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Electrochemical Studies of Poly(mercaptohydroquinone) and Poly(mercapto-*p*-benzoquinone) Film Prepared by Electrochemical Polymerization. IV. Preparation of Palladium Microparticles on the Polymer Film

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The electrodeposition of Pd at microgram levels onto an electroconductive poly(hydroquinone/*p*-benzoquinone) film-coated glassy carbon electrodes is described. The polymer films were chemically modified with Pd pyridine complex and/or with Pd thiolate prior to the Pd electrodeposition. Controlled-potential electrolysis was applied to form Pd microparticles on the polymer film from an acid $PdCl_2$ solution. The nucleation/growth of Pd microparticles was largely promoted by these chemical modifications. The Pd particles on the pyridine complex-modified electrode were closely dispersed and were spherically shaped, while on the thiolate-modified electrode the Pd deposits were irregular in shape. Both the electrodes thus prepared exhibited high activity toward the generation of hydrogen and had good stability in acidic solution.

The electrodeposition of metal microparticles onto polymer films has both scientific and technological importances. In the last decade, many investigations[1] have been intensively carried out using various types of polymers coated on glassy carbon (GC) electrodes. Oyama and Anson[2] showed that poly(vinylpyridine) film could effectively bind transition metal complexes. Recently Bartak et al.[3] reported the electrodeposition of platinum microparticles on three types of poly(4-vinylpyridine) films on GC electrode surface. In a previous paper[4] we reported the preparation of an electroconductive (hydroquinone/*p*-benzoquinone) (SQ) film by an electrooxidation of mercaptohydroquinone. We could attach mercapto group and/or pyridine ring onto an SQ film by means of their addition reactions to the quinone moiety in the SQ film. Mercapto group and pyridine ring can fix a variety of metal ions by forming thiolates and pyridine complexes, respectively. We report here on the nucleation/growth of palladium, on SQ films chemically modified with either Pd thiolate or Pd pyridine complex prior to the Pd electrodeposition and on SQ films without such chemical modifications, by the electroreduction of palladium chloride.

Experimental

Chemicals and Fixation of Pd in SQ Film. Mercaptohydroquinone was synthesized and purified according to the method described in our previous paper.[4] The chemicals used for the synthesis of mercaphohydroquinone were of reagent grade. The palladium chloride used for the electrodeposition and the other inorganic reagents were of reagent grade and used without further purification. The substrate electrode used was a GC electrode 3 mm in diameter. Before polymer coating, the GC electrode was first polished successively with 5.0 and 0.3 μm alumina (Buehler Co.) and then subjected to an ultrasonic cleaning with deionized water for at least 10 min to remove any residual alumina off the surface. The SQ film on the GC electrode was prepared by anodic polymerization of 1 mM (1 M=1 mol dm^{-3}) mercaptohydroquinone at a constant potential of +0.5 V vs. saturated calomel electrode (SCE) in a Britton–Robinson buffer solution of pH 5.0 containing 20 vol% ethanol. The SQ film-coated GC electrode was placed in a Britton–Robinson buffer solution of pH 5.0 containing either 2 mM 4-mercaptopyridine or 2 mM sodium hydrogensulfide under a nitrogen atmosphere for 3 h in order to introduce the mercaptopyridine or the mercapto group, respectively, to the quinone ring in the SQ film. After washing with a large amount of deionized water, the electrode was put in 1 M hydrochloric acid solution containing 0.4 mM palladium chloride in order to form either Pd pyridine complex or Pd thiolate. In this paper, the Pd pyridine complex-modified GC electrode and the Pd thiolate-modified one are referred to as SQ-Py-Pd and SQ-S-Pd, respectively.

Apparatus and Procedures. The apparatus used for the preparation of SQ film on the GC electrode has previously been described.[4] An SCE was used as a reference electrode and all potential values cited in this paper are those referred to the SCE. A controlled-potential electrolysis at −0.1 V was applied to disperse Pd deposit onto both the SQ-Py-Pd and the SQ-S-Pd from a still solution containing 1 M hydrochloric acid and 0.4 mM palladium chloride. The amount of Pd deposit was quantitated from the total charge consumed during the electrochemical process by assuming 100% current efficiency and ignoring a slight amount of the Pd fixed by forming the thiolate and/or the pyridine complex prior to the electrodeposition. Electrode surfaces before and after the electrodeposition were examined by using a scanning electron microscope (SEM) (JEOL JSM-35C). The elemental identity of the deposit was determined with an electron spectroscopy for chemical analysis (ESCA) (Shimadzu ASIX-1000). The surfaces of sample electrodes were washed with deionized water and air dried before ESCA analysis. Voltammetric measurements were carried out with a standard three-electrode system consisting of an SQ film-coated GC working electrode, a Pt plate counter electrode, and an SCE reference electrode having an agar bridge of saturated potassium chloride.

Results and Discussion

Pd Deposition onto SQ Film. An examination of the SQ film by SEM has revealed that the surface of the film is relatively smooth and pinhole free over the whole surface as shown in Fig. 1. The flim thickness was estimated to be ca. 2 μm from the SEM photograph of boundaries between the film and the GC electrode. The "real" SQ film under the electrodeposition will be more bulky and thicker than the SEM image of the SQ film which is air dried. Figure 2 shows the SQ surface image by SEM when the elecrodeposition was carried out for 10 min. Particlelike deposits having various sizes of less than 1 μm in diameter were visible on the surface with very little deposition. These microparticles were identified as Pd deposit by XPS analysis where two peaks based on Pd 3d could be obtained at 335 and 340 eV.

Pd Deposition onto SQ-Py-Pd. Any image of Pd particles was not found by SEM at magnification 5000 on the SQ-Py-Pd film before the electroreduction of palladium chloride, though XPS peaks based on Pd 3d could been obtained. After an electrodeposition for 30 s, obscure Pd ultramicroparticle images ca. 500—700 Å in diameter could be observed by SEM at a higher magnification (Fig. 3). The image size grew with deposition time and after 6 min spherical Pd microparticles of nearly equal size, ca. 1000 Å in diameter, were closely packed together throughout the surface of the SQ-Py-Pd film (Figs. 4-(a) and -(b)). A variation in the brightness of the particle images was observed on the Pd microparticles in Fig. 4-(b). The brightness variation seemed to be independent of the particle size. The darker images probably are particles buried in the SQ film. The particles continued to grow spherically with time and after ca. 7 min began to aggregate partially all over the film surface. In

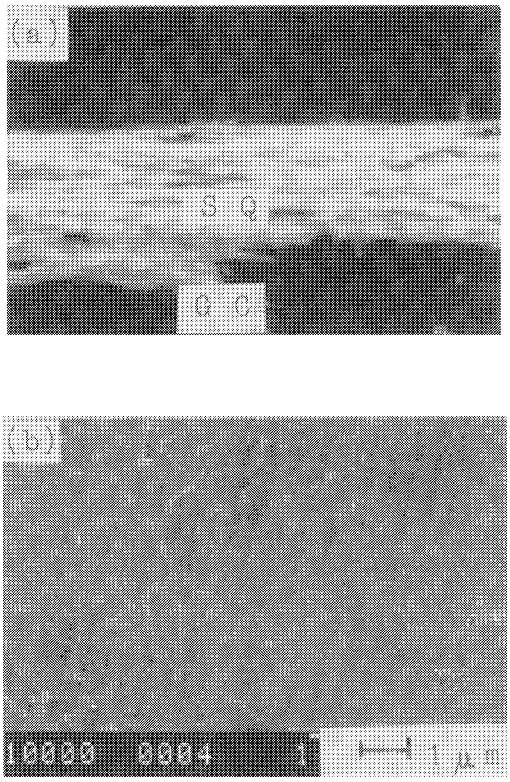

Fig. 1. SEM photograph of a vertical sectional view (a) and the surface (b) of the SQ film on the GC electrode. (a) and (b) are under the same magnification.

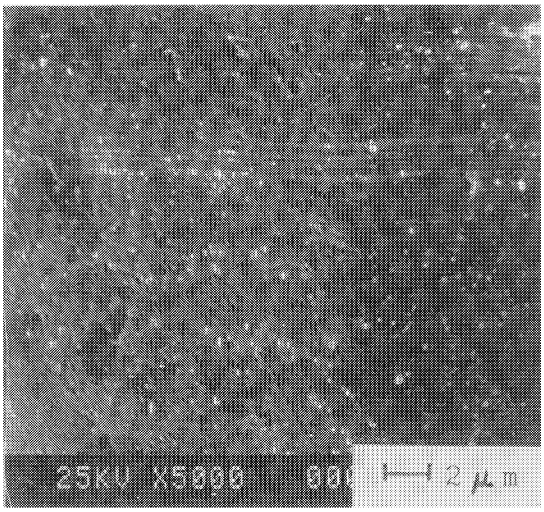

Fig. 2. SEM photograph of Pd microparticles deposited on the SQ film. The microparticles were prepared by the electroreducion of $PdCl_2$ at −0.1 V vs. SCE for 10 min at room temperature using a still 1 M HCl solution containing 0.4 mM $PdCl_2$

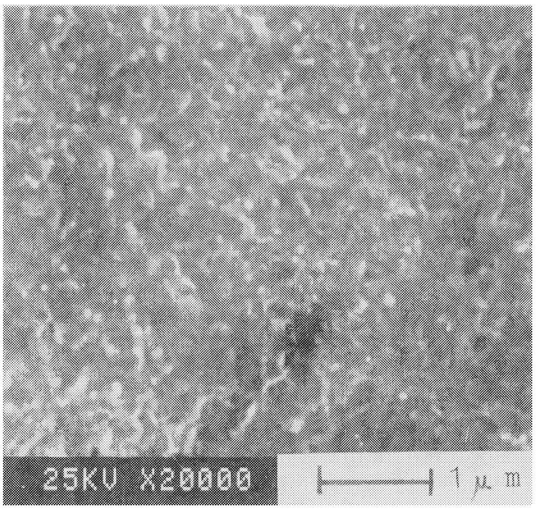

Fig. 3. SEM photograph of Pd ultramicroparticles deposited on the SQ-Py-Pd film. The ultramicroparticles were prepared by the electroreduction of $PdCl_2$ for 30 s. Other electrodeposition conditions were the same as those in Fig. 2.

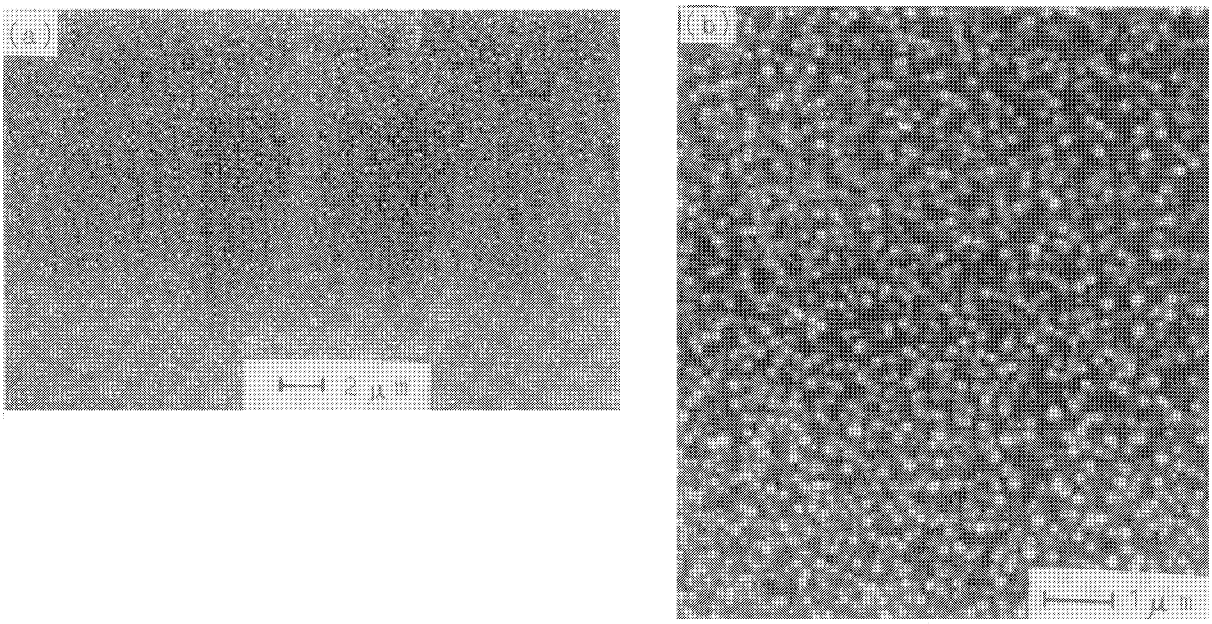

Fig. 4. SEM photograph (a) of Pd microparticles deposited on the SQ-Py-Pd film and an enlargement photograph (b) of (a). The microparticles were prepared by the electroreduction of $PdCl_2$ for 6 min. Other electrodeposition conditions were the same as those in Fig. 2.

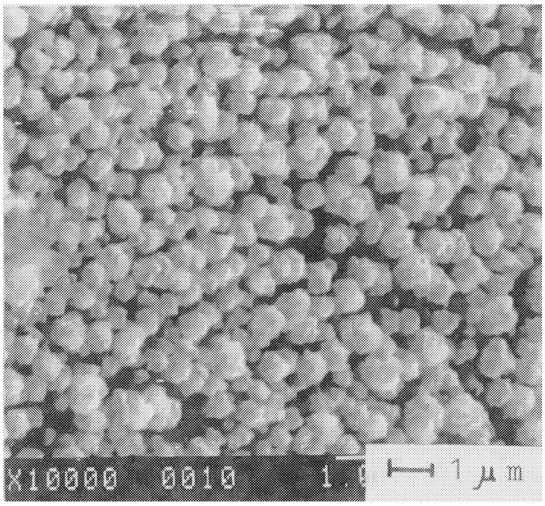

Fig. 5. SEM photograph of Pd particles deposited on the SQ-Py-Pd film. The particles were prepared by the electroreducion of $PdCl_2$ under a slow stirring of the $PdCl_2$ solution. Other electrodeposition conditions were the same as those in Fig. 4.

addition, the nucleation/growth rate of the Pd microparticles seemed to be accelerated by stirring the palladium chloride solution. Figure 5 shows the grown Pd particles on the SQ-Py-Pd film after the electrodeposition for 6 min with a slow stirring. The deposits appear to be made up of aggregated polycrystalline particles or of coalesced particle clusters. The present deposits may be dispersed only two-dimensionally on the surface of the film because all the SEM particle images have nearly equal brightness. Further, it was also observed that an increase in the concentration of palladium chloride resulted in an increase in particle size for a given electrodeposition time. When 2-mercaptopyridine was used for fixing Pd instead of 4-mercaptopyridine, Pd microparticles of nearly equal size could be observed by SEM after an electrodeposition for 5 min under the same deposition conditions as those for the SQ-Py-Pd, though the particle population density appeared to be slightly lower.

Pd Deposition onto SQ-S-Pd. The surface of the SQ-S-Pd film became rougher and increased in brightness, especially at edges of cracks and projections on the film surface, with an increase in the electrodeposition time up to ca. 20 min. Figures 6 and 7 show SEM photographs of surface images of the SQ-S-Pd film after 3 and 6 min, respectively. Any spherical Pd microparticles were observed on neither of them, though the XPS peaks based on Pd 3d appeared at the same binding energy levels as those for the SQ-Py-Pd. After a much longer time, 30 min, freshly deposited spherical Pd microparticles were observed on a rough surface of the film by SEM.

Electrochemical Characterization and Stability. Figure 8 shows a cyclic voltammogram illustrating the catalytic generation of hydrogen at the SQ-Py-Pd with a Pd loading of 8.2 μg cm^{-2} which was prepared by an electrodeposition for 6 min, in 1 M H_2SO_4. The cyclic voltammetric response in the range of +0.2 to +0.7 V is based on the redox reaction of the SQ film itself. A cathodic peak and an ill-defined anodic peak probably

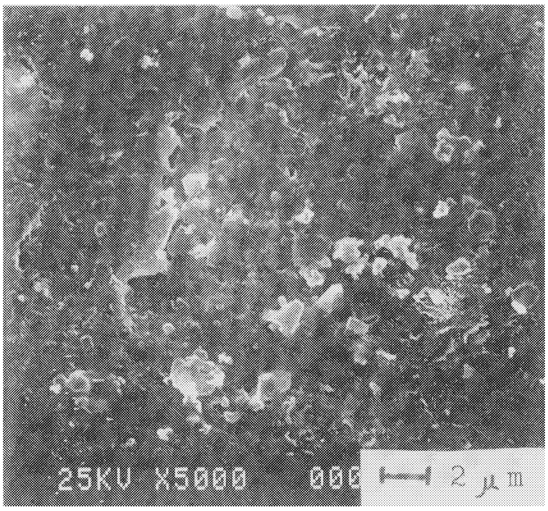

Fig. 6. SEM photograph of Pd deposits on the SQ-S-Pd film. The Pd deposits were prepared by the electrodeposition of $PdCl_2$ for 3 min. Other electrodeposition conditions were the same as those in Fig. 2.

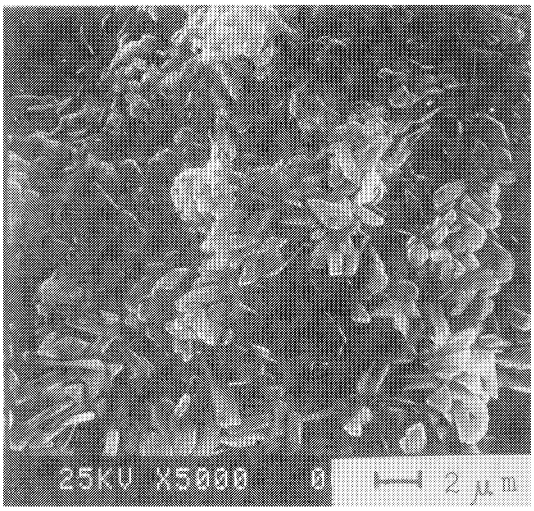

Fig. 7. SEM photograph of Pd deposits on the SQ-S-Pd film. The Pd deposits were prepared by the electroreduction of $PdCl_2$ for 6 min.

based on the adsorption-desorption of hydrogen appeared at −0.22 and in the range of +0.04 to −0.05 V, respectively, and increased in height with electrodeposition time up to ca. 6 min and then gradually decreased. On the other hand, these waves based on the adsorption/desorption of hydrogen were observed to be comparatively small in size on the SQ-S-Pd having a nearly equal amount of Pd loading.

The logarithm of the cathodic current for H_2 evolution was plotted vs. the potential up to the overpotential of ca. 150 mV (Tafel plot). The linear portion of each Tafel plot was extrapolated to the current axis to determine the exchange current. The exchange current density, I_0, appeared to increase up to some critical value with increasing Pd loading on both of the SQ-Py-Pd and the SQ-S-Pd. The I_0 values vs. Pd loading levels are listed in Table 1. The I_0 value on the SQ-Py-Pd with a Pd loading of 8.2 μg cm^{-2} is of the same order of magnitude or larger than the literature value[5] of ca. 1 mA cm^{-2} for smooth Pd in 1 M H_2SO_4. Due to the increasing roughness of the SQ film surface with depositing Pd, all I_0 values listed here are reported on the basis of the GC surface area.

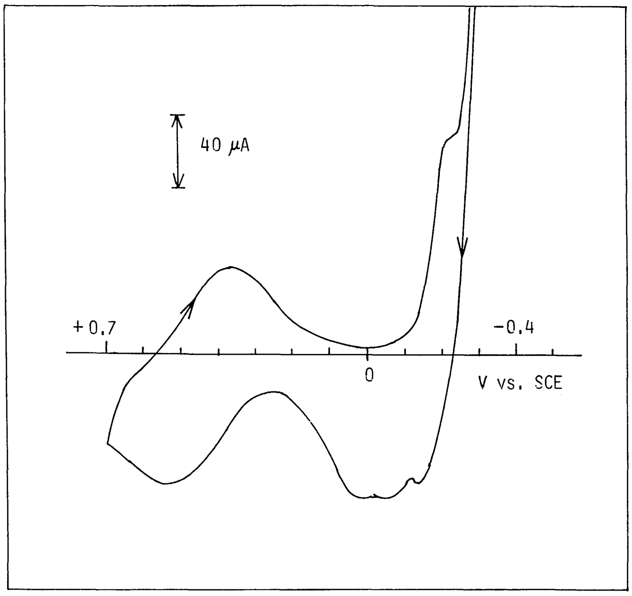

Fig. 8. Cyclic voltammogram for hydrogen evolution at the SQ-Py-Pd having a Pd loading level of 8.2 μg cm^{-2} in a 1 M H_2SO_4 aqueous solution in a N_2 atmosphere at room temperature. The electode used here is the same as that of Fig. 4. Scan rate: 50 mV s^{-1}.

Table 1 shows that the electroreduction of palladium chloride on the SQ film is largely promoted through the palladium fixation in the film prior to the electrodeposition, that is to say, the fixed palladium may behave as an effective electroactive site toward the Pd electrodeposition. This estimation is also substantiated by the SEM analysis of the Pd microparticles electrodeposited on the film surface. Judging from the SEM photograph shown in Fig. 2 where the Pd microparticle images less than 1 μm in diameter were obseved on the surface of the SQ film having a thickness of ca. 2 μm, it is reasonable to assume that the Pd microparticles in Fig. 2 resulted from the electroreduction of palladium chloride on the SQ film rather than on the GC substrate electrode, that is to say, the hydroquinone moiety, an electroactive site in the film, may participate directly in the electroreduction of palladium chloride as well as the fixed Pd prior to the electrodeposition. Table 1 and the SEM analysis also suggest that the electroreduction reaction of palladium chloride on the Pd fixed in the film may

Table 1. Comparison of Pd Loading Levels and Exchange Current Densities (I_0) for Hydrogen Generation on the SQ-Py-Pd, SQ-S-Pd, and SQ films Coated on GC Electrodes

Electrode	Reduction average[a] current density	Deposition time	Loading level[b]	I_0
	A cm^{-2}	min	μg cm^{-2}	mA cm^{-2}
SQ-Py-Pd	41.5	6	8.2	1.4
SQ-S-Pd	38.5	6	7.6	0.8
SQ	18.5	6	3.6	—

a) Average values were obtained from ca. 10 trials. b) The loading levels of the total charge consumed during the electroreduction of $PdCl_2$ by assuming 100% current efficiency.

proceed more rapidly than that on the hydroquinone moiety in the film.

The nucleation step in electrocrystallization on metal surfaces is known to follow either simultaneous or progressive nucleation.[6] In the simultaneous nucleation, many nuclei are formed at nearly the same time with a short induction time, and then these nuclei grow similarly in size. In the progressive nucleation, nuclei are formed over a range of time and grow to produce metal crystals having a variety of sizes. The Pd nucleation/growth on the SQ-Py-Pd film appears to follow the simultaneous nucleation judging from the SEM analysis, while on the SQ-S-Pd film the aggregation of nuclei will occur at relatively early nucleation step and grow progressively to form various shapes of Pd deposits as shown in Fig. 7, because the Pd nuclei strongly bound by a covalent bond will not be torn from the fixed site but grow in size. The detailed mechanism which can explain the present serious difference in the Pd nucleation/growth between the SQ-Py-Pd and the SQ-S-Pd, is obscure now. In order to clarify the mechanism, a more extensive investigation is in progress.

The long-term stability of these electrodes modified with Pd microparticles and/or Pd deposit was examined by continuous soaking in 1 M H_2SO_4 aqueous solution. There was observed neither appreciable peeling of the SQ film nor deterioration of the catalytic activity for hydrogen generation on the surfaces of these electrodes after 24 h of soaking in the above acidic solution. The stability of these electrodes for H_2 generation was tested by controlled potential electrolysis at −0.1 V for 1 h in the above acidic solution. Little change in appearance of the electrode surface was observed by SEM.

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