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Electrochemical Studies of Poly(mercaptohydroquinone) and Poly(mercapto-*p*-benzoquinone) Films Prepared by Electrochemical Polymerization. VI. Electroreduction of L-Cystine on Thiolates Fixed in the Polymer Film

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(Received July 31, 1991)

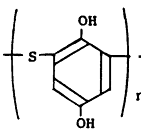
Synopsis. Electrocatalytic reduction of L-cystine (CySSCy) was examined on glassy carbon electrodes coated with the title conductive polymer in which Pt, Pd, Cu, Ag, and Hg thiolates were fixed. Pt and/or Pd thiolate fixed in the polymer behaved as excellent electrocatalytic active sites for reductive cleavage of the sulfur–sulfur bond in CySSCy.

Electroreduction of disulfides has been investigated by many workers.1) Most of them were carried out on an Hg electrode. The reduction mechanism2) at the Hg electrode has been proposed as follows:

$$\mathrm{RSSR} + \mathrm{Hg} \leftrightarrows (\mathrm{RS})_2\mathrm{HG}$$

$$(\mathrm{RS})_2\mathrm{Hg} + 2\mathrm{H}^+ + 2\mathrm{e} \leftrightarrows 2\mathrm{RSH} + \mathrm{HG}$$

Polymer-modified electrodes have recently been in use for immobilization of metal ions and metal complex ions.3) We reported that poly(mercaptohydroquinone) (**1**) and poly(mercapto-*p*-benzoquinone) (**2**) films (abbreviated as SQ films) are easily prepared by electrooxidation of mercaptohydroquinone on a glassy carbon electrode (GCE)4) and that **2** attaches mercapto groups to give a poly(2-thiol-mercaptohydroquinone) film (**3**) by dipping **2**-modified GCE into an aqueous NaHS solution and the resulting **3**-modified GCE gives a poly(2-thiolate-mercaptohydroquinone) film (**4**)-modified GCE by soaking in an aqueous solution of a metal ion of interest.



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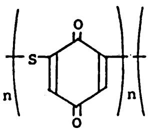

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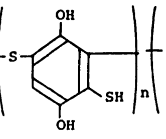

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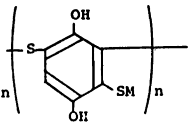

4

Here M denotes a univalent metal ion.5)

Recently we reported that thiolate-modified GCE's function as heavy metal ion sensors6) and execute the electrocatalytic reduction of CO_2.7) Here we describe the electrocatalytic cleavage of the sulfur–sulfur bond in cystine (CySSCy) on thiolate-modified GCE's.

Experimental

Two types of GCE's were used. One (GCE_1), for voltammetric measurements, was a GC disk 3 mm in diameter sealed in a glass tube with an epoxy resin. Another (GCE_2), for controlled-potential electrolysis of CySSCy and determination of the amount of metal ion fixed in the SQ film, was a GC rod 3 mm in diameter and 2 cm in effective length (ca. 1.9 cm^2 in surface area). Both were prepared from a Tokai Carbon glassy carbon electrode 3 mm in diameter. CySSCy was obtained from Tokyo Kasei Co., Ltd. Other chemicals were of reagent grade and used without further purification. Voltammetric measurements and controlled-potential electrolysis were carried out with a three-electrode system consisting of a thiolate-modified GC working electrode, a Pt wire counter electrode, and Ag/AgCl reference electrode having an agar salt bridge of saturated KNO_3. Metal ions fixed in the SQ film were Ag(I), Hg(II), Cu(II), Pd(II), and Pt(IV).

Results and Discussion

SQ films used here were prepared on GCE_1 and/or GCE_2 by electrooxidation at +0.5 V vs. Ag/AgCl for 1 h in a Britton–Robinson buffer solution (pH 5.0) containing 1 mM (1 M=1 mol dm^{-3}) mercaptohydroquinone. The density of quinone moieties in the SQ film thus prepared was ca. 1×10^{16} units/cm^2. The amounts of the metals fixed in the film are given in Table 1. A_1 and A_2 in Table 1 denote the amounts of metal fixed in the SQ film. The A_1 values were determined by either polarography or spectrophotometry based on a decrease in the metal ion concentration after single dipping of the **3**-modified GCE_2 into a small volume of solution (1 cm^3) containing 0.1 mM metal ion for 30 min under N_2 bubbling, and the A_2 values were calculated on an assumption that all the thiol groups in the SQ film participate in the formation of thiolate as follows: Pt(-**3**)$_4$, Pd(-**3**)$_2$, Cu(-**3**)$_2$, Hg(-**3**)$_2$, and Ag(-**3**)$_1$. A_1 is roughly 3 times of A_2 in most cases except for the Cu thiolate. The formal redox potential ($E^{0\prime}$=+0.14 V vs. Ag/AgCl, pH 5.7) of the SQ film (**1**/**2** couple) is signifi-

Table 1. Amount of Metals Fixed in the SQ Film on GCE_2 by Thiolate Formation

Metal	A_1[a)] / μg cm^{-2}	Determination	A_2[b)] / μg cm^{-2}
Pt	2.3—2.4	Spectrophotometric[c)]	0.8
Pd	2.5—2.6	Spectrophotometric[d)]	0.9
Ag	5.1—5.3	Polarographic[e)]	1.8
Hg	5.6—5.8	Polarographic[e)]	1.7
Cu	0.9—1.0	Polarographic[e)]	0.5

a), b) See text. c) by a method described in Ref. 8. d) By a method described in Ref. 9. e) With Yanagimoto GC-P2 glassy carbon electrode.

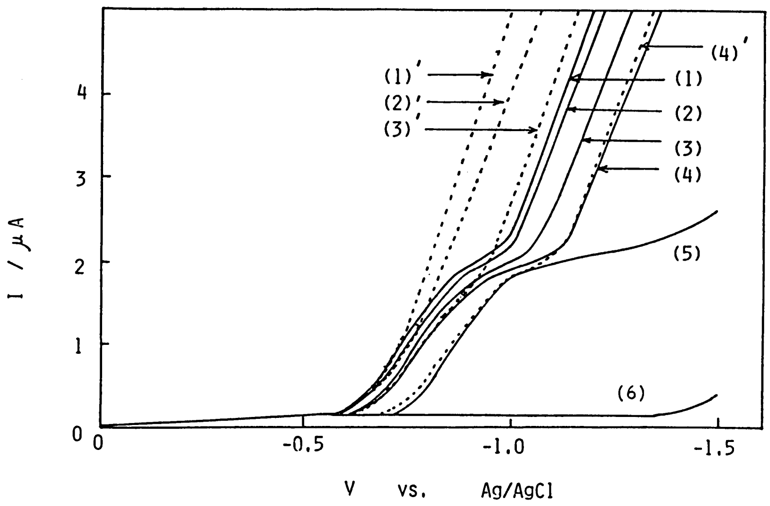

Fig. 1. Cathodic voltammograms of CySSCy in a Britton–Robinson buffer solution (pH 7.0) on various metal-fixed GCE_1's (solid curves) and on bare metal wire electrodes (broken curves) at 2 $mV\,s^{-1}$ in N_2 atmosphere.
(1) Pt, (2) Pd, (3) Ag, (4) Cu, (5) Hg, (6) None, (1)′ Pt wire, (2)′ Pd wire, (3)′ Ag wire, (4)′ Cu wire.

Table 2. Current Density and Current Efficiency for Electroreduction of CySSCy[a] on Metal-Fixed GCE_2's at −0.8 V vs. Ag/AgCl

Metal	Amounts	Current density	Q	Current Efficiency
	n mol cm^{-2}	μA cm^{-2}	mC	%
Pt	12—13	27—29	370—390	97—99
Pd	23—25	24—26	325—350	
Ag	46—48	22—23	300—310	
Hg	28—29	16—19	215—260	
Cu	15—16	19—23	260—310	90—95

a) In 1 mM CySSCy Britton–Robinson buffer solution (pH 7.0).

cantly more negative than those of $PtCl_6^{2-}/PtCl_4^{2-}$ and $PtCl_4^{2-}/Pt$, Pd^{2+}/Pd, Hg^{2+}/Hg, and Ag^+/Ag redox couples. Hence after the formation of thiolate, two electrons may transfer to the metal ions in the SQ film by oxidation of one hydroquinone moiety. As a result, two metal ions may be reduced on a thiolate site[10] in spite of the valency of metal ions to give a nucleus composed of three metal atoms provided that each metal thiolate forms as described above. The predominant cause for the larger A_1 than A_2 in Table 1 therefore may be the nucleation of metals on thiolate sites. Cathodic voltammograms of CySSCy on the SQ film-coated GCE_1's modified with five different thiolates and an SQ film-coated GCE_1 having no thiolate are shown in Fig. 1 by solid curves. Broken curves are the voltammograms of CySSCy on bare metal electrodes. The result reveals that each metal fixed in the SQ film functions as an electroactive site for the reduction of CySSCy. Reduction potentials of CySSCy shifted positively, and the degree of this shift was in the order of Pt >Pd>Ag>Cu>Hg. Especially on the Pt-fixed GCE_1, the reduction of CySSCy initiates at a potential near the redox potential of CySSCy (−0.34 V vs. NHE, pH 7.0).[11] As seen in Fig. 1, such conspicuous reduction currents of CySSCy did not appear on bare Pt, Pd, and Ag wire electrodes owing to H_2 evolution. Controlled-potential electrolysis of CySSCy were carried out with the thiolate-modified GCE_2 at −0.8 V vs. Ag/AgCl for 2 h in a Britton–Robinson buffer solution (pH 7.0) containing 1 mM CySSCy. The result is listed in Table 2. On the other hand, when metal wire electrodes were used, the current efficiency appeared to be lower than 3% for Pt and Pd and ca. 10% for Ag wire electrodes under the same reduction conditions as in the thiolate-modified GCE_2. The reductive cleavage of CySSCy, $CySSCy+2H^++2e \leftrightarrows 2$ Cysteine, was confirmed by a well-known spectrophotometric measurement (CMB method)[12] widely used for both qualitative and quantitative analyses of thiol compounds. Even after 2 h of electrolysis, no appreciable change was noted in the shape of their voltammograms. These results show that Pt and/or Pd metals bound to the conductive polymer chain behave as excellent electrocatalytic active sites for the reductive cleavage of the sulfur–sulfur bond in CySSCy.

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