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HEAVY METAL ION SENSORS PREPARED FROM QUINONOID POLYMER ELECTRODES MODIFIED WITH MERCAPTIDES

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Quinonoid polymer electrode, prepared by the electrochemical oxidation of mercaptohydroquinone, was modified with mercaptide of heavy metal ions of interest, such as Ag^+ ion, Hg^{2+} ion, Cd^{2+} ion, Cu^{2+} ion, and Pb^{2+} ion. The quinonoid polymer electrodes modified with mercaptides showed a function as selective ion sensors for heavy metal ions in solution.

Chemically modified electrodes have been of interest recently, since they possess some characteristic functions such as selectivity in redox reaction,[1)] electrocatalysis[2)] and analytical sensors.[3)] In previous papers we have described the preparation and the electrochemical properties[4)] of the quinonoid polymer electrode with glassy carbon electrode and the selective redox reaction of species in solution on this modified electrode. We wish to report here an application of the quinonoid polymer electrode to selective heavy metal ion sensors by means of the modification of quinone rings with various mercaptides which are slightly soluble in water. The quinonoid polymer film was prepared on Pt wire (0.5 mm diameter and ca. 3 mm long) by electrochemical polymerization of mercaptohydroquinone (0.4 mM, 1 M = 1 mol dm^{-3}) at a constant potential of + 0.3 V vs. SCE for 10 min in a Britton-Robinson buffer solution (pH 5.0) containing 20 vol % ethanol at room temperature and other polymerization conditions were identical to those previously used on glassy carbon electrode.[4)] This polymer film on Pt wire gave similar cyclic voltammetric behaviors to that on glassy carbon electrde, i.e., quite similar peak currents and peak potentials vs. potential scan rate relations were obtained. The polymer on Pt wire is then said to have a structure (1) shown in Fig. 1. This quinonoid polymer electrode was rinsed with pure water and was soaked in the Britton-Robinson buffer solution (pH 5.0) containing 1 mM

$Na_2S_2O_3$ for 30 min under a nitrogen atmosphere to attach $S_2O_3^{2-}$ ion to the quinone ring[5)] in the film (step 1 shown in Fig. 1). Then the electrode (2) was thoroughly rinsed with pure water and reduced thiosulfo group on (2) at - 0.5 V vs. SCE for 10 min in the buffer solution (pH 5.0) to give mercapto groups (-SH)(3).[6)] The modified electrode with mercapto group (3) was soaked in a solution of heavy metal ion of interest for 30 min to form the mercaptide with the heavy metal ion (4)(step 3 shown in Fig. 1) and then the reduced form of the polymer (SQE_{Red}) was electrochemically oxidized to the oxidized form of the polymer (SQE_{Ox}) at + 0.3 V vs. SCE in a 1 mM KNO_3 solution.

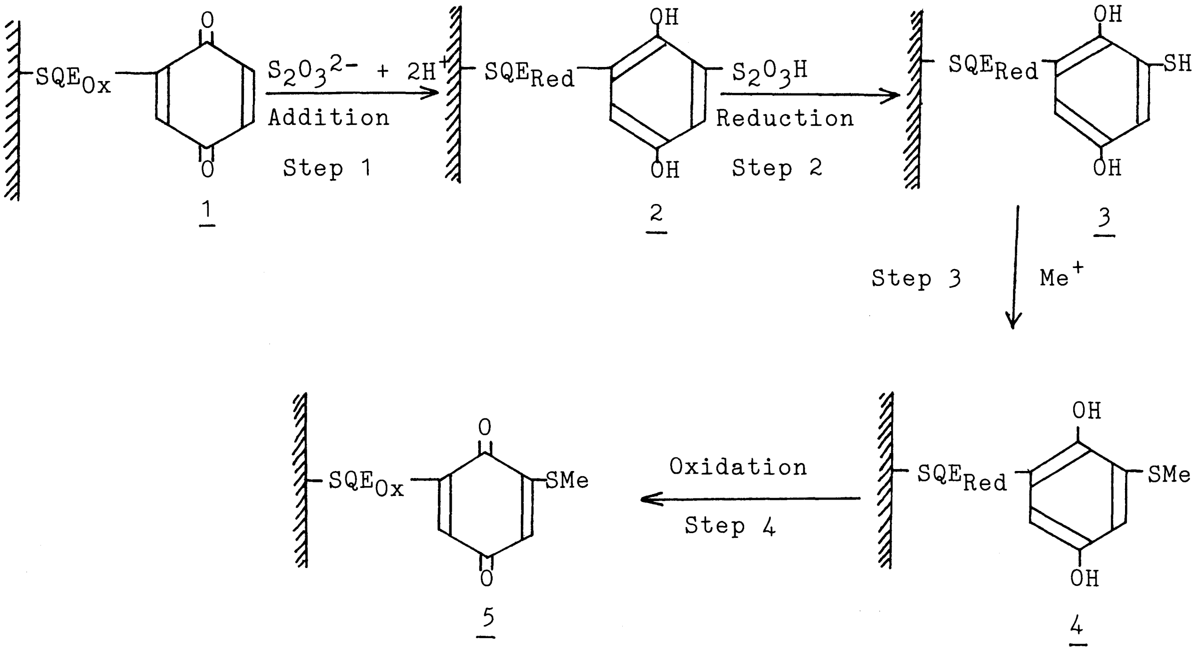

Fig. 1. Scheme of the preparation of the mercaptide-modified quinonoid polymer electrode.

SQE_{Ox} : Poly(mercapto-p-benzoquinone)polymer film (the oxidized form)

SQE_{Red}: Poly(mercaptohydroquinone)polymer film (the reduced form)

Me^+ : Heavy metal ion

The mercaptide-modified quinonoid polymer electrodes (5) were kept in 0.1 M KNO_3 solutions containing 10^{-3} M the heavy metal ions and were carefully rinsed with pure water before measurement. Potentials of the mercaptide modified electrodes (abbreviated as E_{el}) were measured with electrometer (Toho Chemical Research Co., Model EM-02). The reference electrode used was an SCE with an agar salt bridge of saturated KNO_3. As shown in Fig. 2, E_{el} of the Ag mercaptide-modified electrode (abbreviated as Ag-ME) showed a nearly Nernstian response against log activety of Ag^+ ion (log a_{Ag^+}) over three orders of magnitude in concentration and the detection limit for Ag^+ ion was found to be about 10^{-5} M. Plots of E_{el} against log a_{Ag^+} shown in Fig. 2 were reproduced fairly well for at least one month when stored in a 0.1 M KNO_3 solution containing 1 mM $AgNO_3$. E_{el} of Ag-ME in a 10^{-4} M $AgNO_3$ solution was affected by the presence of 10^{-6} M Hg^{2+} ion, but not affected by the presence of either 10^{-2} M Cd^{2+} ion or 10^{-2} M Cu^{2+} ion. The maximum deviation on the plots of E_{el} vs. log a_{Ag^+} was within 5% in four different measurements with four Ag-ME's prepared separately with a great care. It should be pointed out here that the preparation condition of the quinonoid polymer electrodes such as purification of the electrode surface, potentials chosen in oxidation and purity of mercaptohydroquinone, etc. may affected seriously the function of the mercaptide-modified electrodes as ion sensors. The quality of the quinonoid polymer electrodes could be examined by a cyclic voltammetric method. The Ag-ME usually required ca. 10 s for response time. Moreover, for other heavy metal ions such as Hg^{2+}, Cd^{2+}, Cu^{2+}, and Pb^{2+} ions, each E_{el} of the heavy metal mercaptide-modified electrode showed a linear response to log $a_{Me^{2+}}$ (Me^{2+} : heavy metal ion). As shown in Table 1, all E_{el}'s of the Cu(II)-, Cd(II)-, and Pb (II) mercaptide-modified electrodes (abbreviated as Cu-ME, Cd-ME, and Pb-ME, respectively) showed almost Nernstian responses against log $a_{Cu^{2+}}$, log $a_{Cd^{2+}}$, and log $a_{Pb^{2+}}$, respectively, but E_{el} of the Hg(II) mercaptide-modified electrode (abbreviated as Hg-ME) showed a remarkable deviation from a Nernstian response. The deviation shown on the Hg-ME will probably arise from the difference of mercaptide formation between the Hg-ME and the other mercaptide-ME's. But the cause of the deviation is not yet clear. The characteristic data for heavy metal ion sensors of the mercaptide-modified electrodes were shown in Table 1. Response times of the Hg-ME, Cu-ME, Cd-ME, and

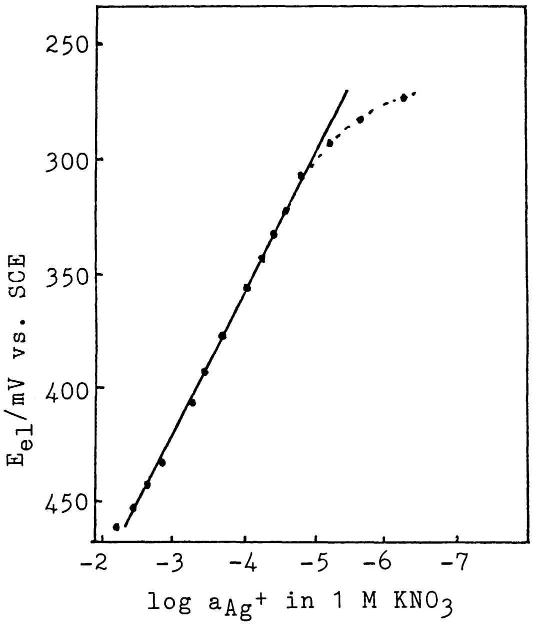

Fig. 2. Relationship between potentials (E_{el}) of the Ag mercaptide-modified electrode and log activity of Ag^+ ion (log a_{Ag^+}).

Pb-ME were nearly equal to that of the Ag-ME. E_{el} of the Hg-ME in a 10^{-4} M $Hg(NO_3)_2$ solution was not affected even by the presence of 10^{-2} M of either Ag^+, Cu^{2+}, Cd^{2+}, or Pb^{2+} ions. These results show that the Hg-ME possesses an excellent function as a selective Hg^{2+} ion sensor.

Table 1. Response characteristics of the mercaptide-modified quinonoid polymer electrodes

Electrodes	Slope(mV/log a)[a]	Linear range(M)	Selectivity coefficients (K)[b]
Ag-ME	60 — 61	10^{-2} — 10^{-5}	$Hg^{2+}(10^2)$, $Cu^{2+}(10^{-2})$
Hg-ME	90 — 91	10^{-3} — 10^{-5}	Ag^+, $Cu^{2+}(>10^{-2})$
Cu-ME	27 — 28	5×10^{-3} — 10^{-5}	$Hg^{2+}(10^3)$, $Ag(10^2)$
Cd-ME	30 — 31	5×10^{-3} — 10^{-5}	$Hg^{2+}(10^3)$, Ag^+, $Cu^{2+}(10^2)$
Pb-ME	26 — 27	5×10^{-3} — 10^{-5}	$Hg^{2+}(10^3)$, Ag^+, $Cu^{2+}(10^2)$

a) All values were obtained on average for five or six measurements.

b) K=[A]/[B] ; [A] is the concentration of mercaptide forming metal ion and [B] is that of interfering metal ion.

It was found that the mercaptide-modified quinonoid polymer electrodes may be used as convenient ion selective sensors for various heavy metal ions which form slightly soluble mercaptides because these mercaptide-modified electrodes can be easily prepared in a short time and probably their sizes may be able to be miniaturized by the use of smaller Pt wire than those used in the present study.

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