Preparation of Microparticle Palladium Incorporating Poly[*N*-(5-hydroxypentyl) pyrrole] Film-Coated Electrode

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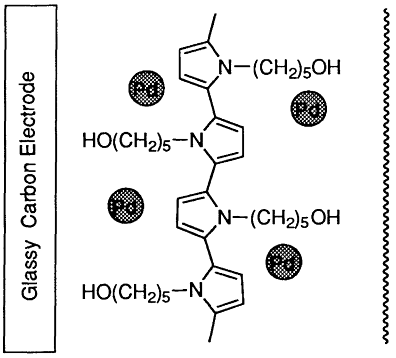
The preparation of the palladium microparticles incorporated poly [*N*-(5-hydroxypentyl) pyrrole] film-coated electrode is described. This electrode exhibited catalytic activity with regard to the hydrogenation of acetylene compound.

Recent recognition of the importance of using recyclable metal catalysts in environmentally benign synthesis has evoked a renewed interest in polymer immobilized catalysts. On the other hand, many developments of the organic polymer coated electrodes, which are useful in the electrochemically catalytic reaction have been carried out in recent years.[1] Furthermore a few conducting polymers have been also used for the immobilization of metal catalysts.[2] In this paper we describe the preparation and characteristic of a new conducting polymer catalytic electrode that incorporates fine palladium particles at which hydrogenation occurs. The catalytic activities of this polymer electrode in the hydrogenation of unsaturated compound will be shown.



The *N*-(5-hydroxypentyl) pyrrole monomer (PAPy)[3] was prepared according to literature method.[4] The polymer film (PPAPy) onto a polished glassy carbon disk (0.071 cm^2) or plate (4.5 cm^2) surface was coated by the cyclic voltammetry or the controlled-potential electrolysis at +1.10 V vs. SCE in the acetonitrile solution of 10 mmol dm^{-3} monomers containing 0.1 mol dm^{-3} Bu_4NBF_4 as a supporting electrolyte. The PPAPy film-coated electrode was immersed in 50 mmol dm^{-3} Na_2PdCl_4 solution for 30 min. and rinsed by water several times. The palladium metal deposition in film was carried out by the electroreduction at -0.30 V in 0.1 mol dm^{-3} KCl solution. The quantity of incorporated palladium metal in films was calculated based on electricity during the electroreduction of $PdCl_4^{2-}$ to Pd^0. The current-voltage curves were measured by a linear sweep potential method. The observation of cathodic current for hydrogen evolution of the PPAPy (Pd) film electrode and the electrolysis of acetylene compound were performed under the controlled-potential condition at -0.4 V in 0.1 mol dm^{-3} HCl buffer solution (pH = 1) containing 50% ethanol.

The polymer film was easily coated under the relatively lower electrolysis potential condition, *ca.* +1V on a glassy carbon electrode surface by the anodic oxidation of 10 mmol dm^{-3} PAPy monomer in acetonitrile containing 0.1 mol dm^{-3} Bu_4NBF_4. This thin polymer film was smooth and strongly adhered on the glassy carbon electrode. As shown in Figure 1 the cyclic voltammograms of the PPAPy film electrode showed at about +0.6 V a reversible redox peak current couple, which is characteristic for conducting polymer. This peak current couple is based on doping-dedoping of anion, BF_4^- in the film.

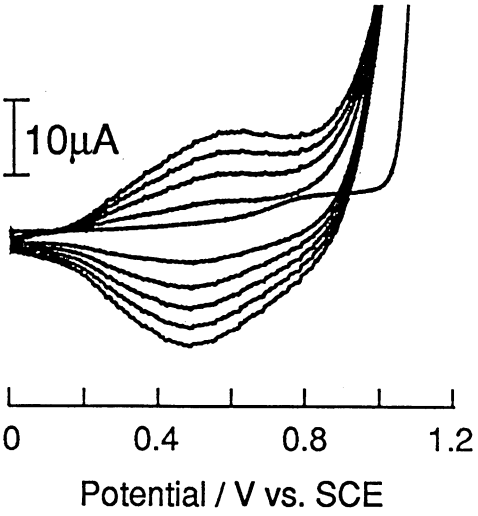


Figure 1. Cyclic voltammograms of 10 mmol dm^{-3} PAPy on the glassy carbon disk electrode in 0.1 mol dm^{-3} Bu_4NBF_4-CH_3CN, scan rate 100 mV s^{-1}.

The incorporation of palladium metals into the hydrophilic polymer film electrodes was achieved by immersion treatment in Na_2PdCl_4 solution, followed by the electrochemical reduction of permeated tetrachloropalladium ion, $PdCl_4^{2-}$ in the films. In the case of the disk film electrode (the passed electricity for anodically polymerization, Q = 10 mC), the palladium metal was incorporated *ca.* 9.3 μg cm^{-2} in the PPAPy film. This incorporated amount was proportional to the thickness of coated film. The palladium metals can clearly be observed as microparticles with *ca.* 0.3 μm in diameters on the PPAPy (Pd) film electrode surface by the scanning electron microscopy (SEM) as shown in Figure 2.

The increase of cathodic current based on hydrogen evolution is clearly observed at ca. -0.2 V, when the resulting PPAPy (Pd) film electrode is subject to potentiostatic sweeping in aqueous ethanol solution (Figure 3).

In order to test the stability and the catalytic activity of the PPAPy (Pd) film electrode, we observed the variation in the cathodic current with electrolysis time by potentiostatic

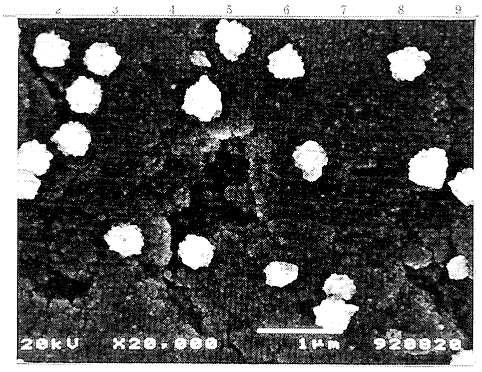


Figure 2. SEM photograph of PPAPy (Pd) film plate electrode surface.

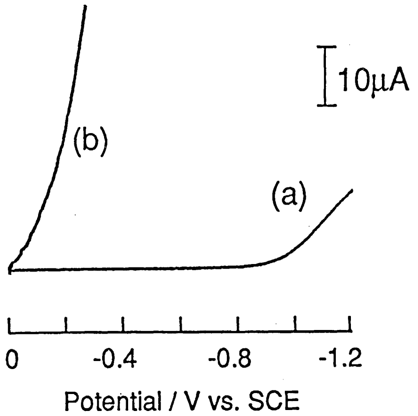


Figure 3. Cathodic current-voltage curves for hydrogen evolution in 0.1 mol dm^{-3} HCl buffer solution (pH = 1) containing 50 % ethanol, scan rate 100 mV s^{-1}.
(a) : PPAPy film, (b) : PPAPy (Pd) film disk electrode.

examination in aqueous solution. As shown in Figure 4, the PPAPy (Pd) film plate electrode showed a remarkable stability over 100 hours and the current density for hydrogen evolution was maintained at *ca.* 0.07 mA cm^{-2}. In particular, there was no peeling of film from the glassy carbon surface, which was observed in the case of unsubstituted polypyrrole film. This was probably because of the strongly interaction of hydroxyl groups of polypyrrole with the glassy carbon surface.

For the purpose of investigation of electrocatalytic hydrogenating possibility for unsaturated organic compounds, the reduction of diphenylacetylene was also carried out by semi-microscale electrolysis in aqueous ethanol solution. Diphenylacetylene (25 μmol) significantly decreased after 4 hours (< 8 %). As hydrogenated products, *cis*-stilbene (1 %) and 1, 2-diphenylethane (91 %) were obtained and the catalytic ability of the resulting PPAPy (Pd) film electrode was confirmed. Further investigations in condition for electrocatalytic hydrogenation using PPAPy (Pd) film electrode are now in progress.

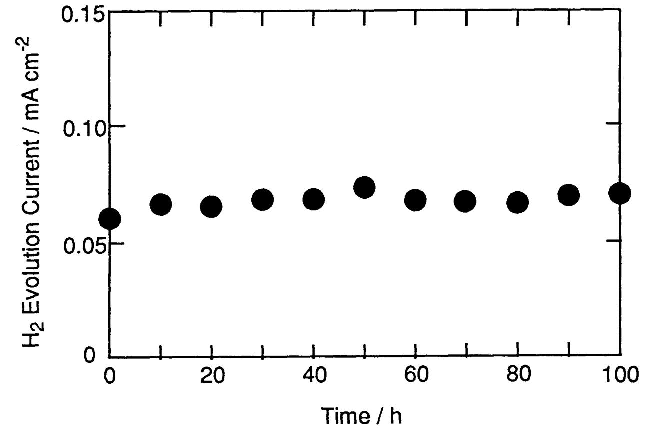


Figure 4. Hydrogen evolution current vs. electrolysis time on the PPAPy (Pd) film plate electrode (S = 4.5 cm^2) in 0.1 mol dm^{-3} HCl buffer solution (pH = 1) containing 50 % ethanol at -0.4 V vs. SCE

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References and Notes

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3 Bp 161~2 °C / 13 torr ; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.21~1.32 (m, 2H, CH_2), 1.43~1.53 (m, 2H, CH_2), 1.65~1.76 (m, 3H, CH_2 and OH), 3.51 (t, 2H, J = 6.5 Hz, CH_2-O), 3.80 (t, 2H, J = 7 Hz, >N-CH_2), 6.05 (t, 2H, J = 2 Hz, Pyrrole), 6.57 (t, 2H, J = 2 Hz, Pyrrole) ; ^{13}C NMR (68 MHz, $CDCl_3$) δ 120, 108, 63, 50, 32, 31, 23 ; IR (neat) 3355, 2936, 2865, 1501, 1453, 1360, 1281, 1090, 1061, 725, 617 cm^{-1}.

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