1 cm^2: 20 μg (2.6×10^{-7} mol of pyridine unit) for PBpy, 50 μg (2.6×10^{-7} mol of thiophene unit) for P3OcTh, and 41.6 μg (2.6×10^{-7} mol of pyridine unit) for P6HexPy.

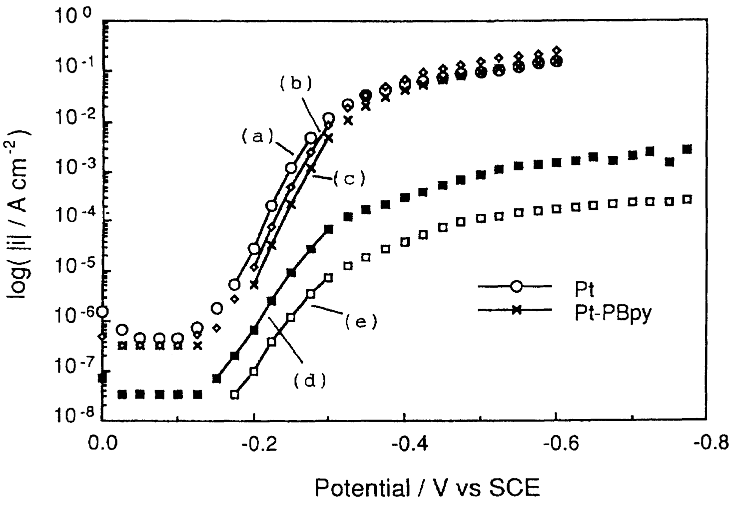


Fig. 2. Log i–V relation of the data shown in Fig. 1. (a)—(e) as in Fig. 1.

Table 1. The β (Eq. 1) and ΔE (Eq. 2) Values for the Polymer Modified Pt Electrode in H_2 Evolution in 0.5 M H_2SO_4 (aq)

No.	Polymer	Amount[a)] $\mu g\,cm^{-2}$	$-\Delta E$/V[b)]	$\beta/10^{-2}$ V	Range,[c)] $-\log(i/A\,cm^{-2})$
	Electrode = Pt				
1	None			3.2	2—5.5
2	PPy	10	0.00	3.2	2—5.5
3	PPy	20	0.01	3.2	2—5.5
4	PPy	30	0.02	3.3	2—5.5
5	PBpy	10	0.01	3.3	2—6
6	PBpy	20	0.01	3.3	2—6
7	PBpy	30	0.02	3.2	2—5.5
8	P3OcTh	25	0.06	4.4	4.5—7.5
9	P3OcTh	75	0.09	5.3	5—7.5
10	P6HexPy	21	0.04	4.5	5—7.5
11	P6HexPy	42	0.11	4.7	5.5—8
12	P(2,6-Q)	32	0.01	4.0	2.5—4.5
13	PQx(diTol)	40	0.02	4.9	3.5—5.5
14	PQx(diEt)	48	0.01	4.8	2.5—5
15	P(2Me-1,4-AQ)	57	0.05	8.7	4.5—5.5
16	PAE-2	50	0.05	8.8	4.5—5.5
17	PTh(OH)	74	0.04	8.0	4.5—5.5

a) 20 μg of PPy, 20 μg of PBpy, 50 μg of P3OcTh, and 41.6 μg of P6HexPy correspond to 2.6×10^{-7} mol of aromatic units. b) At $i=10^{-5}$ $A\,cm^{-2}$. c) Range to obtain the parameter β.

pattern (at 500 m $V\,s^{-1}$) as the bare Pt electrode (with two typical symmetric redox couples at −0.02 and −0.12 V vs. SCE in the hydrogen absorption–desorption region of the Pt electrode.[25)]

On these bases, we take the ΔE value as a measure for the barrier to transportation of H^+ in the polymer film, which seems to be correlated to hydrophilicity and chemical reactivity of the polymer film against H_2SO_4, as discussed below.

Table 2 lists contact angle θ of the polymer films against water; this angle can be taken as a measure for the hydrophilicity of the polymer film. As shown in Table 2, PPy and PBpy without the alkyl substituent give smaller θ values (smaller than 70 °C of nylon[26)]), whereas the θ values of P3OcTh and P6HexPy are large (comparable to 94—95 ° of polyethylene and polypropylene[26a)] but smaller than 117.0 ° of vacuum deposited poly(*p*-phenylene)[26b)]). Thus, comparison of the electrochemical data obtained with the polymer-modified Pt electrodes (Table 1) and the θ values reveals the effect of the hydrophilicity of the polymer on the ΔE value:

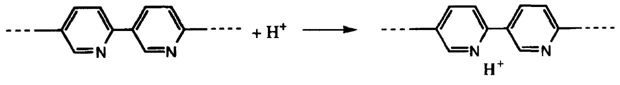
Table 2. Contact Angle θ of the Polymer Film against Water

Polymer	θ/°
PPy	64.7
PBpy	65.0
P6HexPy	99.6
P3OcTh	97.1
P(2,6-Q)	89.7
PQx(diTol)	94.3
PQx(diEt)	78.9
P(2Me-1,4-AQ)	92.8
PAE-2	89.6
PTh(OH)	91.0

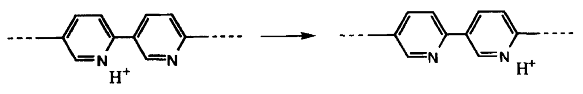
$$\begin{array}{lll} & \text{PPy, PBpy} \quad < & \text{P3OcTh, P6HexPy, P(2Me-1,4-AQ)} \\ & & \text{PAE-2, PTh(OH)} \\ \Delta E/\text{V} & < 0.02 & > 0.04 \\ \theta/° & < 90 & > \text{ca. } 90 \end{array} \tag{3}$$

In cases of P(2,6-Q), PQx(diEt), and PQx(diTol), they give small ΔE values of 0.01—0.02 V (Nos. 12—14 in Table 1), in spite of their relatively large θ values (78.9—94.3 ° in Table 2) against pure water. However, this result is attributable to a large affinity of the polymers toward acidic water, as discussed later.

In cases of the polymers with nitrogen, H^+ seems to be carried through protonated nitrogen, e. g.,



(4)



(5)

In the process of the proton transfer, the counter anion SO_4^{2-} is considered to stay at an averaged position and not to move over a long distance.

$$\begin{array}{c|c|c} \text{Pt} & \text{polymer} & \text{solution} \\ & \text{layer} & \\ & \leftarrow H^+ \quad H^+ \quad H^+ & \leftarrow H^+ \\ & SO_4^{2-} \quad SO_4^{2-} & \end{array}$$

As for the protonation of the nitrogen-containing polymers, the following results have been obtained.

Although yellow powders of PPy and P(2,6-Q) form protonated reddish brown powdery products by chemical reactions with acids under stirring, no apparent color change of the polymer film is observed when the polymer-modified electrode is immersed in the aqueous solution of 0.5 M H_2SO_4. It is considered to be due to the difficulty for the inner part of the polymer film, which is apart from the surface area, to react smoothly with H_2SO_4. The IR spectrum of the P(2,6-Q) film obtained after dipping in 0.5 M H_2SO_4 (aq) (chart b in Fig. 3) is almost identical to that of the original P(2,6-Q) (chart a) and shows no apparent sign of the protonation.

On the other hand, when the negative potential for the H_2 evolution is applied, the color of the polymer film rapidly changes from yellow to reddish brown. As shown in Fig. 3, FT-IR spectrum of the reddish brown product obtained from the P(2,6-Q) film (chart c) is much different from that of original P(2,6-Q) (chart a), and resembles the IR spectrum of the reaction product of P(2,6-Q) with HCl (chart d). The reddish brown product gives rise to an additional broad absorption band of $SO_4{}^{2-}$ at about 1200 cm^{-1}. Application of the negative potential seems to allow moving of H^+ into the inner part of the polymer film, thus making the salt formation possible.

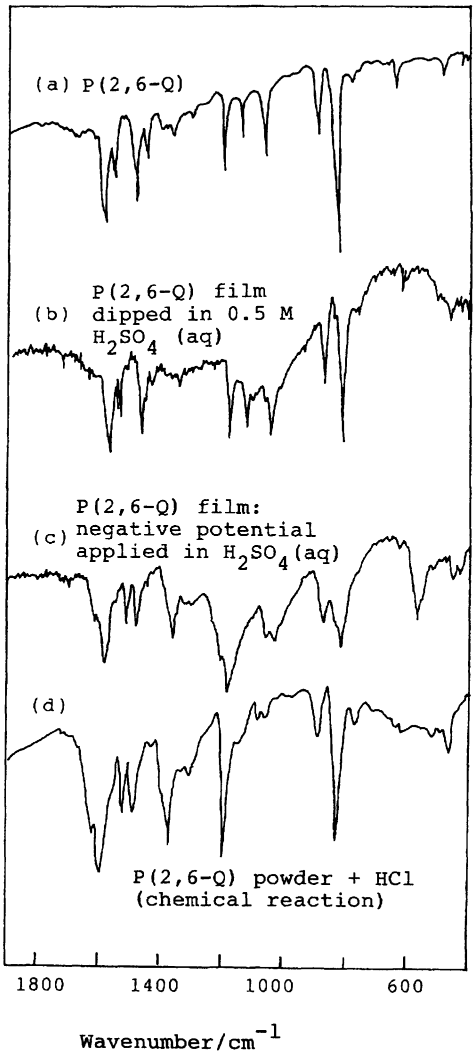


Fig. 3. IR spectra of (a) P(2,6-Q), (b) cast film of P(2,6-Q) (after dipping in 0.5 M H_2SO_4 (aq), washing with H_2O, and drying under vacuum), (c) cast film of P(2,6-Q), after application of the negative potential in 0.5 M H_2SO_4 (aq), and (d) reaction product of P(2,6-Q) with HCl ($(C_9H_5N\cdot 0.62HCl)_n$).

Recently a variety of H^+-transporting solid electrolytes including polymer electrolytes like Nafion have been reported and applied to make practical items such as electrochromic devices,[27] fuel cells,[28—30] and sensors. The observed correlation between the H^+-transporting ability of the polymer film and its hydrophilicity will contribute to comprehension of the H^+-transporting properties of the solid electrolytes. Due to the good H^+-transporting ability, as well as their high chemical and thermal stability,[9,12] PPy, PBpy, and P(2,6-Q) may also be useful materials as polymer electrolytes.

Transportation of H^+ in Polymer Film. PPy, PBpy, and P(2,6-Q) give limiting currents $i_{\lim}$ essentially in agreement with that of the basal Pt electrode (e.g., $i_{\lim}$=about 0.2 A cm^{-2} for curves a and b in Fig. 2). On the contrary, the hydrophobic polymers such as P3OcTh and P6HexPy affords an $i_{\lim}$ value considerably smaller than that of Pt (e.g., curves d and e in Fig. 2).

If $i_{\lim}$ is determined by the rate of transport of H^+ through the polymer film, it is related to the following diffusion equation.

$$i_{\lim}/F = D\frac{\Delta C}{d}. \tag{6}$$

Here, F, D, ΔC, and d stand for Faraday constant, diffusion coefficient, difference in the concentration of H^+ between the aqueous solution of 0.5 M H_2SO_4 and surface of Pt, and thickness of the polymer film, respectively.

If ΔC can be taken as approximately 1 M, one can calculate the D value from the $i_{\lim}$ value; the D values thus obtained are summarized in Table 3. As shown in Table 3, PPy, PBpy, and P(2,6-Q) have relatively large D values, whereas PQx(diEt) gives a medium D value and the other hydrophobic polymers (Eq. 3) show smaller D values. In the cases of PQx(diEt) and P3OcTh, they give essentially the same D value at different thicknesses of the film.

pH Dependence for P(2,6-Q)-modified Electrode. The P(2,6-Q)-modified Pt electrode shows the unique pH dependence of the i–V curve, reflecting a chemical change of P(2,6-Q) due to the protonation in the acidic medium. For example, the bare Pt electrode and the P(2,6-Q)-modified electrode give almost the same i–V curve in 0.5 M H_2SO_4 (aq), and the P(2,6-Q)-modified Pt electrode gives only a small ΔE value: ΔE=0.01 V, as shown in Table 1. However, the ΔE value increases with increase in the pH value, and ΔE values of 0.05, 0.10, and 0.20 V are observed at pH=4.20, 6.95, and 9.87, respectively. Decrease in hydrophilicity of P(2,6-Q) by raising the pH value, which is consistent with the large θ value of P(2,6-Q) against water (Table 2), accounts for the increase in the ΔE value with pH. It is reported that protonated quinoline, the monomer unit of the polymer, has a pK_a value of 4.97.

Other Metal Electrodes. Use of Ag with a larger overpotential than Pt leads to the shift of the i–V curves to the negative potential side. Use of W and Cu electrodes gives

Table 3. Limiting Current i_{lim} and Diffusion Coefficient D for the H_2 Evolution on the Polymer-Modified Pt Electrode

No.	Polymer	Thickness[a]	Limiting current[b]	Diffusion coefficient[c]
		μm	$A\,cm^{-2}$	$cm^2\,s^{-1}$
1	PPy, PBpy	0.1—0.3	larger or comparable to that of bare Pt electrode (ca. 1.5 $10^{-1}\,A\,cm^{-2}$)	$>5\times10^{-8}$
2	P3OcTh	0.25	5×10^{-3}	1.3×10^{-9}
3	P3OcTh	0.5	2×10^{-3}	1.0×10^{-9}
4	P6HexPy	0.42	3×10^{-4}	1.2×10^{-10}
5	P(2,6-Q)	0.97	As in No. 1	$>1.5\times10^{-7}$
6	PQx(diTol)	2.34	2×10^{-2}	4.7×10^{-8}
7	PQx(diEt)	0.7	2×10^{-2}	1.4×10^{-8}
8	PQx(diEt)	1.4	1×10^{-2}	1.4×10^{-8}
9	P(2Me-1,4-AQ)	1.67	2×10^{-2}	3.3×10^{-10}
10	PAE-2	1.45	4×10^{-5}	5.8×10^{-11}
11	PTh(OH)	2.16		

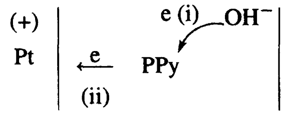
a) Calculated by assuming that the density of the polymer is 1. b) Limiting current obtained from the i–V relationship or maximum current below $|E|=0.7$ V. c) Calculated according to Eq. 6 by assuming $\Delta C=1$ M or 10^3 mol dm^{-3}.

analogous results.

O_2 Evolution. Figure 4a shows i–V relations for anodic (O_2 evolution) reactions of bare Pt and PPy-modified Pt electrode in 1 M KOH (aq); the log i–V plots for the reactions are depicted in Fig. 4b. These polymers and other polymers used have high stability against oxidation.[19]

As shown in Fig. 4, a PPy-modified electrode gives a larger electric current than the bare Pt electrode at a low potential region, suggesting that the polymer assists the oxidation of OH^-. However, at a higher potential region, the electric current becomes smaller than that observed with bare Pt, presumably due to the limited velocity of the transportation of OH^- in the polymer film. Similar results are observed with PBpy-modified and P3OcTh-modified (Fig. 5) Pt electrodes.

Since PPy has n-type conducting properties,[9] one of the most probable processes of the oxidation of OH^- in the polymer film, if it occurs, will involve electron transfer from OH^- to PPy and movement of electron in the PPy film to reach the Pt anode: (Scheme 1) However, a shift of lone pair electrons at nitrogen of PPy toward the Pt anode is also conceivable, and it may be responsible for the oxidation of OH^-.



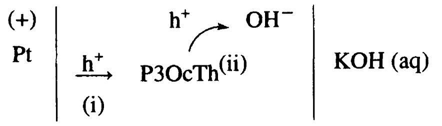
(i) electron of OH^- shifts to electron-accepting [9] PPy

(ii) electron accepted by PPy moves to the Pt electrode through the n-type PPy

Scheme 1. Model for oxidation of OH^- in the PPy-modified Pt electrode.

On the other hand, P3OcTh serves as a p-type conducting material;[10,11] in this case, the oxidation seems to take place with hole h^+ (positive carrier) formed in the P3OcTh film (Scheme 2). It is reported that poly(thiophene-2,5-diyl) and its derivatives like P3OcTh accept holes from electrodes and serve as hole-transporting material.[31—33] It is also reported that oxidation (or p-doping) of poly(3-alkylthiophene) to generate the h^+ carrier starts at about 0.6—0.7 V vs. SCE.[10,11]

In contrast to the cases of the PPy-, PBpy-, and P3OcTh-modified Pt electrodes, P6HexPy- P(2,6-Q)-, and PQx(diEt)-modified Pt electrodes give lower oxidation current than the bare Pt electrode. The blocking effect of the P6HexPy, P(2,6-Q), and PQx(diEt) films, in spite of their n-type conducting properties similar to those of PPy and PBpy,[9,12,14] suggests that subtle differences in chemical and physical properties of the polymer film (e.g., redox potential, hydrophilicity, and



(i) P3OcTh accepts hole from the Pt electrode (or give electron to the Pt electrode) [31,32] and the hole moves in the P3OcTh film

(ii) the hole in the P3OcTh is accepted by OH^- (or electron of OH^- shifts to the hole).

Scheme 2. Model for oxidation of OH^- in the P3OcTh-modified Pt electrode.

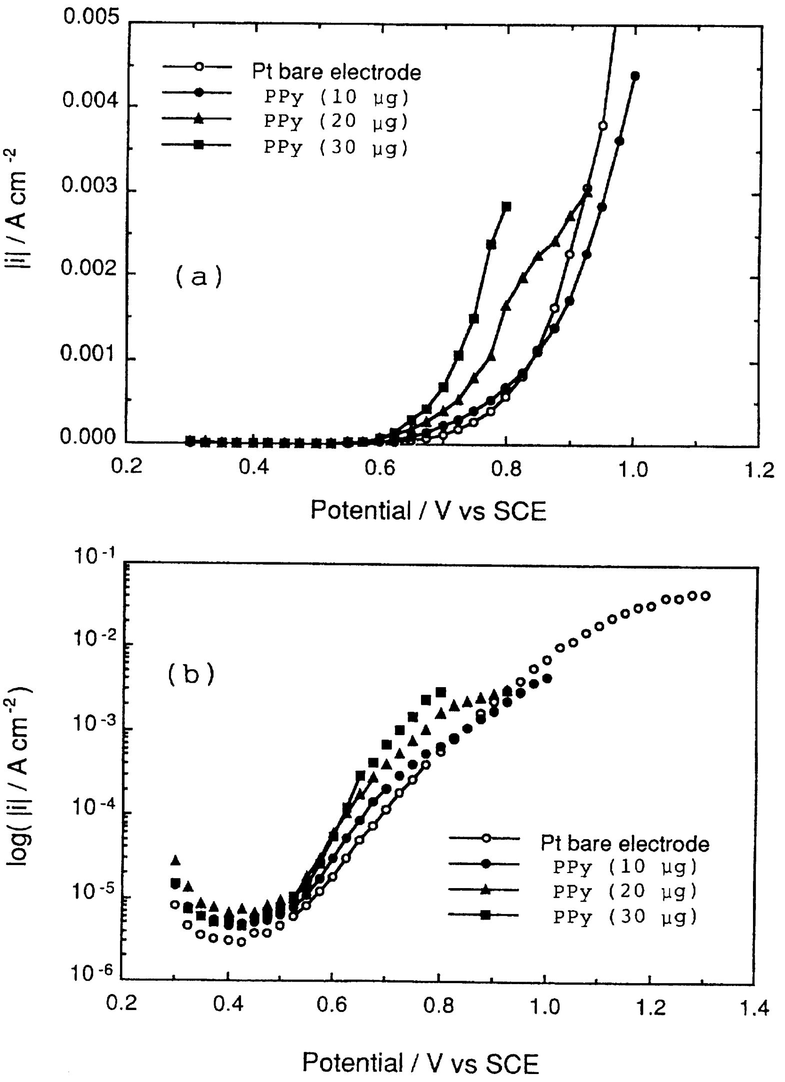


Fig. 4. (a) *i*–*V* relationships for anodic (O_2 evolution) reactions of bare Pt (○) electrode and PPy-modified Pt electrode (amount of PPy=10 μg cm^{-2} (●), 20 μg cm^{-2} (s), and 30 μg cm^{-2} (■)) in 1 M KOH (aq) and (b) their log *i*–*V* plots.

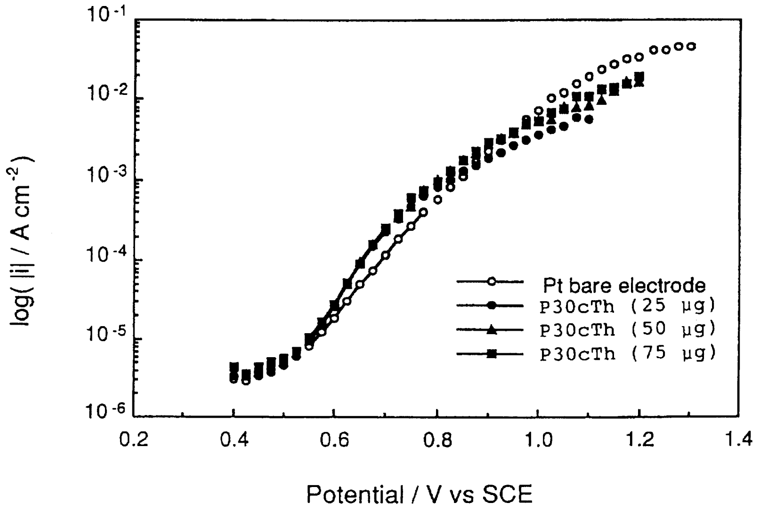


Fig. 5. Log *i*–*V* relation for the O_2 evolution reactions of bare Pt (○) electrode and P3OcTh-modified Pt electrode (amount of P3OcTh=25 μg cm^{-2} (●), 50 μg cm^{-2} (▲), and 75 μg cm^{-2} (●)) in 1 M KOH (aq).

morphology) determine whether the polymer film serves as the active layer or the blocking layer in the anodic reaction. PPy and PBpy films also behave as similar active layers in polymer-modified ITO electrodes used for the anodic reaction (O_2 evolution).

Conclusion and Scope. Hydrophilic PPy, PBpy, and P(2,6-Q) serve as the H^+-carrying polymer electrolytes for the H_2 evolution in 0.5 M H_2SO_4, and the Pt electrodes modified with these polymers give an i–V curve similar to that of a bare Pt electrode. On the other hand, use of hydrophobic polymers such as P3OcTh, P6HexPy, and PAE-2 to modify the Pt electrode leads to the shift of the i–V curve to a more negative potential side. Films of PPy, PBpy, and P3OcTh in the polymer-modified Pt electrodes work as active layers for the anodic reaction in 1 M KOH (aq). Application of the polymer-modified electrodes to electrolytic reactions (e.g., some organic synthetic reactions), which require higher level potentials and thus lead to the sufficient p- and n-doping of the polymer, may reveal more remarkable acceleration effects of the polymers in the electrolytic reactions.

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