SHORT COMMUNICATIONS

Acceleration Effect of a π -Conjugated Polymer-Modified Electrode for Electrolytic Evolution of H₂ in H₂SO₄(aq)

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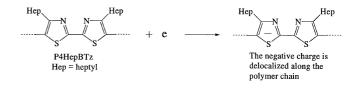
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KEY WORDS Polymer-Modified Electrode / Poly(bithiazole) / Electrolysis / Hydrogen Evolution / Acceleration Effect /

Electrically conducting π -conjugated polymers are the subject of many recent papers.^{1,2} They are electrochemically active, and application of the polymers to electrochemical devices such as battery³⁻⁵ and electrochromic devices⁶ has been reported. Previously we reported electrochemical response of π -conjugated polymer-modified platinum electrodes in electrolysis of aqueous 1 M NaOH and 0.5 M H₂SO₄.⁷ For electrochemical evolution of O2 from the NaOH aqueous solution, we observed an acceleration effect of poly(3alkylthiophene-2,5-diyl). This polymer is a typical ptype conducting polymer which easily receives electrochemical oxidation when connected to an anode, and the acceleration effect is considered to be due to facile acceptance of electron of OH⁻ by the p-doped poly(3alkylthiophene-2,5-diyl).

$$OH^- + \cdots + S^R \longrightarrow O_2 + \cdots + S^R$$

For similar acceleration effect for electrolytic evoluiton of H₂ in aqueous 0.5 M H₂SO₄, however, we were not able to observe such an acceleration effect with previously tested π -conjugated polymers. We recently noticed that Schultze and coworkess had also reported electrochemical evolution of hydrogen on polyaniline-modified metal electrodes in 0.5 M H₂SO₄(aq).⁸ However, they could not observe the acceleration effect, either. We now report that a recently prepared π -conjugated polymer, poly(4,4'diheptyl-2,2'-bithiazole-5,5'-diyl), P4HepBTz,⁹ gives such an acceleration effect for cathodic evolution of H₂ in 0.5 M H₂SO₄. P4HepBTz is one of typical n-type conducting polymers, and susceptible to electrochemical reduction to generate negative carriers in its film by applying reducing potential through metallic electrodes such as a platinum electrode.⁹



EXPERIMENTAL

P4HepBTz was prepared as previous reported.⁹ P4HepBTz was soluble in organic solvents, and painting a platinum plate ($\phi = 6.1 \text{ mm}$) with a trifluotoacetic acid solution of P4HepBTz and drying up under vacuum gave a smooth thin film on the platinum plate, which was purchased from Tokuriki Co, Ltd. Pt and washed with concd HNO₃, formic acid, acetone, and hexane in this order in an ultrasonic cleaner.

Figure 1 exhibits a sketch of the cell constructed with the P4HepBTz-modified platinum electrode. The measurement was carried out under stirring after bubbling N₂ gas for 2 h. Bubbles of hydrogen were smoothly removed under the stirring conditions. By using a Hokuto Denko HAB-151 potentiostat, the potential was moved to a negative direction with a velocity of 1 mVs^{-1} . Every 25 s after a shift of 25 mV, the sweep was stopped and the potential was fixed for 180 s, and the electric current read during 170 and 180 s interval time was adopted as the *i* value at the potential V. Stable and constant electric current was observed during about 100 and 250 s.

RESULTS AND DISCUSSION

Figure 2 shows comparison of i-V relationships obtained with the bare platinum electrode and the

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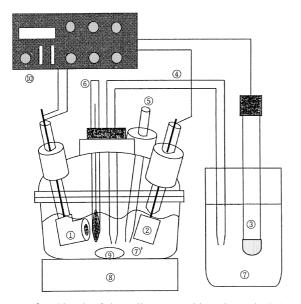


Figure 1. Sketch of the cell. ①: working electrode (P4Hep-BTz-modified platinum disk; diameter = 6.1 mm; area = 0.30 cm^2 ; platinum electrode was washed with dil. HNO₃, formic acid, acetone, and hexane); ② counter electrode (platinum plate; 20 mm × 20 mm × 0.10 mm); ③: reference electrode (Toa HS-305D AgCl/Ag electrode); ④: salt bridge (agar bridge with 4 M KCl(aq)); ⑤: N₂ gas inlet; ⑥: thermometer; ⑦ & ⑦': aqueous solution of $0.5 \text{ M H}_2\text{SO}_4$ (in distillated water) ⑧: magnetic stirrer; ⑨: stirring bar; ⑩: potentiostat.

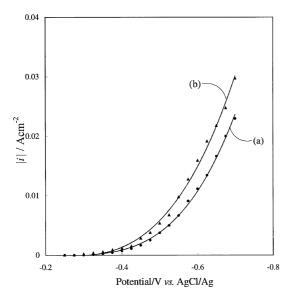


Figure 2. *i*-V relationship for evolution of H_2 from an aqueous solution of 0.5 M H_2SO_4 . Curve a (\bullet): data for bare platinum electrode. Curve b (\blacktriangle): data for P4HepBTz-modified platinum electrode. Amount of P4HepBTz = 0.046 mg / 0.30 cm² or 0.015 mg cm⁻². Measured under N₂ at 25°C.

P4HepBTz-modified platinum electrode under the same measurement conditions. As shown in Figure 2, modification of the platinum electrode with P4HepBTz led to an increase in the cathodic current. The acceleration effect (or catalytic effect) observed with the P4HepBTz-modified electrode was reproducible. The

data depicted in Figure 2 were obtained with a sample amount of $(0.046 \text{ mg} (2.5 \times 10^{-4} \text{ mmol of the thi-azole unit})$ of P4HepBTz)/ $(0.30 \text{ cm}^2$ of the platinum electrode) corresponding to about 1 µm thickness of the polymer film covering the platinum electrode, and essentially the same *i*-V relationship was obtained for the amount ranging from (0.023 mg of P4HepBTz) to $(0.069 \text{ mg of P4HepBTz})/(0.30 \text{ cm}^2 \text{ of the platinum})$ electrode). When the potential is swept to a highly negative potential beyond -0.75 V vs. AgCl/Ag, the electric current is considered to be saturated.^{7, 8} When concentration of sulfuric acid was decreased, the cathodic current decreased as previously observed.⁷ Similar acceleration effect is also expected for other protic acids, and we will continue our research in this line.

Other π -conjugated polyarylenes, including poly-(pyridine-2,5-diyl),¹⁰ poly(2,3-ditolylquinoxalenes-5,8diyl),¹¹ poly(2-methylanthraquinone-1,4-diyl),¹² and vacuum-deposited poly(p-phenylene),¹³ did not show such an acceleration effect. Since all of these polymers are also susceptible to n-doping,¹⁴ delicate difference in the polymer structure affects the hydrogen evolution with the polymer-modified electrode. For the present case using P4HepBTz as the modifying polymer, the hydrogen evolution may take place by electron transfer through the *n*-doped polymer Among *n*-dopable π -conjugated polymers, to H^+ . polybithiazoles have especially a strong tendency to form an ordered π -stacked structure,¹⁵ and this π -stacked structure may be related to smooth electron transfer through P4HepBTz. Further study on the π -conjugated polymer-modified electrode will give basis for development of electrolytic syntheses using π -conjugated polymer-modified electrodes.¹⁶

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