Bull. Chem. Soc. Jpn., 73, 745—746 (2000)

Electrochemical Hydrogenation of Organic Compounds on Poly[*N*-(5-carboxyhexyl)pyrrole] Film-Coated Electrodes Incorporating Palladium

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(Received September 6, 1999)

Poly[*N*-(5-carboxyhexyl)pyrrole] coated carbon-fiber electrodes incorporating palladium metal were prepared for the electrocatalytic hydrogenation of methyl α-oxobenzeneacetate, 2-cyclohexen-1-one, and diphenylacetylene in an ethanol-buffer solution. The reactions using these electrodes proceeded smoothly to give hydrogenated products in good yields.

Conducting polymers have recently been suggested as new coating materials on electrode surfaces.[1] The electrohydrogenation of organic compounds using substituted polypyrrole modified electrodes as catalysts has been reported in Moutet's[2] and our papers[3] previously. Furthermore, we have also demonstrated the preparation of new film electrodes which were coated with poly[*N*-(carboxyalkyl)pyrrole] films.[4] However, these electrodes have never been applied to the hydrogenation catalysts of organic compounds. The effect of film having a carboxylic acid group has not been clarified either. In the present work, we describe syntheses of poly[*N*-(5-carboxyhexyl)pyrrole] (PCHPy) film-coated electrodes incorporating palladium metal microparticles by using carbon-fiber having a wider surface area and we report their catalytic activity in the hydrogenation of methyl α-oxobenzeneacetate, 2-cyclohexen-1-one, and diphenylacetylene (Fig. 1).

The PCHPy film on a carbon-fiber ($S = 37$ cm^2) was prepared by controlled-potential electrolysis (CPE) at 1.10 V vs. SCE in an acetonitrile solution of 10 mM (mM=mmol dm^{-3}) *N*-(5-carboxyhexyl) pyrrole (CHPy) containing 0.1 M tetrabutylammonium tetrafluoroborate. During the electropolymerization, 1.85 C (50 mC cm^{-2}) of electricity was passed. The resulting PCHPy film electrode was immersed in a 50 mM sodium tetrachloropalladate(II) aqueous solution for 30 min and tetrachloropalladate dianions were permeated in the film. The electroreductive deposition of palladium metal ($W_{Pd} = 1.5$ μmol) in the film was carried out by the CPE or controlled-current electrolysis (CCE) in a 0.1 M potassium

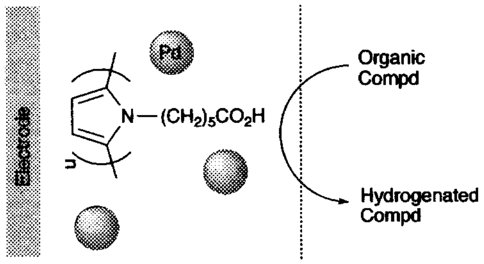

Fig. 1. The electrocatalytic hydrogenation on the PCHPy-(Pd) electrodes.

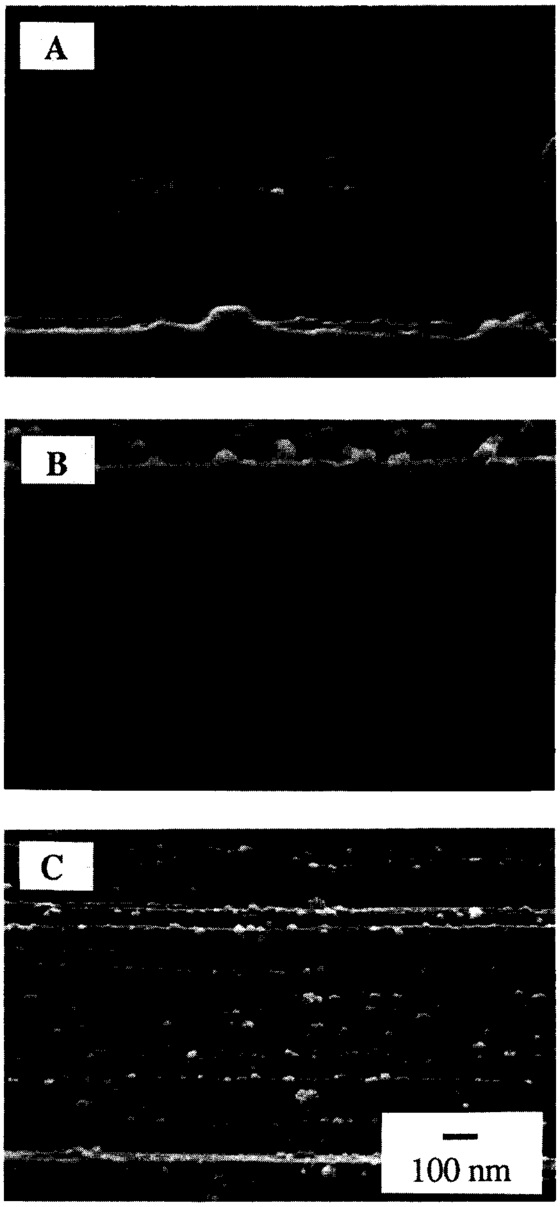

Fig. 2. The scanning electron micrographs on the surface of PCHPy(Pd) electrodes. A) Palladium metal was deposited by CPE ($E_p = -0.3$ V). B) CCE (Current density = 27 μA cm^{-2}). C) CCE (270 μA cm^{-2}).

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

Entry No.	PCHPy(Pd) electrode[a)]	D[b)] nm	Substrate[c)]	Time[d)] h	Product	Yield[e)] %	C.E.[f)] %
1	A	30—100	Methylα-oxobenzeneacetate	3.5	Methyl mandelate	55	42
2	B	20—80	Methylα-oxobenzeneacetate	3.5	Methyl mandelate	78	60
3	C	10—60	Methylα-oxobenzeneacetate	3.5	Methyl mandelate	92	70
4	C	10—60	2-Cyclohexen-1-one	3.5	Cyclohexanone	80	61
5	C	10—60	Diphenylacetylene	6.3	1,2-Diphenylethane	98	83

a) Film electrodes were prepared by the method as described in the text. b) Particle size of palladium metal on the surface of PCHPy(Pd) electrode. c) Molecularity of substrate is 50 μmol. d) Controlled-current electrolysis (27 μA cm^{-2}). e) Determined by gas chromatography. f) Current efficiency.

chloride solution. In the PCHPy(Pd)-A electrode, the palladium metal was deposited by the CPE at −0.30 V. The PCHPy(Pd)-B and -C electrodes were prepared by the CCE at 27 and 270 μA cm^{-2} at current densities, respectively.

The incorporated palladium metals could be observed as microparticles on a film electrode surface by the scanning electron microscope, as shown in Fig. 2. The particle size on the PCHPy(Pd)-A electrode surface varies over ca. 30—100 nm in diameter (Fig. 2A). In the PCHPy(Pd)-B and -C electrodes, an increase of the depositioning current density clearly resulted in a decrease in the particle size of palladium metals (Figs. 2B and 2C).

In all film electrodes, a cathodic current based on hydrogen evolution was observed at ca. −0.4 V in an aqueous ethanol solution. These electrodes showed remarkable stability for electrochemical hydrogenation experiments without peeling of the coated film. The physical stability of the electrodes is probably due to the strong interaction of substituted carboxyl groups in the film with the carbon-fiber surface.

The electrohydrogenation reactions of organic compounds were performed by the CCE (27 μA cm^{-2}). As shown in Table 1, using three film electrodes methyl α-oxobenzeneacetate was hydrogenated to methyl mandelate (Entries 1, 2, and 3). In the case of PCHPy(Pd)-C electrode, the electrohydrogenation proceeded with the highest current efficiency to give the product in the highest yield. These results suggest that a decrease in the particle size (D) of the metal catalyst results in an increase of its surface area, which consequently promotes the hydrogenation on the catalyst. The PCHPy(Pd)-C electrode was also applied to the reaction of an α, β-unsaturated carbonyl compound, 2-cyclohexen-1-one, which was converted to 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). Furthermore, the electrohydrogenation of diphenylacetylene having a triple bond provided 1, 2-diphenylethane with high current efficiency (Entry 5).

The catalytic activity of these film electrodes for the electrohydrogenation was about three times that of the poly [*N*-(hydroxyalkyl) pyrrole] film-coated electrodes.[3]

Experimental

CHPy was prepared according to a previous paper.[4] The preparation of film electrodes, cyclic voltammetric measurements, and electrolysis experiments were carried out as explained in our previous paper.[3] The surface of prepared film electrodes was examined using a scanning electron microscope (JEOL JSM-6320F). Electrolysis was carried out in a cylindrical two-compartment cell equipped with a platinum anode (2×3×0.01 cm), a film cathode, and a glass filter diaphragm. After argon gas deaeration, electrolysis was performed in 10 ml of a 50% ethanol–hydrochloric acid buffer solution (pH = 1) containing 50 μmol substrate at a room temperature. The electrolysis solution was treated in the ordinary manner and was analyzed in a gas-chromatograph (GL Sciences GC-380).

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