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Redox Reaction of Quinones at a Silver-Deposited Gold Electrode in Acetonitrile and Aqueous Solutions

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Silver-deposited gold electrodes were prepared in order to investigate the role of deposited silver onto a gold electrode in the electrochemical behavior of *p*-benzoquinone at the electrode. Using the electrodes as a working electrode, the electrochemical behavior of *p*-benzoquinones was examined in acetonitrile and aqueous solutions. In the acetonitrile solution, cyclic voltammograms for *p*-benzoquinone derivatives were measured and the relations between the potentials of the second-redox peak and the sum of Hammett's σ value were examined. A potential-pH diagram was obtained for *p*-bezoquinone in an aqueous solution. Both relations were also obtained at other solid electrodes. The mechanism for a redox reaction at a silver-deposited gold electrode was considered based on a comparison of the observation data at the electrode with different materials.

Biological substances have been widely studied electrochemically using solid electrodes. However, for many compounds, the electrochemical behavior at a solid electrode has often been affected by the condition of the electrode surface. This is sometimes ascribed to a poisonous substance adsorbed on the electrode, an unfavorable adsorptive orientation of redox species for electron transfer from an electrode, thermodynamically unfavored solvent structures around the electrode for electron transfer, and so on.[1–9] Accordingly, many different strategies have been employed to modify the electrode surface.[10–13] We found that an electrochemical pretreatment of the working electrode is effective for the oxidation of L-ascorbic acid.[14]

Quinone-hydroquinone redox systems have been studied extensively over many decades. Quinones comprise a redox reaction of classical and current importance to organic and biological chemistry, and represent one of the oldest and most basic redox processes.[15] They show a two-electron/two-proton redox process in aqueous solution, whereas a one-electron two-step process is observed separately in an aprotic solvent. Furthermore, quinone redox reactions are very sensitive to the condition of the electrode surface. Therefore, quinones can be employed as a probe system to investigate the effect of the electrode surface condition on redox reactions.

We found that the electrochemical behavior of *p*-benzoquinone was significantly affected by the addition of a trace amount of silver ion.[6] It is pointed out that the underpotential deposited silver onto the electrode should play an important role in the redox process of quinones. In this study, in order to investigate the role of deposited silver in the redox process, *E*–pH diagrams of *p*-benzoquinone were examined in aqueous solution and the electrochemical behaviors of quinone derivatives with different electron density in the quinone ring were measured in an acetonitrile solution, using the working electrodes of different materials involving a silver-deposited gold electrode.

Experimental

Materials and Solutions. The quinones used in this study were tetramethyl- (Tokyo Kasei), 2,5-dimethoxy- (Tokyo Kasei), 2,5-di-*tert*-butyl- (Tokyo Kasei), 2,5-dimethyl- (Tokyo Kasei), 2-methyl- (Wako), 2-chloro- (Aldrich), 2,5-dichloro- (Tokyo Kasei), tetrachloro-*p*-benzoquinone (Wako), and *p*-benzoquinone (Wako). 2-Methyl-*p*-benzoquinone was purified by sublimation and 2-chloro-*p*-benzoquinone was recrystalized twice from a water-ethanol mixture. Other quinones were used without further purification. All other reagents were of guaranteed grade and were used without further purification. Sodium sulfate and tetrabutylammonium hexafluorophosphate were used as a supporting electrolyte for electrochemical measurements at a concentration of 0.10 mol dm^{-3} in an aqueous solution and in an acetonitrile solution, respectively. For measurements in an aqueous solution, the pH of a sample solution was adjusted to 1.8 with sulfuric acid, whereas sulfate, acetate, and phosphate buffer systems were used at concentrations of 0.1 to 2.0 mol dm^{-3} for pH adjustment of the sample solutions in determining *E*–pH diagrams. All sample solutions were deaerated with nitrogen gas before each measurement.

Electrochemical Measurements. Electrochemical measurements were carried out by a BAS 100B/W electrochemical workstation using a three-electrode assembly. AgCl/Ag and Ag$^+$/Ag electrodes were used as a reference electrode in aqueous and acetonitrile solutions, respectively. An Ag$^+$/Ag electrode was customarily constructed with immersing a silver wire into a 0.01 mol dm^{-3} AgNO$_3$ acetonitrile solution, and was used by connecting with a sample solution through a liquid junction of an acetonitrile solution of 0.10 mol dm^{-3} tetrabutylammonium hexafluorophosphate. The counter electrode was a platinum coil. The working electrodes were a polycrystalline gold, silver, platinum, and palladium disk, and a glassy carbon disk with a diameter of 6 mm embedded in Teflon. Furthermore, silver-deposited gold electrodes were prepared as described below and were used as a working electrode. The working electrodes other than the silver-deposited gold electrodes were polished to a bright mirror finish with slurries of 1.0, 0.3, and 0.05 μm alumina powder, and washed by sonication for 5 min in 0.05 mol dm^{-3} sulfuric acid. Sweeps were initiated at 50 mV s^{-1} in the cathodic direction, unless otherwise noted.

The silver-deposited gold electrodes were prepared for measurements in aqueous and acetonitrile solutions, respectively, in the following way. For measurements in an aqueous solution, silver deposited at an underpotential (Ag-UPD) gold electrode was prepared by holding a gold electrode in an aqueous solution of 1.0×10^{-4} mol dm^{-3} $AgNO_3$ and a 0.10 mol dm^{-3} supporting electrolyte at 0.45 V vs (AgCl/Ag) for 500 s. The amount of deposited silver was calculated to be 6.8×10^{14} atoms from the charge on dissolution in Fig. 3-A and the coverage was estimated as less than half a monolayer from the charge density for one monolayer of Ag.[16–18] For measurements in an acetonitrile solution, on the other hand, Ag-UPD and bulk silver-deposited (bulk-Ag) gold electrodes were prepared by holding a gold electrode in an acetonitrile solution of 1.0×10^{-3} mol dm^{-3} $AgNO_3$ and a 0.10 mol dm^{-3} supporting electrolyte at 0.3 and -0.05 V vs (Ag^+/Ag), respectively, for 500 s.[19] The amount of deposited silver was calculated to be 1.1×10^{15} and 4.6×10^{15} atoms from the charge upon dissolution shown in Fig. 3-B for the Ag-UPD and bulk-Ag gold electrodes, respectively. The coverage was also estimated to be less than one monolayer and 2.5 layers for the Ag-UPD and bulk-Ag gold electrodes, respectively, as mentioned above.[16–18] These electrodes were washed with a solvent and used immediately for each measurement after the electrode was prepared. The conditions for preparing the electrodes are mentioned in the next section.

Results and Discussion

The addition of silver ion caused an anomaly in the electrochemical behavior of *p*-benzoquinone at a gold electrode.[6] In an aqueous solution, the addition of a trace amount of silver ion made the cyclic voltammogram to be more irreversible. It was demonstrated by the Ag-UPD gold electrode that the anomaly was ascribed to the deposited silver at an underpotential onto a gold electrode. In an acetonitrile solution, on the other hand, only the second waves were influenced, and their reversibility was gradually improved with increasing the concentration of silver ion added. The influence of the addition of silver ion in the acetonitrile solution was significantly different from that in an aqueous solution.[6] In order to clarify the influence of the deposited silver on the electrochemical behavior of quinones, the deposition feature of silver ion onto a gold electrode was re-examined in an aqueous solution, and was also investigate in an acetonitrile solution.

Silver-deposited gold electrodes were prepared by holding at various potentials in a manner similar to that mentioned in the experimental section. Differential pulse voltammograms of the dissolution of the deposited silver were measured for the prepared gold electrodes to determine the condition for preparing Ag-UPD and bulk-Ag gold electrodes in aqueous and acetonitrile solutions. Figure 1-A shows the voltammograms of dissolution of the deposited silver onto the gold electrode in an aqueous solution reported previously.[6] The voltammograms exhibited a dissolution peak of the deposited bulk-Ag at 0.43 V vs (AgCl/Ag), two obscured peaks for the dissolution of the Ag-UPD in the UPD region, and a peak for dissolution of the Ag-UPD overlapped with the surface-oxidation peak of the polycrystalline gold electrode at about 1.1 V vs (AgCl/Ag).[18,20,21] As can be seen from Fig. 1-A, the amount of deposited silver decreased with increasing the deposition potential and no dissolution of the bulk-Ag was observed for the gold electrode silver-deposited at more positive potentials. The voltammograms for the dissolution of the silver could be deconvoluted into the peak for the dissolution of the bulk-Ag and several peaks for the dissolution of the Ag-UPD by subtracting the residual current from the voltammograms and using the deconvolution program GRAMS/32, as shown in Fig. 2-A. These dissolution peaks of the Ag-UPD correspond to UPD of Ag on Au(111) surface or other Au surface.[16,22,23] The dissolution peaks of the Ag-UPD was difficult to deconvolute in the voltammograms at a more positive deposition potential. Thus, in order to obtain a tentative criterion for preparing bulk-Ag and the Ag-UPD gold electrodes, the peak areas for the dissolution of the bulk-Ag and the totally deposited silver are plotted against the deposition potential of silver in Fig. 3-A. The

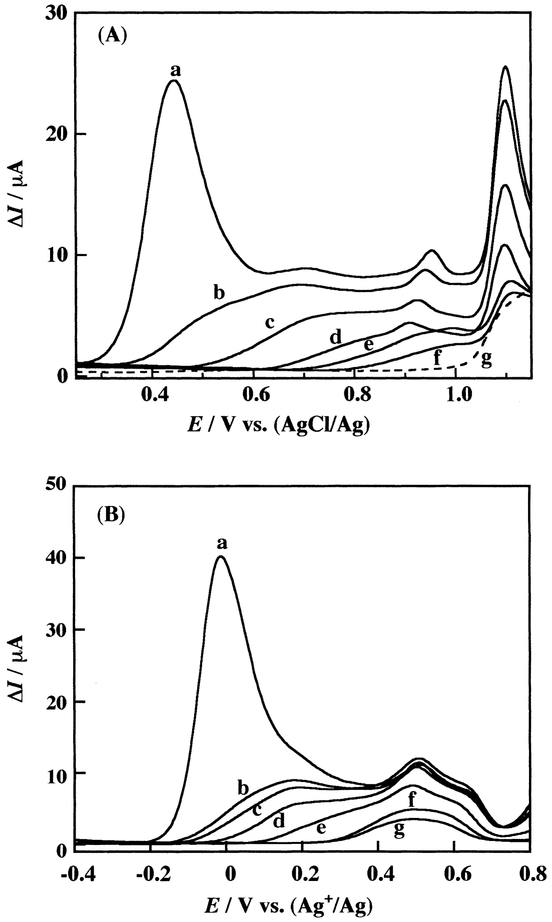

Fig. 1. Differential pulse voltammograms of dissolution of silver deposited on gold electrode in aqueous solution of supporting electrolyte, reported in Ref. 6 (A) and in acetonitrile solution of supporting electrolyte (B). (A) Silver was deposited for 500 s in aqueous solution of 1.0×10^{-4} mol dm^{-3} silver ion at (a) 0.35, (b) 0.4, (c) 0.6, (d) 0.7, (e) 0.8, and (f) 0.9 V vs (AgCl/Ag). Curve (g) is a voltammogram of gold electrode (blank). (B) Silver was deposited for 500 s in acetonitrile solution of 1.0×10^{-3} mol dm^{-3} silver ion at (a) -0.05, (b) 0, (c) 0.05, (d) 0.1, (e) 0.3, and (f) 0.5, and (g) 0.6 V vs (Ag^+/Ag).

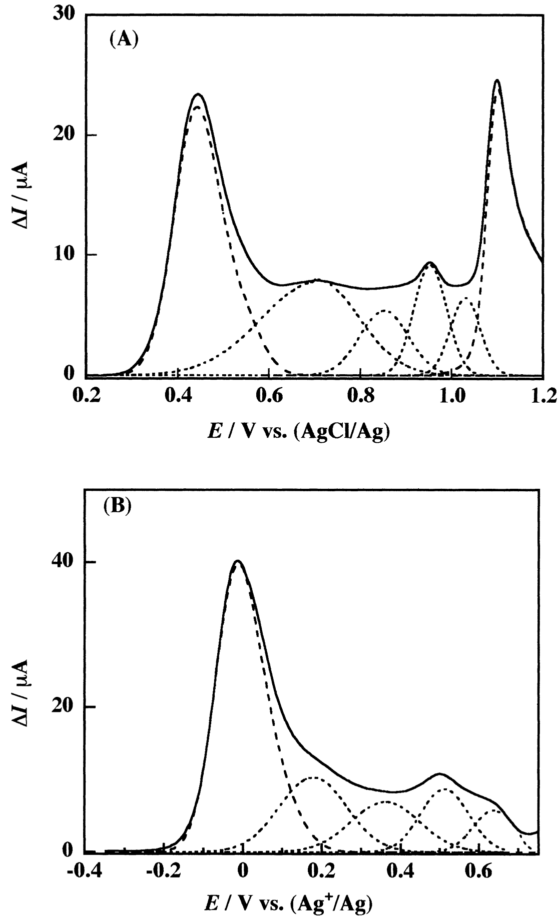

Fig. 2. Deconvoluted voltammogram of the curves (a) in Fig. 1 in the aqueous solution (A) and in the acetonitrile solution (B).

total amount of the deposited silver abruptly decreased up to a deposition potential of 0.46 V vs (AgCl/Ag); after that it gradually decreased with increasing the deposition potential. The deposition potential at the inflection point approximately agreed with the deposition potential at which no dissolution of the bulk-Ag could be observed.

Similar results were obtained in an acetonitrile solution, as shown in Fig. 1-B, Fig. 2-B, and Fig. 3-B. The deconvoluted peaks correspond to the deposited bulk-Ag and the UPD of Ag on different surfaces of Au, similar to those in aqueous solution.[16,22,23] The deposition potential of the inflection point was 0.05 V vs (Ag^+/Ag) and also agreed with the deposition potential at which no dissolution of the bulk-Ag could be observed. In both aqueous and acetonitrile solutions, the amount of the silver deposited was independent of the deposition time in the range of 120 s to 1000 s at the deposition potential in the UPD region. Accordingly, for use in an aqueous solution, an Ag-UPD gold electrode was prepared by holding a gold electrode in an aqueous solution of silver ion at 0.5 V vs (AgCl/Ag) for 500 s. For use in an acetonitrile solution, on the other hand, bulk-Ag and Ag-UPD gold electrodes were prepared by holding a gold electrode in an acetonitrile solution of silver ion for 500 s at −0.05 and 0.3 V vs (Ag^+/Ag), respectively.

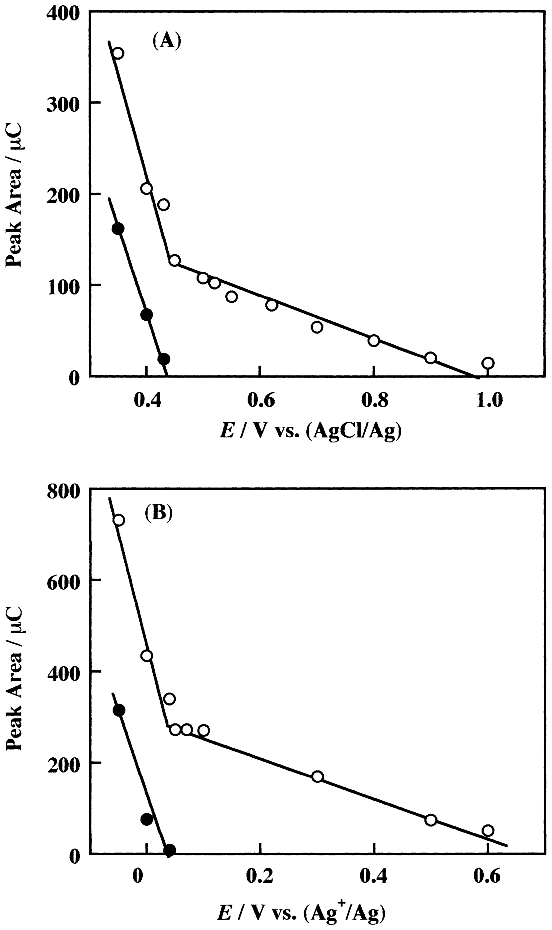

Fig. 3. Relationship between the deposition potential and the peak area for dissolution of the deposited silver on gold electrode in the aqueous solutions (A) and in the acetonitrile solution (B). Symbols (●) and (○) represent the peak areas for dissolution of the bulk-Ag and the total of silver deposited, respectively.

As previously reported,[6] the anomaly in an aqueous solution was caused by the Ag-UPD. In an acetonitrile solution, however, the addition of silver ion influenced only the second redox process of *p*-benzoquinone to make it reversible. The effect of the addition of silver ion on the electrochemical behavior of *p*-benzoquinone was investigated using these prepared electrodes as a working electrode. Cyclic voltammograms were measured at the Ag-UPD and bulk-Ag electrodes in an acetonitrile solution. The results are shown in Fig. 4 together with those at a gold electrode in both the absence and presence of silver ion. *p*-Benzoquinone shows two redox couples at −0.8 V and −1.6 V vs (Ag^+/Ag) in acetonitrile. At a gold electrode, although the first redox couple exhibited reversibility (a peak separation of 70 mV), the second one was extremely irreversible (a peak separation of 300 mV), as shown in Fig. 4-a. However, the reversibility of the second redox process could be improved more and more by increasing the silver-ion concentration, and the peak separation was reduced to 120 mV at a silver-ion concentration of 5×10^{-4} mol dm^{-3} (the voltammogram d in Fig. 4). This silver-ion effect was not so marked as that in an aqueous solution, and was in the opposite direction. The voltammogram at the Ag-UPD electrode was similar

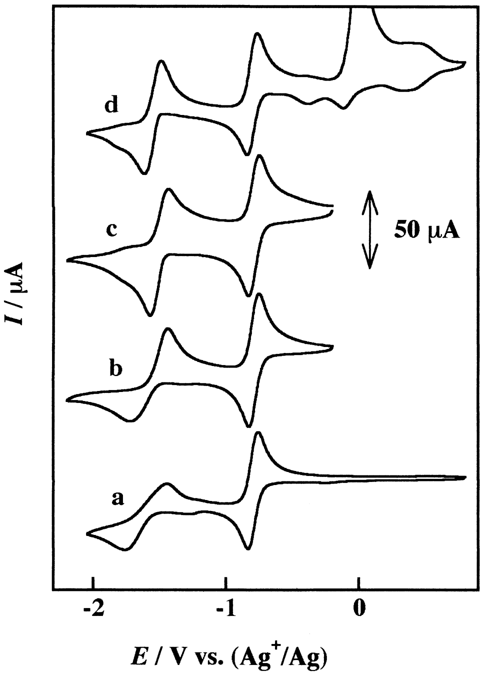

Fig. 4. Cyclic voltammograms of *p*-benzoquinone at a concentration of 5×10^{-4} mol dm^{-3} in acetonitrile solution, using a polycrystalline gold electrode and the silver-deposited gold electrodes prepared as a working electrode. Voltammograms (a) and (d) are at a polycrystalline gold electrode in the absence and presence of 5×10^{-4} mol dm^{-3} silver ion, and (b) and (c) are at the Ag-UPD gold electrode and the bulk-Ag gold electrode, respectively.

to that at gold electrode in the absence of silver ion, though the deposited silver slightly influenced the electrochemical behavior of *p*-benzoquinone. At a bulk-Ag electrode, however, the reversibility of the second redox couple of *p*-benzoquinone was markedly improved in the voltammogram. This indicates that the change in the voltammogram by the addition of silver ion in an acetonitrile solution is not responsible for the Ag-UPD but for the bulk silver deposited on the gold electrode.

Cyclic voltammograms were measured for *p*-benzoquinone derivatives in acetonitrile solution at various working electrodes, including the prepared silver-deposited electrodes, in order to investigate the role of the deposited silver. As a typical example, the voltammograms of tetramethyl-*p*-benzoquinone are shown in Fig. 5. The first redox waves of the quinone were well-defined, and were almost independent of the electrode materials. However, the electrode material influenced the second redox waves: the second waves became more ill-defined as the electrode material went on from a glassy carbon to a platinum. This trend was also obtained for other quinones.

The Hammett equation was applied to correlate various equilibrium constants, rate constants, and physical quantities.[24] It is known that there is a linear correlation between the redox potentials and the sum of the substituent constants (σ_p) for polysubstituted quinonoid compounds.[25] The correlation between the peak potentials and $\Sigma\sigma_p$ was examined for *p*-benzoquinone derivatives in this study. The results at a gold electrode are shown in Fig. 6. Figure 6 indicates good linear relationships between the peak potential and $\Sigma\sigma_p$. There was no difference in the slope of the linear relation between the reduction and oxidation processes for the first redox step. For the second redox step, on the other hand, the slope about the reduction process was significantly different from that about the oxidation process. Similar results were obtained at other working electrodes; the obtained slopes are listed in Table 1. The slopes for the second redox process at a palladium and platinum working electrodes were evaluated only from the data of *p*-benzoquinone and its chloro-derivatives, since the voltammograms for methyl-, methoxy-, and *tert*-butyl-derivatives exhibited extremely ill-defined redox peaks for the second redox process. The slopes for the first redox process were independent of the electrode materials. On the other hand, the slopes for the second redox process varied with the electrode materials, and were different between the reduction and oxidation processes. These facts indicate that the susceptibility of substituent effect is dependent on the electrode materials for the second redox process, though independent of that for the first step.

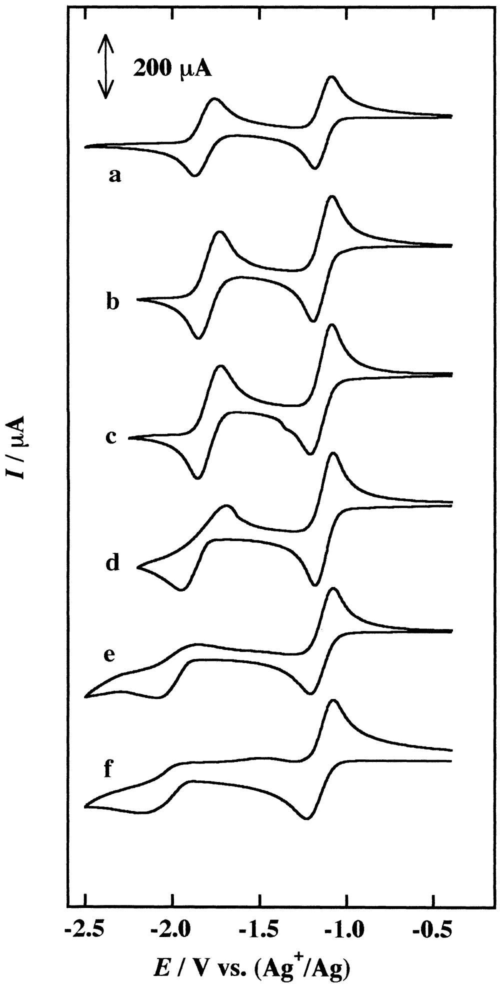

Fig. 5. Cyclic voltammograms of tetramethyl-*p*-benzoquinone in acetonitrile at various working electrodes; (a) a glassy carbon, (b) a silver, (c) the bulk-Ag gold, (d) a gold, (e) a palladium, and (f) a platinum.

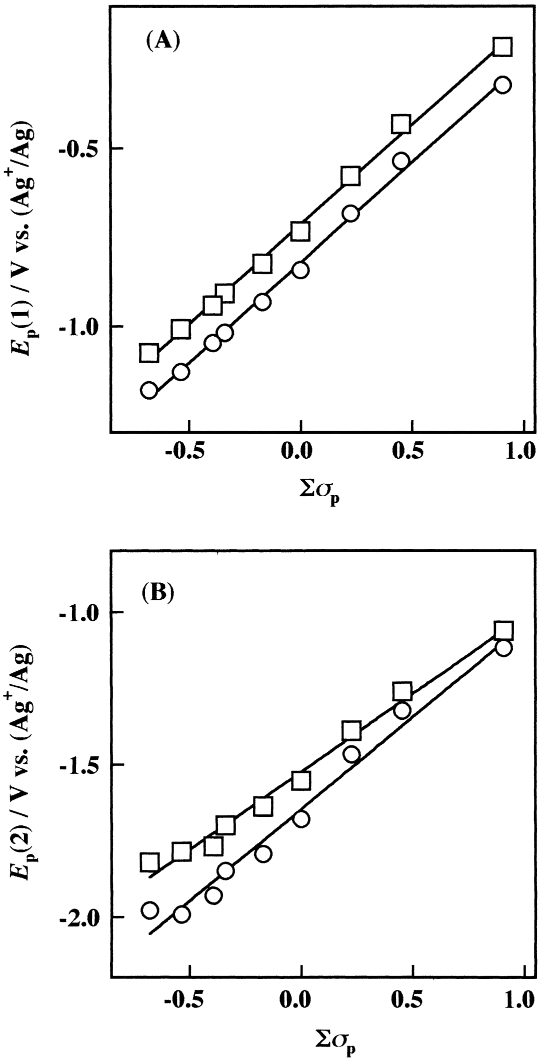

Fig. 6. Correlation between the sum of substituent constants σ_p values for the substituents and the peak potentials obtained from the cyclic voltammograms of *p*-benzoquinone derivatives at a gold electrode. (A) and (B) are the plots for the peak potentials of the first and the second redox process, respectively. Symbols (□) and (○) denote the oxidation and the reduction peak potentials, respectively.

An inspection was made of the slopes of the second redox process. For the oxidation, the slopes are almost independent of the electrode materials, but are smaller than those for the first redox process. The smaller slope indicates that a dianion (two-electron reduced form of quinone) with a smaller $\Sigma\sigma_p$ value is less oxidizable. C. Rüssel reported that although the dianion of *p*-benzoquinone was associated with the tetrabutylammonium cation, its monoanion (one-electron reduced form of quinone) was not in an acetonitrile solution.[26] This association interprets the smaller slope for the oxidation of the second redox process; that is, the dianion is more stabilized for quinones with a smaller $\Sigma\sigma_p$ value.

For reduction, on the other hand, the slopes are divided into three groups: smaller than (at a glassy carbon, a silver, and the bulk-Ag gold electrode), equal to (at the Ag-UPD gold and a gold electrode), and greater than that for the first redox process (at a palladium and a platinum electrode). The bulk-Ag and Ag-UPD gold electrodes were divided into separate groups in spite of no significant difference between the slopes at both electrodes, because the reduction peak of the second process is unquestionably different at both electrodes, as can be seen from Fig. 4. The stabilization of the dianion by association with the tetrabutylammonium cation causes the smaller slope for the first group. For the second and the third groups, another opposite effect may participate in addition to the above-mentioned effect. The increasing order for the slopes corresponds to the order of the increasing work functions of metals.[27,28] It is known that there is a linear relation between the work function and the potential of zero charge (pzc).[29,30] The pzc may significantly influence the reaction and the orientation of a solvent at a metal electrode surface.[31] The pzc of a silver (−0.7 V vs NHE) is the potential region of the second redox process of quinones. On the other hand, the pzc of gold and platinum is more positive, and their electrode surface may be more negatively charged than that of a silver one in the potential region of the second redox process of quinones. Osawa pointed out from results by surface enhanced IR absorption spectroscopy that the orientation of water molecules at the surface of a gold electrode varied in the potential region of more positive and more negative than pzc in an aqueous solution, depending on the potential.[31] Thus, a reorientation of solvent molecules at the electrode surface should also occur in an ace-

Table 1. Slopes for Plots in Fig. 6 at Various Working Electrodes

Electrode	Slope/V			
	1st redox process		2nd redox process	
	Reduction	Oxidation	Reduction	Oxidation
Glassy carbon	0.56 ± 0.02	0.56 ± 0.02	0.46 ± 0.02	0.45 ± 0.01
Silver	0.58 ± 0.01	0.55 ± 0.02	0.43 ± 0.01	0.46 ± 0.02
Bulk-Ag gold	0.57 ± 0.01	0.56 ± 0.02	0.45 ± 0.05	0.45 ± 0.03
Ag-UPD gold	0.57 ± 0.02	0.56 ± 0.02	0.56 ± 0.08	0.43 ± 0.02
Gold	0.56 ± 0.01	0.56 ± 0.01	0.59 ± 0.03	0.50 ± 0.02
Palladium	0.57 ± 0.02	0.56 ± 0.02	0.72 ± 0.08*	0.39 ± 0.03*
Platinum	0.56 ± 0.01	0.58 ± 0.02	0.79 ± 0.02*	0.44 ± 0.03*

*These values were evaluated from the data for *p*-benzoquinone and the chloro-derivatives.

tonitrile solution with an intermediate polarity when silver with a different pzc value is deposited onto a gold electrode. It is speculated that this difference in the orientation of acetonitrile molecules may be reflected in the slope of the second reduction process. The solvation of quinones may also influence the slope, since their solvation is dependent on the electron density of the quinone ring.[32] Accordingly, it is concluded that the deposition of silver onto a gold electrode causes a change in the orientation of solvents toward the electrode, and brings about a modification of the reversibility in the second redox process of quinones (including the reduction to the dianion) in an acetonitrile solution.

In an aqueous solution, quinones show the two-electron/two-proton redox process. The role of silver deposited onto a gold electrode was investigated from the aspect of the mechanism of the electrode reaction of *p*-benzoquinone in an aqueous solution. Cyclic voltammograms of *p*-benzoquinone were obtained at various working electrodes with different electrode materials in aqueous solution at various pH values. The peak potentials were plotted against the pH, and *E*–pH diagrams were obtained, as shown in Fig. 7. Their slopes are summarized in Table 2. The *E*–pH diagrams exhibited linear relationships with a slope of about −60 mV/pH at gold, palladium, and platinum working electrodes in the pH region of the present study. This indicates that the redox reaction of the quinone proceeds through the two-electron/two-proton mechanism at these working electrodes, as reported so far.[15] However, their average peak separation increased from that at the gold electrode (ca. 50 mV) to that at the platinum electrode (ca. 150 mV). This tendency corresponds to the overpotential for oxygen evolution. At a Ag-UPD gold electrode, in which silver with the smallest overpotential for oxygen evolution was deposited at an underpotential, the *E*–pH diagram varied according to the pH range; the oxidation peak potential was independent of the pH below pH 5, but was strongly dependent on the pH above pH 5, although the slope for reduction process remained constant over the pH range in this study.

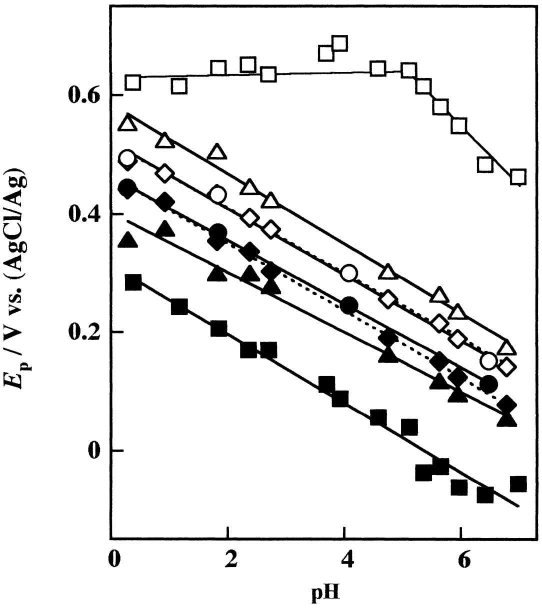

Fig. 7. *E*–pH diagrams for the redox process of *p*-benzoquinone at various working electrodes; a gold (○, ●), a palladium (◇, ◆), a platinum (△, ▲), and the Ag-UPD gold electrode (□, ■). Open and solid symbols denote the peak potentials for oxidation and reduction, respectively.

Table 2. Slopes of *E*–pH Diagram at Various Working Electrodes

Electrode	Slope/(mV/pH)	
	Reduction	Oxidation
Gold	−54 ± 1	−56 ± 3
Palladium	−57 ± 1	−55 ± 1
Platinum	−51 ± 3	−59 ± 2
Ag-UPD gold	−58 ± 3	8 ± 4 (pH < 5) −88 ± 10 (pH > 5)

At an Ag-UPD gold electrode, the redox reaction of quinone may proceed as follows. The reduction proceeds as follows in a similar manner:

$$Q + 2H^+ + 2e^- \rightarrow QH_2 \tag{1}$$

as that at the other working electrode. Q and QH_2 represent quinone and hydroquinone, respectively. The *E*–pH diagram for the oxidation is explained as follows:

$$QH_2 \rightarrow QH_2^{2+} + 2e^- \tag{2}$$

$$QH_2^{2+} \rightarrow Q + 2H^+ \tag{3}$$

$$QH_2 \rightarrow Q^{\bullet -} + 2H^+ + e^- \tag{4}$$

$$2Q^{\bullet -} \rightarrow Q + Q^{2-} \tag{5}$$

QH_2^{2+}, $Q^{\bullet -}$, and Q^{2-} represent the protonated quinone, the semiquinone anion radical, and the deprotonated hydroquinone, respectively. Below pH 5, hydroquinone oxidizes to QH_2^{2+} without the transfer of a proton at the electrode surface, and subsequently releases protons in bulk, according to Eqs. 2 and 3. A proton transfer does not participate in the electrode reaction. This implies that the hydroquinone and/or their reduced product exist at the surface of the silver-deposited electrode as a less acidic form than that in bulk, though pK_a for QH_2^{2+} in bulk has a value smaller than zero.[15] It is speculated that a kind of water structure may be formed at the surface of the silver-deposited electrode and hydroquinone and/or their reduced product are confined in their hydrogen-bond network. This confinement could prevent deprotonation accompanied by electron transfer. In a lower hydrogen concentration range, above pH 5, the slope with a large negative value (−88 mV/pH) for the *E*–pH diagram shows that the oxidation of hydroquinone proceeds through the concurrent paths of a one-electron/two-proton process, i.e. Eq. 4, in addition to the process of Eq. 2 at the electrode surface; the resultant semiquinone anion radical successively disproportionates to quinone and deprotonated hydroquinone in bulk, according to Eq. 5.

It is concluded that deposited silver onto a gold electrode caused the change in the solvent structures at the surface of the electrode and brought about a change in the voltammograms in both acetonitrile and aqueous solutions. In an aqueous solution, the oxidation process was markedly influenced by the silver deposited at an underpotential.

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