Electrocatalytic Hydrogenation of Organic Compounds on a Poly[*N*-(5-hydroxypentyl)pyrrole] Film-Coated Electrode Incorporating Palladium Microparticles

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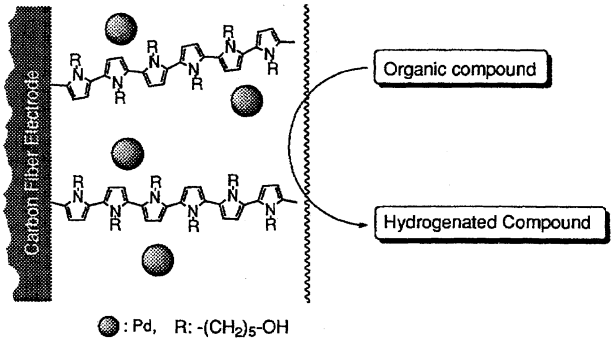
A poly[*N*-(5-hydroxypentyl)pyrrole] film-coated carbon-fiber electrode incorporating palladium metal microparticles was prepared and the catalytic ability in the electrochemical hydrogenation of organic compounds was investigated. This electrode exhibited a high catalytic ability and a strong physical stability with respect to hydrogen evolution. By using this electrode, the electrocatalytic hydrogenation for organic compounds in an organic solvent–buffer solution led to an efficient formation of hydrogenated products, such as saturated compounds, amino compounds, and hydroxy compounds, in high yields and current efficiencies. Furthermore, a catalytic polymer film electrode was successfully applied to the hydrogenative deprotection of a benzyl group and the dehalogenation of bromobenzene in electroreduction media.

Catalytic metal incorporated in polymer-coated electrodes has been accepted to have potential applications in electrocatalytic reactions.[1] On the other hand, recently, conducting polymers have been noted to be new coating materials.[2] The electrohydrogenation of organic compounds using poly(viologen-linked pyrrole) film modified catalytic electrodes has been reported by Moutet and co-workers.[3] We have also demonstrated the preparation of a new catalytic polymer film electrode, as discussed in a previous paper.[4] This electrode is coated with a poly[*N*-(5-hydroxypentyl)pyrrole] film (P5HPy) and incorporates fine small palladium catalysts. We report herein on the synthetic application of a P5HPy-coated carbon-fiber electrode incorporating palladium metal microparticles for the hydrogenation of organic compounds, such as diphenylacetylene, 2-cyclohexen-1-one, nitrobenzene, 1,4-benzoquinone, methyl benzoylformate, benzyl benzoate, and bromobenzene (Scheme 1).

Experimental

General. The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 spectrometer. IR spectra were recorded on a JEOL JIR-DIAMOND 20 FT-IR spectrophotometer. A high-performance liquid-chromatographic analysis (HPLC) was performed on a GL Sciences Inertsil ODS-2 column (2.1 mm inner diameter×250 mm length) with a system comprising a Shimadzu LC-5A pump and a SPD-2AM UV spectrophotometric detector. Gas-chromatographic analyses (GC) were carried out with a GL Sciences GC-380 instrument equipped with a GL Sciences TC-WAX capillary column (0.53 mm inner diameter×15 m length). The electrode surfaces were examined using a JEOL JSM-6320F scanning electron microscope (SEM).



Scheme 1.

Preparation of Monomer. *N*-(5-Hydroxypentyl)pyrrole monomer (5HPy) was prepared according to a literature method[5] involving the palladium-catalyzed cyclization of 2-butene-1,4-diol with 5-amino-1-pentanol: Bp 161—162 °C/13 Torr (1 Torr = 133.322 Pa) ; ^{1}H NMR ($CDCl_3$) 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 $H_{3,4}$), 6.57 (t, 2H, J = 2 Hz, Pyrrole $H_{2,5}$); ^{13}C NMR ($CDCl_3$) δ = 120, 108, 63, 50, 32, 31, 23; IR (neat) ν 3355, 2936, 2865, 1501, 1453, 1360, 1281, 1090, 1061, 725, 617 cm^{-1}.

Preparation of a Catalytic Polymer Film Electrode. The electrolysis experiments and electricity measurements were carried out with a Nikko Keisoku NPGS-2501 potentiogalvanostat and a NDCM-4 digital coulomb meter. The P5HPy on the bundle of a carbon-fiber (Asahi Kasei Carbon Fiber CO., Ltd., Hi-Carbolon-3KS, Surface area, S = 37 cm^2) surface was coated by controlled-potential electrolysis at 1.10 V vs. SCE in an acetonitrile solution of 0.01 M (1 M = 1 mol dm^{-3}) 5HPy containing 0.1 M Bu_4NBF_4 as a supporting electrolyte. The passed electricity for electrochemical polymerization on the carbon fiber was 0.05C cm^{-2}. The P5HPy electrode was immersed in a 50 mM $Na_2[PdCl_4]$ aqueous solution for 30 min. and rinsed with water several times. The palladium metal deposition in the P5HPy was carried out by electroreduction at −0.30 V in a 0.1 M KCl solution. The quantity of incorporated palladium metal in the P5HPy was calculated based on the electricity during the electroreduction of $[PdCl_4]^{2-}$ to Pd^0. Current–voltage

curves for hydrogen evolution of the prepared P5HPy(Pd) electrode were measured by a linear sweep potential method in a 0.1 M HCl buffer solution (pH = 1.0) containing 50% ethanol. The Observation of current for hydrogen evolution of the prepared P5HPy(Pd) electrode was carried out by a controlled-potential electrolysis at −0.4 V in a 50% ethanol 0.1 M HCl buffer solution (pH = 1.0).

Voltammetric Measurement. For cyclic voltammetric measurements, a Nikko Keisoku NPGS-2501 potentiogalvanostat, an NFG-5 function generator, and a GRAPHTEC WX1200 XY-recorder were employed. A glass undivided cylindrical cell equipped with a platinum-wire auxiliary electrode (0.1×50 mm), a working electrode, and an SCE reference electrode was used for the measurements.

Electrolysis for Organic Compounds. Controlled-current electrolyses were carried out in a cylindrical two-compartment cell equipped with a platinum plate anode (2×3 cm), a catalytic polymer film cathode, and a glass filter diaphragm. After deaeration by argon electrochemical hydrogenation of organic compounds was performed in a buffer solution containing 50% organic solvent (10 ml) at room temperature under an argon atmosphere. When the substrate and/or products were of low boiling point, the electrochemical hydrogenation was run in a sealed cell. After the reaction came to an end, the electrolysis solution was neutralized with a 0.1 M potassium carbonate solution, and then extracted with ether. After the extract was washed with water several times and dried over anhydrous sodium sulfate, it was analyzed by GC and HPLC.

Results and Discussion

Catalytic Polymer Film Electrode. The polymer film, a P5HPy-coated electrode, was prepared by the electrooxidation of 10 mM monomer, 5HPy, at 1.10 V vs. SCE in an acetonitrile containing 0.1 M Bu_4NBF_4. For this electro-polymerization 0.05 C cm^{-2} of electricity was passed. In an acetonitrile solution containing 0.1 M Bu_4NBF_4 the cyclic voltammograms of the P5HPy electrode showed a reversible redox peak current couple, which is characteristic for a conducting polymer, as shown in Fig. 1. This peak-current couple is based on the doping–dedoping of an anion, $[BF_4]^-$, in the P5HPy. This shape of this peak couple did not change during 5 sweep cycling.

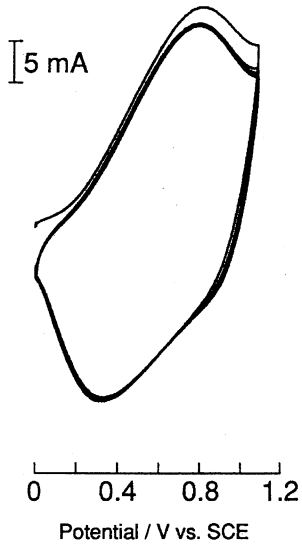


Fig. 1. Cyclic voltammograms of the P5HPy(Pd) electrode in a 0.1 M Bu_4NBF_4–acetonitrile. Scan rate = 100 m V s^{-1}.

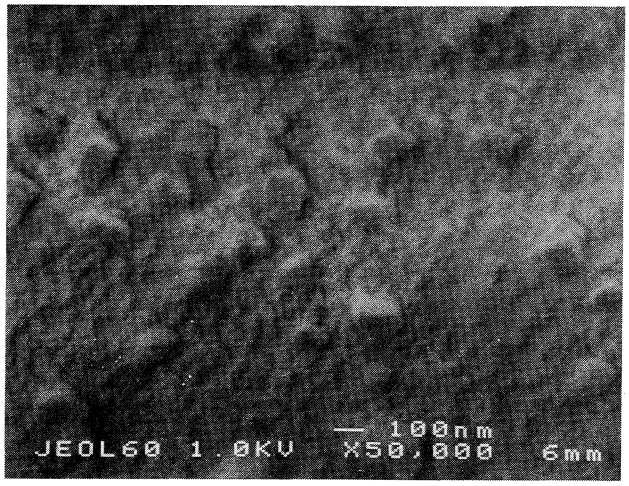


Fig. 2. SEM photograph of the P5HPy(Pd) electrode surface.

The resulting P5HPy electrode was dipped in a 50 mM $Na_2[PdCl_4]$ aqueous solution. The incorporation of palladium metal in the P5HPy was accomplished by the controlled-potential electrolysis technique in a KCl solution. The quantity of incorporated palladium metal (W_{Pd}) in this P5HPy could be calculated based on the electricity passed during the electroreduction of $[PdCl_4]^{2-}$. The incorporating palladium metals could be clearly observed as microparticles with ca. 0.1 μm in diameter on the catalytic polymer film, a P5HPy(Pd) electrode surface, by the SEM, as shown in Fig. 2.

An increase of in the cathodic current, based on hydrogen evolution, was clearly observed at ca. −0.3 V, when the resulting P5HPy(Pd) electrode was subjected to potentiostatic sweeping in an ethanol-containing aqueous solution (Fig. 3, a). The P5HPy electrode without incorporating palladium metal did not show any cathodic current for hydrogen evolu-

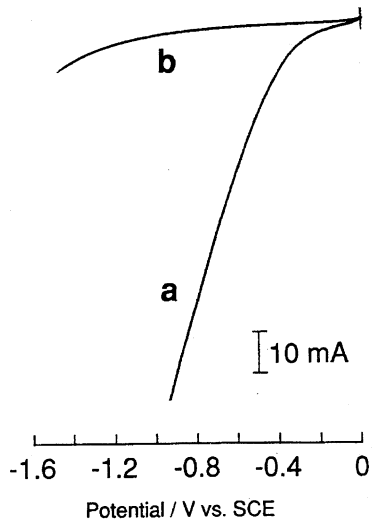


Fig. 3. Cathodic current–voltage curves for hydrogen evolution on the P5HPy(Pd) electrode (a) and the P5HPy electrode without incorporating of palladium metal (b) in a 0.1 M HCl buffer solution (pH = 1.0) containing 50% ethanol. Scan rate = 100 mV s^{-1}.

tion between 0 to −1.5 V (Fig. 3, b). The P5HPy(Pd) electrode showed remarkable stability for electrochemical hydrogenation experiments without peeling of the coated film from the carbon fiber surface. As shown in Fig. 4, although the current for hydrogen evolution in the controlled-potential electrolysis at −0.4 V decreased to ca. 0.3 mA cm^{-2} by half after 30 h, this electrode preserved sufficient catalytic activity in hydrogenation experiments. In the cyclic voltammetry of this P5HPy electrode in an anodic potential region, the shape of the reversible redox couple was also similar to that before the above-mentioned hydrogen evolution experiment. The physical stability of this electrode was probably due to the strong interaction of substituted hydroxy groups in the P5HPy with the carbon-fiber surface.

Electrocatalytic Hydrogenation of Organic Compounds. All of the electrocatalytic hydrogenation experiments for organic compounds were carried out in an organic solvent–buffer solution in a divided cell at room temperature. The electrohydrogenation of organic compounds was performed by controlled-current electrolysis as a simpler electrolysis technique. Using the P5HPy electrode without incorporating of palladium metal, the electroreduction of organic compounds at −1.0 V did not take place, indicating that they were not hydrogenated directly on the P5HPy electrode in a 50% ethanol–HCl buffer (pH = 1.0) solution.

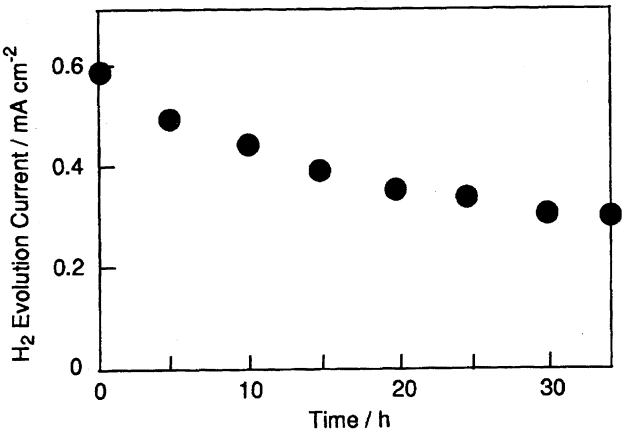


Fig. 4. Plots of current density for hydrogen evolution vs. time of controlled-potential electrolysis at −0.4 V vs. SCE on the P5HPy(Pd) electrode (S = 37 cm^2) in a 0.1 M HCl buffer solution (pH = 1.0) containing 50% ethanol.

As shown in Table 1, when the P5HPy(Pd) electrode containing palladium metal was applied to the electrohydrogenation of an unsaturated compound having a triple bond, diphenylacetylene provided 1, 2-diphenylethane via the formation of *cis*-stilbene in good yield and in high current efficiency (Entry 1). A decrease in the amount of palladium incorporated in the films almost left the efficiency of the reaction unaltered (Entry 2). As shown in Fig. 5, the diphenylacetylene had been almost completely consumed during the latter half of the reaction course, and the hydrogenation of the formed stilbene proceeded because the reactivity of stilbene is lower than that of diphenylacetylene. When the amount of the substrate increased, 1, 2-diphenylethane was obtained in quantitative yield and high current efficiency in 50% tetrahydrofuran (THF) instead of ethanol as an organic solvent used to dissolve (Entry 3). The ratio of the amount of the final product, 1, 2-diphenylethane, to the incorporated catalyst metal was greater than 100.

In a 50% ethanol–HCl buffer (pH = 1.0) solution, α,β-unsaturated carbonyl compound, 2-cyclohexen-1-one was converted into cyclohexanone by the selective hydrogenation of a double bond in the ring, without the formation of other products, such as cyclohexanol and 2-cyclohexen-1-ol (Entry 4). Nitrobenzene in an acidic solution was hydrogenated to the aniline in good yields (Entry 6). When the amount of passed current was low, the decrease in the yield and the current efficiency resulted in a large extension of the

Table 1. Electrocatalytic Hydrogenation of Organic Compounds on the P5HPy(Pd) Electrode in a 50% Ethanol–HCl Buffer (pH = 1) Solution[a)]

Entry	Substrate	Molecularity	W_{Pd}	Current	Time	Hydrogenation product	Yield[b)]	Current efficiency
		μmol	μmol	μA cm^{-2}	h		%	%
1	Diphenylacetylene	25	6.6	54	1.4	1,2-Diphenylethane	99	95
2	Diphenylacetylene	25	2.3	54	1.4	1,2-Diphenylethane	98	94
3	Diphenylacetylene	250[d)]	2.3	108	7.0	1,2-Diphenylethane	100	96
4	2-Cyclohexen-1-one	40	2.3	54	1.6	Cyclohexanone	99	66
5	Nitrobenzene	40	1.5	27	6.7	Aniline	84[c)]	81
6	Nitrobenzene	40	1.5	82	2.1	Aniline	100[c)]	100
7	1,4-Benzoquinone	40	1.5	20	2.9	Hydroquinone	100[c)]	100
8	Methyl benzoylformate	40	1.5	50	3.2	Methyl mandelate	97	35
9	Methyl benzoylformate	40	2.3	50	3.1	Methyl mandelate	98	37
10	Benzyl benzoate	40[e)]	1.5	25	8.0	Benzoic acid Toluene	100[c)] 99[c)]	29 29
11	Bromobenzene	40[e)]	1.5	50	2.0	Benzene	98[c)]	57

a) Electrolyses were carried out as described in the text. b) Yields were based on substrates and were determined by GC. c) Determined by HPLC. d) This reaction was run in a 50% THF–HCl buffer (pH = 1) solution. e) This reaction was run in a 50% ethanol–1/15 M phosphate buffer (pH = 7.0) solution.

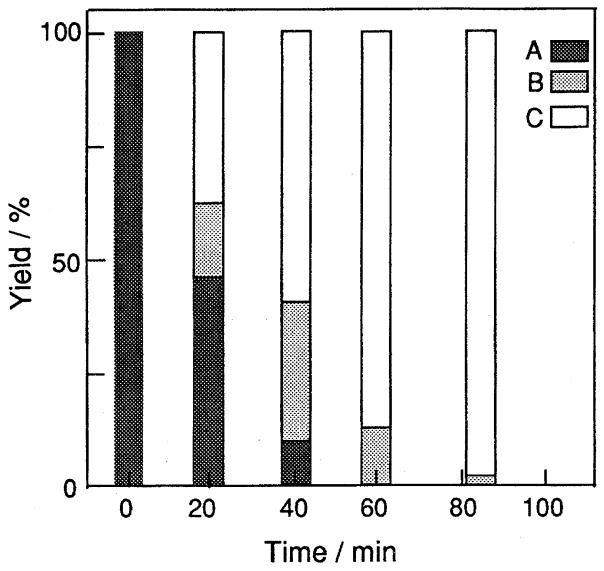


Fig. 5. Time course for the electrocatalytic hydrogenation of diphenylacetylene on the P5HPy(Pd) electrode in a 50% ethanol–0.1 M HCl buffer solution (pH = 1.0). Electrode: S=37 cm^2, W_{Pd}=2.3 μmol. Passed current, I=54 μA cm^{-2}. A : Diphenylacetylene (25 μmol); B : *cis*-Stilbene; C : 1, 2-Diphenylethane.

electrolysis time. The electrolysis of 1, 4-benzoquinone gave hydroquinone in spite of the low amount of passed current in almost quantitative yields and high current efficiencies (Entry 7). Although methyl benzoylformate was also hydrogenated to methyl mandelate as a corresponding alcoholic compound in good yields, the current efficiency was very low (Entry 8 and 9).

Furthermore, the P5HPy(Pd) electrode was applied to the electrochemical removal of a carboxyl-protecting group. Although the hydrogenation of benzyl benzoate under mild conditions in a 50% ethanol–phosphate buffer solution (pH=7.0) produced benzoic acid and toluene in equal yield, the current efficiencies were poor (Entry 10). This reaction took a long time to complete because both the rate of hydrogen production and substrate hydrogenation on catalysts were slow. The electrohydrogenative removal of the benzyl group proceeded selectively without producing benzyl alcohol, which is produced under acidic conditions.

We also tried an experiment for the dehalogenation of an aromatic halogenated compound. Bromobenzene was debrominated by electrohydrogenation under mild conditions in a 50% ethanol–phosphate buffer solution (pH = 7.0) to benzene in high yield (Entry 11). Although dehalogenations usually proceeds under basic conditions,[6] it was suggested from this result that dehalogenations take place even under neutral conditions.

Conclusion

A poly[*N*-(5-hydroxypentyl)pyrrole] conducting polymer film, P5HPy, was coated by electrooxidative polymerization on carbon fiber, and palladium metal microparticles were incorporated into the film by electroreduction. The resulting catalytic polymer film, a P5HPy(Pd) electrode, exhibited a high catalytic ability and physical stability. This electrode could be applied to not only hydrogenation for an unsaturated compound, nitro compound, quinone, and carbonyl compound, but also to removing a carboxyl-protecting group and the dehalogenation of an aromatic halogenated compound. Electrohydrogenation for organic compounds using the P5HPy(Pd) electrode provided corresponding products in both high yields and high efficiencies.

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