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Electrochemical Studies of Poly(mercaptohydroquinone) and Poly(mercapto-*p*-benzoquinone) Films Prepared by Electropolymerization. II. Fixation of Heavy Metals and Their Electrochemical Properties

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Heavy metal ions, Ag^+, Hg^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Pd^{2+}, Fe^{3+}, and Pt^{4+}, were each fixed on a conductive redox film of poly(mercapto-*p*-benzoquinone) or poly(mercaptohydroquinone) by mercaptide formation. Of these mercaptide-modified electrodes, the Pt(IV)-, Pd(II)-, and Ag(I)-modified electrodes possess some catalytic properties for electrochemical hydrogen evolution. These mercaptide-modified electrodes display a nearly Nernstian response to their respective heavy metal ions in aqueous solution and exhibit good durability when stored under appropriate conditions. Especially, the Hg(II)-modified electrode displays an excellent function as an Hg^{2+} ion sensor. The effect of miniaturization of substrates upon response ability was investigated by using two different-sized Pt wires (0.5 mm and 0.03 mm in diameter).

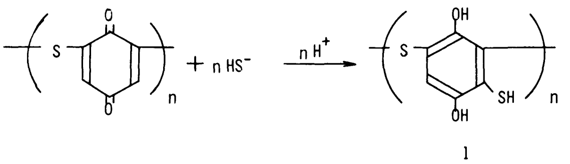
Electrode surface modification using various electrocatalytic materials has been investigated in the field of electrocatalysis. Catalytic electrodes modified at the monolayer level have not successfully been utilized because they lack stability and conductivity.[1] Polymer-modified electrodes have recently been used for immobilization of metal ions and metal complex ions.[2] Many investigations have thus far been undertaken to devise more active and stabler catalyst systems for the electrochemical evolution of hydrogen,[3] the electrochemical reduction of oxygen,[4] and other inorganic and organic reactions.[5] Some basic applications[6] of catalytic electrodes have been reported. We prepared poly(mercapto-*p*-benzoquinone) (SQE_{Ox}) and poly(mercaptohydroquinone) (SQE_{Red}) films,[7] and reported their electrochemical properties.[8] Many heavy metal ions were fixed on the redox polymers (SQE, standing for SQE_{Red} and/or SQE_{Ox}) in the form of mercaptides. This fixation is easy and can be carried out under mild conditions as described below. Mercaptide-modified electrodes (ME–M's) are stable and possess a characteristic structure in which heavy metal atoms or particles are connected with a substrate electrode via a conductive polymer of SQE. As described in our previous paper,[7] the thickness of SQE can be controlled by the duration of electrolysis of mercaptohydroquinone. We report here on the method of fixing heavy metal ions on SQE and on some items of basic electrochemical behavior of various ME–M's.

Experimental

Mercaptohydroquinone was synthesized and purified according to the method described in our previous paper.[7] The chemicals used for the synthesis of mercaptohydroquinone were of reagent grade. The other inorganic reagents were of reagent grade and used without further purification. Deionized water was used for the preparation of solutions, final washing of electrode surface, and rinsing SQE. The substrate electrodes used were two different-sized platinum wires ($Pt_{0.5}$ and $Pt_{0.03}$), 0.5 and 0.03 mm in diameter, respectively, and both ca. 5 mm in effective length,[9] and a Yanagimoto GC-P2 glassy carbon electrode (GCE) 3 mm in diameter. The apparatus used for the preparation of SQE on these electrodes was the same as that used in the previous paper.[7] The reference electrode used was a saturated calomel electrode (SCE). Voltammetric measurements were carried out with a three-electrode system consisting of an ME–M working electrode, a Pt plate counter electrode, and an SCE reference electrode having an agar salt bridge of saturated KNO_3. Purified nitrogen gas was bubbled for 30 min to remove dissolved oxygen. Current–potential curves were recorded on a Yanagimoto P-8 polarograph. Potentiometric measurements were carried out in the conventional manner. An ME–M was set in a glass beaker containing a test solution. An SCE was set in another beaker containing an aqueous solution saturated with KCl. The two glass beakers were connected with each other by an agar salt bridge of saturated KNO_3. Potentials of ME–M's were measured with a Toho Chemical Research EM-02 electrometer. Each test solution contained 0.1 M ($1\ M=1\ mol\ dm^{-3}$) KNO_3 to provide a constant ionic strength ($\mu=0.1$) and was brought to pH 5.0 ± 0.1 by addition of an appropriate quantity of dilute nitric acid. The test solution was prepared just before potentiometric measurement to avoid the dissolution of atmospheric carbon dioxide. All potentiometric measurements were carried out at 25 ± 0.1 °C.

Results and Discussion

Fixation of Heavy Metal Ions on SQE. SQE_{Ox} was prepared on $Pt_{0.03}$, $Pt_{0.5}$, and GCE by an electrochemical oxidation of 0.4 mM mercaptohydroquinone at a constant potential of +0.3 V for 30 min in a Britton–Robinson buffer solution of pH 5.0 containing 20 vol% ethanol. When $0.3\ mC\ cm^{-2}$ was passed during the electropolymerization under the conditions described above, the surface density of quinone units in the SQE_{Ox} thus prepared was found to be ca. $8\times 10^{14}\ cm^{-2}$ on each electrode surface by measurement of the charge associated with the reduction of the SQE_{Ox}. After finishing the electropolymerization, the SQE_{Ox}-modified electrodes were thoroughly rinsed with water and then immersed in a Britton–Robinson buffer solution containing 1 mM NaHS for 1 h at room temperature under a nitrogen atmosphere for the conversion to **1** by the reaction



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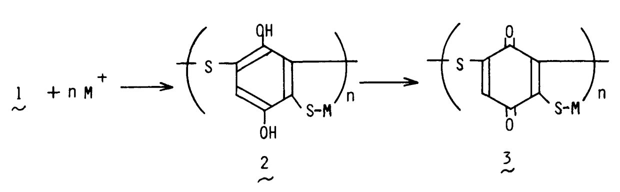
In order to confirm the above-described addition to have proceeded effectively, spectrophotometric measurements were carried out by using a pH 5.0 Britton–Robinson buffer solution containing 1 mM NaHS and 0.4 mM *p*-benzoquinone under a nitrogen atmosphere. The absorption spectrum with $\lambda_{max}=246$ nm due to *p*-benzoquinone rapidly decreased with lapse of time, while a new absorption spectrum with $\lambda_{max}=298$ nm increased. This absorption maximum is in fair agreement with that of 0.4 mM mercaptohydroquinone in wavelength and absorbance. On the basis of this spectrophotometric measurement, it is clear that the addition of HS^- ions to the majority of the quinone rings in SQE_{Ox} has occurred to give **1**. After thorough rinsing with water, the **1**-modified electrodes were immersed in an aqueous solution containing 1 mM heavy metal ion for more than 1 h under a nitrogen atmosphere in order to fix the heavy metal ion on **1** by allowing its mercaptide to be formed which is insoluble or sparingly soluble in aqueous solution. Thus far Ag^+ or Hg^{2+} has been used for the titration of mercapto groups in various proteins.[11] After rinsing with a large amount of water to remove unreacted heavy metal ion, the **2**-modified electrodes were kept for 10 min at +0.3 V in 0.1 M KNO_3 solution in order to reduce **2** into **3** because the latter is superior to the former in durability:



where M^+ indicates a univalent heavy metal ion. The **3**-modified electrodes thus prepared were kept in an aqueous solution containing the same heavy metal ion (1 mM) and were rinsed with water just before use for measurement. In order to confirm the mercaptide formation described above, the reaction between mercaptohydroquinone and Ag^+ was followed spectrophotometrically in aqueous solution. Figure 1 shows that mercaptohydroquinone and Ag^+ rapidly undergo an equimolar reaction to give an insoluble Ag-mercaptide. The mercaptide formation was confirmed for the other heavy metal ions, Hg^{2+}, Pd^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Fe^{3+}, and Pt^{4+}. Hence it has been established that these heavy metal ions can be fixed on SQE via the formation of mercaptide **2** or **3**.

Voltammetric Behavior in Aqueous Solution. Voltammetric measurements were performed with a GCE as the substrate electrode because of its higher hydrogen overvoltage than that of Pt. Each ME–M gave a cathodic voltammogram characteristic of the metal ion species fixed on SQE. Their cathodic voltammograms were reproducible except those obtained during initial two or three potential scannings. As shown in Fig. 2, hydrogen evolution potentials become more positive in the order: Pt≈Pd>Ag>Cu≈Cd>Hg. The order observed here is inversely proportional to the magnitude of their hydrogen overvoltages. Of the SQE's having no mercapto groups, only those which had been immersed in Pt^{4+} or Pd^{2+} solution in the same manner, were observed to show small positive shifts in hydrogen evolution potential even after repeated rinsings with a large quantity of water. However, these small positive shifts decreased quickly with repeated potential scannings between 0 V and the hydrogen evolution potential. This salient difference in voltammetric behavior between SQE having mercapto group and SQE alone which were each

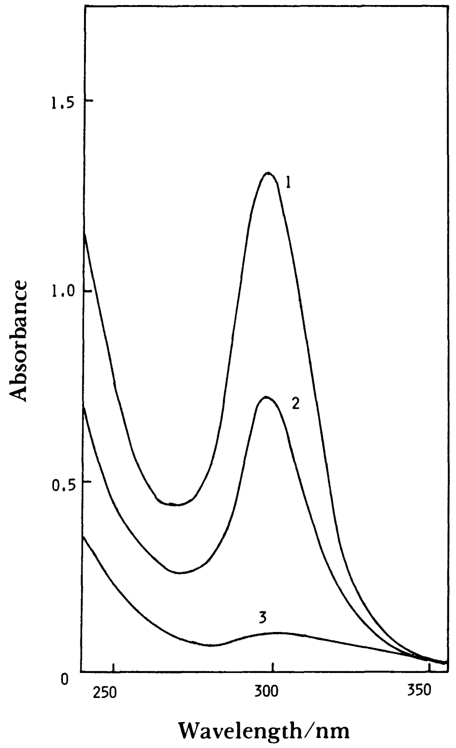


Fig. 1. Absorption spectra of mercaptohydroquinone (0.4 mM) in aqueous solution in the presence of Ag^+ in N_2 atmosphere. Concentration of $AgNO_3$: 1, 0 M; 2, 0.2 mM; 2, 0.4 mM.

immersed in the metal ion solution, strongly supports the above-mentioned judgment that the addition of HS^- ion to SQE_{Ox} gives **1**. Figure 3 shows that the hydrogen evolution potential of ME–Ag shifts negatively with an increase in the pH of buffer solution. This negative shift in hydrogen evolution potential was observed also with the other ME–M's. These results indicate that the electroactive sites where the hydrogen evolution occurs are solely the metals fixed on SQE and are neither the surface of GCE nor the SQE itself. Moreover, the above information strongly suggests that many metals which can form mercaptides may be electrochemically nucleated and grown on the electroactive sites, i.e., the metals fixed on SQE by means of the electroreduction of these metal ions in aqueous solution. The metal nucleation on the heavy metals fixed on SQE will be reported elsewhere.

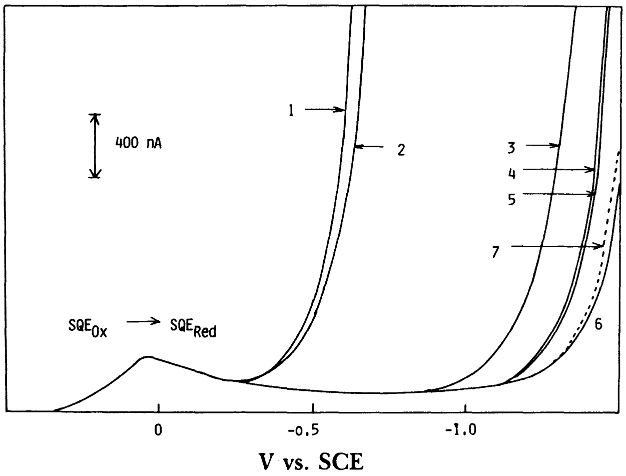


Fig. 2. Current-potential curves of ME–M's in the Britton-Robinson buffer solution having pH 5.0 in N_2 atmosphere. The potential was scanned at 3.3 mV s^{-1}.
1, ME-Pt(IV); 2, ME-Pd(II); 3, ME-Ag(I); 4, ME-Cu(II); 5, ME-Cd(II); 6, ME-Hg(II); 7, SQE alone.

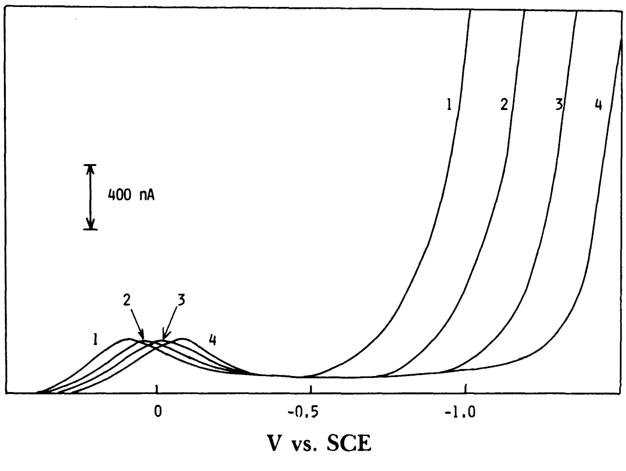


Fig. 3. Effect of pH on the current-potential curves of ME-Ag(I) using the Britton-Robinson buffer solution in N_2 atmosphere. The potential was scanned at 3.3 mV s^{-1}.
1, pH 3.0; 2, pH 4.0; 3, pH 5.0; 4, pH 6.0.

Potentiometric Behavior in Metal Ion Solution. We reported that Pt electrodes modified with a few species of mercaptides show a nearly Nernstian response to the same heavy metal ion as that of the mercaptide in 0.1 M KNO_3 aqueous solution.[12] In this work, potentiometric measurements were carried out by using two different-sized Pt electrodes, $Pt_{0.5}$ and $Pt_{0.03}$, modified with **3** in order to investigate on the deterioration in durability caused by the miniaturization of the substrate electrode. As a result of this investigation, no marked difference in the response characteristics such as response time and response concentration range was found to exist between the two electrodes. However, $Pt_{0.03}$ modified with **3** was occasionally dislodged or bent on insertion of the electrode into a test solution containing heavy metal ions. These defects encountered are obviously attributed to the fine flexible body of $Pt_{0.03}$ itself and need, therefore, to be overcome by fixation of $Pt_{0.03}$ on some hard substrate. As shown in Fig. 4, ME–Ag(I) displays a good Nernstian response to Ag^+ and has good durability. The response characteristics of various mercaptide-modified $Pt_{0.5}$'s are summarized in Table 1. The ME–M's show an almost Nernstian

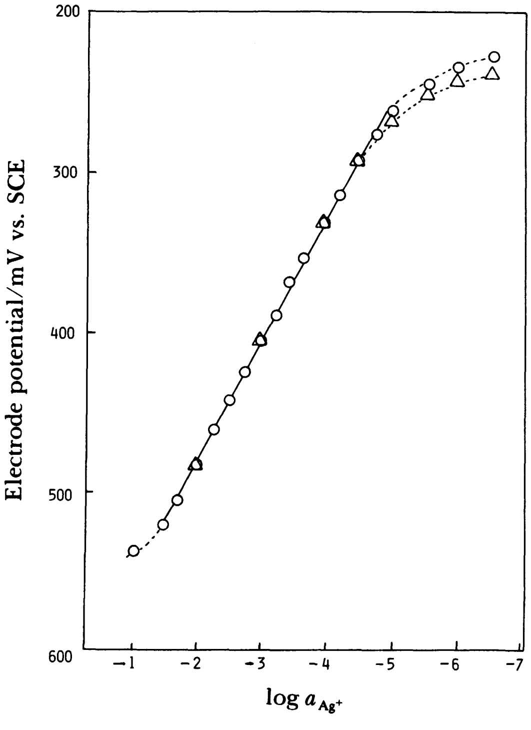


Fig. 4. Relationship between potential of ME-Ag(I) ($Pt_{0.5}$) and $\log a_{Ag^+}$ in 0.1 M KNO_3.
○: By Me-Ag(I) prepared just before the measurement, △: by ME-Ag(I) permitted to stand for one month.

Table 1. Response Characteristics of ME-M's ($Pt_{0.5}$)

Electrode	Test ion	Slope[a)] mV/−log *a*	Range of linear response/M
ME-Ag(I)	Ag^+	60—61	$10^{-1.5}$—10^{-5}
ME-Hg(II)	Hg^{2+}	90—91	10^{-3}—10^{-5}
ME-Cu(II)	Cu^{2+}	27—28	5×10^{-3}—10^{-5}
ME-Pb(II)	Pb^{2+}	26—27	5×10^{-3}—10^{-5}
ME-Cd(II)	Cd^{2+}	30—31	5×10^{-3}—10^{-5}
ME-Fe(III)	Fe^{3+}	54—55	10^{-2}—10^{-5}

a) Each value range was obtained as the average from five or six measurements.

Table 2. Selectivity Coefficients (K_{Sel}'s) of ME-M's and Standard Redox Potentials (E^0's) of Mercaptide-Forming Heavy Metals

Electrode	K_{Sel}[a)]	E^0[b)] V vs. SHE
ME-Hg(II)	Ag^+, Cu^{2+}, Pb^{2+}, Cd^{2+}, Fe^{3+} ($<10^{-2}$)	+0.920($2Hg^{2+}/Hg_2^{2+}$)
ME-Ag(I)	Hg^{2+}(10^2), Fe^{3+}(1), Cu^{2+}, Pb^{2+}, Cd^{2+}(10^{-2})	+0.799(Ag^+/Ag)
ME-Fe(III)	Hg^{2+}(10^2), Ag^+(1), Cu^{2+}, Pb^{2+}, Cd^{2+}(10^{-2})	+0.771(Fe^{3+}/Fe^{2+})
ME-Cu(II)	Hg^{2+}(10^3), Ag^+, Fe^{3+}(10^2), Pb^{2+}, Cd^{2+}(10^{-2})	+0.337(Cu^{2+}/Cu)
ME-Pb(II)	Hg^{2+}(10^3), Ag^+, Cu^{2+}, Fe^{3+}(10^2), Cd^{2+}(1)	−0.126(Pb^{2+}/Pb)
ME-Cd(II)	Ag^+, Hg^{2+}, Fe^{3+}(10^3), Cu^{2+}(10^2), Pb^{2+}(1)	−0.403(Cd^{2+}/Cd)

a) K_{Sel}=[A]/[B] where [A] is the concentration of mercaptide-forming metal ion and [B] is that of interfering metal ion.
b) Ref. 15.

response to the heavy metal ions except ME-Hg(II) and ME-Fe(III). All of them respond within 10 s and usually have long service lives when stored in 1 mM nitrate solution weakly acidified with nitric acid. Especially, in the case of ME-Ag(I), its response behavior shown in Table 1 is fairly reproducible for at least one month when stored in a weakly acidic 1 mM $AgNO_3$ solution in a dark place. As we expected, the response characteristics, such as response range and response slope, of ME-Ag(I) were observed to be in good agreement with those of a naked Ag wire 0.5 mm in diameter, though the naked wire could respond more quickly. Similar agreement in response characteristics was also observed between ME-Cu (II) and a naked Cu wire. The potentiometric characteristics observed of ME-M's support the idea that some degree of interaction between heavy metals fixed on SQE and heavy metal ions in aqueous solution should cause the change in electrode potential of ME-M's, and suggest that the interaction between them is fundamentally equal to the reversible reduction-oxidation reaction between any naked metals and their ions in aqueous medium. The divalent and trivalent heavy metals fixed on SQE in the form of mercaptide should have more complicate bond structures than that given by -S-M in **2** or **3**. Especially, in the case of ME-Hg(II) and ME-Fe(III), large deviations in response slope from the Nernstian response expected for Hg^{2+} and Fe^{3+} were observed with the two electrodes, though their response characteristics were reproducible in five different measurements with five ME-Hg(II)'s or five ME-Fe(III)'s each prepared separately. Stricks et al.[13)] have reported that the mercapto group in cystein (RSH) reacts with Hg^{2+} to give mercaptides such as $(RS)_2Hg$, $(RS)_2Hg_2{}^{2+}$, and $(RS)_2Hg_3{}^{4+}$ depending upon reaction conditions. However, from the fair reproducibility in response behavior observed of the two electrodes, it can be presumed that the two electrodes have certain definite bond structures under the preparation conditions used in this work. The selectivity coefficients (K_{Sel}'s) of the ME-M's and the standard redox potentials (E^0's) of the mercaptide-forming heavy metals are presented in Table 2. The K_{Sel}'s were determined by the mixed solution method described by Rechnitz et al.[14)] These data show that ME-Hg(II) has an excellent selectivity to Hg^{2+} and that the electrode is subjected to negligible interference from the other heavy metal ions used here. Hence ME-Hg(II) possesses a useful function as a selective Hg^{2+} sensor. In addition, Table 2 shows that K_{Sel}'s are correlated closely to E^0's that is, the potential of any mercaptide-modified electrodes is very sensitive to interfering ions having more positive E^0's but is insensitive to those having more negative ones. This correlation between K_{Sel} and E^0 strongly suggests that certain redox reaction should occur in aqueous solution between any one species of heavy metal fixed on SQE and any one other species of heavy metal ion having more positive E^0, and supports the idea that the function of ME-M's as heavy metal ion sensors results from a redox interaction between the fixed heavy metal and its ion. Judging from their voltammetric and potentiometric characteristics observed in this work, it may be concluded that ME-M's are applicable to many catalytic or selective electrochemical reactions and to the preparation of new types of metal ion sensors.

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