

Figure 1. Sketch of the cell. ①: working electrode (P4HepBTz-modified platinum disk; diameter = 6.1 mm; area = 0.30 cm²; 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 M H₂SO₄ (in distilled water) ⑧: magnetic stirrer; ⑨: stirring bar; ⑩: potentiostat.

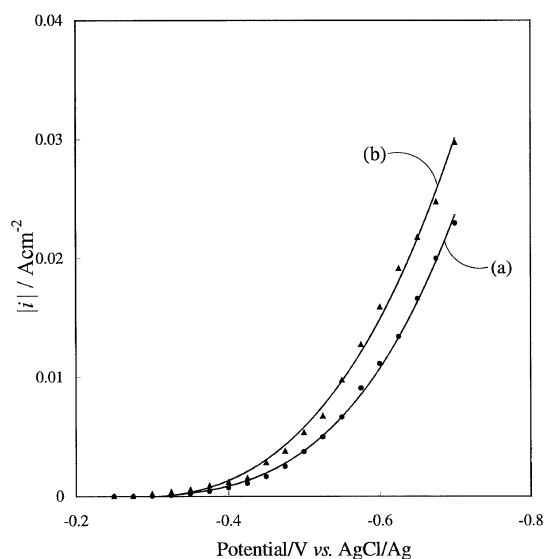


Figure 2. *i*-V relationship for evolution of H₂ from an aqueous solution of 0.5 M H₂SO₄. Curve a (●): data for bare platinum electrode. Curve b (▲): data for P4HepBTz-modified platinum electrode. Amount of P4HepBTz = 0.046 mg / 0.30 cm² or 0.015 mg cm⁻². Measured under N₂ at 25°C.

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 mg (2.5 × 10⁻⁴ mmol of the thiazole unit) of P4HepBTz)/(0.30 cm² 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 mg of P4HepBTz)/(0.30 cm² 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-5,8-diyl),¹¹ poly(2-methylantraquinone-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 to H⁺. Among *n*-dopable π-conjugated polymers, 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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