Electrochemical Studies of Poly(mercaptohydroquinone) and Poly(mercapto-*p*-benzoquinone) Films Prepared by Electropolymerization. I. Preparation of pH Microsensor and Its Fundamental Characteristics

Gorou ARAI,* Takashi KOIKE, and Iwao YASUMORI
Department of Applied Chemistry, Faculty of Engineering, Kanagawa University, Kanagawa-ku, Yokohama 221

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Synopsis. Carbon fibers were electrochemically modified with poly(mercaptohydroquinones). These modified carbon fiber electrodes showed excellent Nernstian response to pH from ca. 2 to 10 and could respond within 2s in the pH range from 3 to 8. These electrodes could work well one month after kept stored in a weak acidic buffer solution and could be easily restored by electroreduction even after their functions had been lowered by successive pH measurements.

In recent years, there has been considerable interest in chemically modified electrodes because of their novel properties such as selective electrolysis,[1] electrocatalysis,[2] and selective ion sensing.[3] Polymeric quinone-hydroquinone systems have been investigated because of their usefulness as specific regenerable redox reagents.[4] Hence, electrodes modified with several poly(benzoquinone) films have been prepared by either the dip-drying or the adsorption method, and their electrochemical behavior and applications in electrocatalysis have been examined by many workers.[5] Recently, we have prepared a poly(mercapto-*p*-benzoquinone) film (PQ) by electrooxidation of mercaptohydroquinone on a glassy carbon electrode[6] and have reported its basic electrochemical behavior.[7] Electrodes modified with PQ thus prepared or poly(mercaptohydroquinone) film (PH_2Q) obtainable by electroreduction of PQ, are expected to possess several novel properties such as mentioned above. More recently, it has been observed that a fine carbon fiber electrode (CFE) modified with PH_2Q (PH_2Q/CFE) is capable of excellent Nernstian response to pH.[8] But its durability was occasionally observed to get lowered after successive pH measurements. In order to reveal the cause for this poor durability, effects of several pretreatments on CFE have been examined by means of a scanning electron microscope. Moreover, three polymer films, namely poly(mercaptomethylhydroquinones)[9] ($PMeH_2Q$), poly(3-mercapto-2,5-dimethylhydroquinone)(PMe_2H_2Q), and PH_2Q films, were prepared on CFE under the same preparation conditions (with respect to, e.g., supporting electrolyte, pH of electrolytic solution, concentration of mercaptohydroquinones, and oxidation potential) and their behavior as pH sensors were investigated in detail. We report here on preferable pretreatment of CFE for the preparation of PH_2Q's/CFE with good durability and their excellent functions as pH microsensors.

Experimental

Mercaptohydroquinones used were synthesized and purified according to the method of Alcolay.[10] Chemicals used for the synthesis of mercaptohydroquinones were of reagent grade. All the other chemicals were of analytical grade and were used without further purification. Electropolymerization of mercaptohydroquinones was performed under potentiostatic conditions with a three-electrode system consisting of a CFE (Torayca T-300, Toray Industries Co., 7 μm in diameter) working electrode, a Pt wire counter electrode, and a saturated calomel electrode (SCE) in a conventional two-compartment glass cell. Potentiostatic electrolysis and cyclic

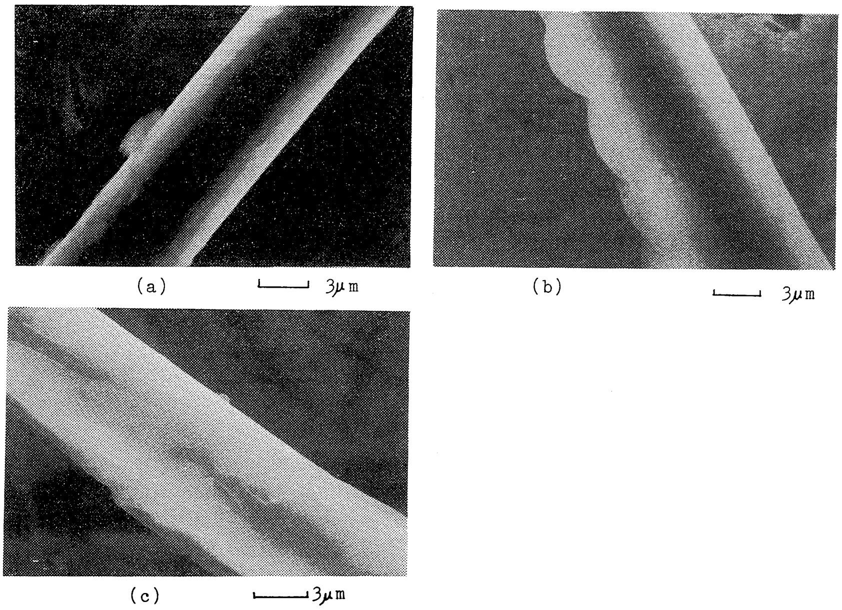


Fig. 1. Scanning electron micrographs of (a) PH_2Q/CFE_0, (b) PH_2Q/CFE_1, and (c) PH_2Q/CFE_2.

voltammetry were performed by using a potentiostat/galvanostat (Model HA-304, Hokuto Denko Co.). PH_2Q/CFE, $PMeH_2Q$/CFE, and PMe_2H_2Q/CFE were attached with Ag paste to an end of a Cu wire which was in a coaxial wire as shown in the previous paper,[8] and their electrode potentials in a buffer solution were measured with an electrometer (Model EM-02, Toho Chemical Research Co.). Scanning electron micrographs were taken on a scanning electron microscope (SEM) (JEOL JSM-35C).

Results and Discussion

Three types of pretreatments were examined on CFE: *Procedure 1* in which a CFE was thoroughly rinsed with deionized water; the CFE thus treated is denoted as CFE_0. *Procedure 2* in which a CFE was thoroughly rinsed with acetone and then washed with deionized water; the CFE thus treated is denoted as CFE_1. *Procedure 3* in which a CFE was rinsed with acetone, then electrochemically cleaned at −1.5 V (vs. SCE), where hydrogen evolution occurs in a Britton-Robinson buffer solution of pH 5.0, for ca. 30 min, and finally washed with deionized water; the CFE thus treated is denoted as CFE_2. CFE_o, CFE_1, and CFE_2 were modified with PQ by potentiostatic electropolymerization using a Britton-Robinson buffer (20 vol% ethanol) solution of pH 6.0 of mercaptohydroquinone (4×10^{-4} mol dm^{-3}) at +0.7 V (vs. SCE) for 30 min under a nitrogen atmosphere at room temperature. Then the PQ's thus prepared were reduced at −0.5 V (vs. SCE) for 30 min in a buffer solution of pH 5.0 to give PH_2Q's. PH_2Q/CFE_0, PH_2Q/CFE_1, and PH_2Q/CFE_2 were stored in a weakly acidic buffer solution and were thoroughly rinsed with deionized water just before SEM measurement. Figure 1 shows scanning electron micrographs of PH_2Q/CFE_0 (a), PH_2Q/CFE_1 (b), and PH_2Q/CFE_2 (c). These micrographs reveal that CFE_2 is uniformly coated over the whole surface with a relatively large amount of PH_2Q, whereas CFE_1 is partially coated with PH_2Q, and that CFE_0 is scarcely coated. Only PH_2Q/CFE_2 displayed good durability. Moreover, PMe_2H_2Q could not be prepared on CFE_1 or CFE_2. These results obtained by SEM indicate that uniform coating of PH_2Q on CFE is required for PH_2Q/CFE to possess good durability as a pH sensor and that the electrochemical cleaning method used here is a preferable pretreatment of the CFE surface. Unless otherwise stated, subsequent examinations were carried out with the CFE_2 prepared as described above. Cyclic voltammograms of CFE's modified with PH_2Q, $PMeH_2Q$, or PMe_2H_2Q are shown in Fig. 2. The anodic and cathodic current integrals of these cyclic voltammograms indicate that the amount of electroactive sites developed on CFE's are in the order: PH_2Q (2.9×10^{-1} mC cm^{-2}) > $PMeH_2Q$ (1.5×10^{-1} mC cm^{-2}) > PMe_2H_2Q (1.1×10^{-1} mC cm^{-2}). The scanning electron micrographs (Fig. 3) of $PMeH_2Q$/CFE and PMe_2H_2Q/CFE surfaces indicate that $PMeH_2Q$ and PMe_2H_2Q, as well as PH_2Q (Fig. 1), are coated uniformly over the whole surfaces of CFE's. Characteristics of their pH responses are summarized in Table 1. Of these three electrodes, only PMe_2H_2Q/CFE could hardly get wetted in an acidic buffer solution having pH lower than 4.5, while in alkaline solution PMe_2H_2Q/CFE was superior to the others in Nernstian response and durability. As seen from Fig. 2, hydroquinone moieties which provide redox sites in PH_2Q, $PMeH_2Q$, and PMe_2H_2Q have an increasing tendency to shift their redox potentials towards negative with increasing number of methyl groups. This tendency is consistent with the fact that redox potentials of hydroquinones are usually shifted more negative with increasing number of electron-releasing substituents such as methyl group.[11] Furthermore, it has been known that acid-base dissociation constants of hydroquinones substituted by electron-releasing groups are smaller than that of unsubstituted hydroquinone

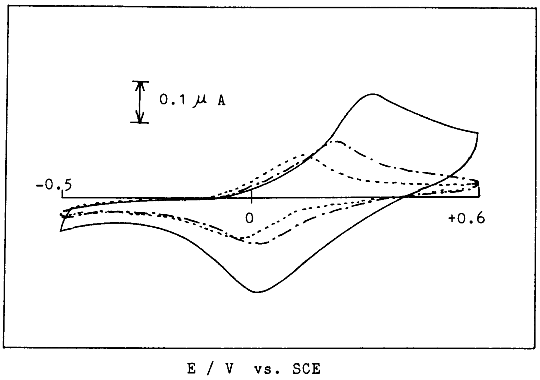
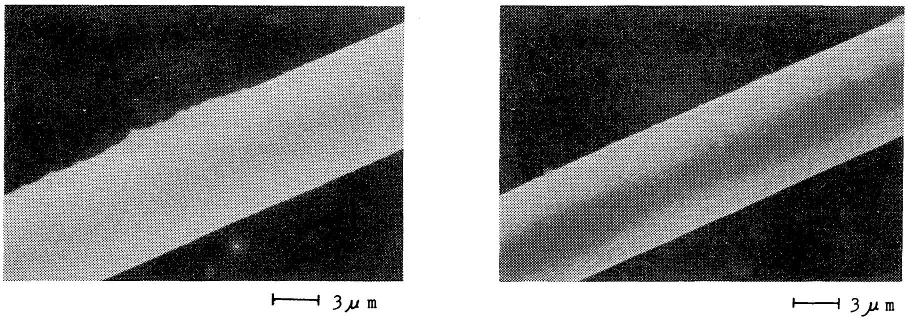


Fig. 2. Cyclic voltammograms of PH_2Q/CFE(——), $PMeH_2Q$/CFE(–·–·–), and PMe_2H_2Q/CFE(······) in the Britton-Robinson buffer solution of pH 6.0 in an atmosphere of nitrogen at 25°C. Scan rate: 50 mVs^{-1}. Effective lengths of these electrodes dipped into the buffer solution were 3 cm.



(a) (b)

Fig. 3. Scanning electron micrographs of $PMeH_2Q$/CFE (a) and PMe_2H_2Q/CFE (b).

Table 1. pH Response Characteristics of PH_2Q/CFE, $PMeH_2Q$/CFE, and PMe_2H_2Q/CFE at 25 °C[a]

Electrode[b]	Slope	Response range	Response-time pH range (I) within 2s
	mV/pH	pH	(II) within 10s
PH_2Q/CFE	59.0 ± 0.4[c]	1.8—8.5	(I) 3.0—8.0
	30.0 ± 0.8[c]	<10.0	(II) 1.8—3.0, 8.0—9.0
$PMeH_2Q$/CFE	58.9 ± 0.4[c]	2.0—9.0	(I) 3.0—8.0
	30.0 ± 0.8[c]	<10.0	(II) 2.0—3.0, 8.0—9.5
PMe_2H_2Q/CFE	58.9 ± 0.3[c]	4.5—10.0	(I) 4.5—9.0
	30.0 ± 0.7[c]	<11.0	(II) 9.0—10.0

a) Britton-Robinson buffer ($2<\mathrm{pH}<11$) and Clark-Lubs buffer ($\mathrm{pH}<2$) were used as standard pH solutions. b) The effective length immersed into the buffer was ca. 1 mm. c) The standard deviation for slopes obtained with multiple calibrations over 20 times.

in aqueous solution.[12] As can be seen in the response ranges in Table 1, the upper limit of linear response with a slope of ca. 59 mV/pH for each electrode is in the order of PMe_2H_2Q/CFE > $PMeH_2Q$/CFE > PH_2Q/CFE. Consequently, it would be reasonable to judge that the upper limits of linear response (ca. 59 mV/pH) for PH_2Q/CFE, $PMeH_2Q$/CFE, and PMe_2H_2Q/CFE are dependent on the dissociation constants of hydroquinone moieties in PH_2Q, $PMeH_2Q$, and PMe_2H_2Q, respectively. All these electrodes could work well for at least one month when kept stored in a weak acidic buffer solution. But their pH responses gave rise to apparent deviations from the Nernstian behavior after successive measurements in alkaline buffer solution. It is considered that this undesirable behavior results from oxidation of the hydroquinone to quinone moieties in PH_2Q, $PMeH_2Q$, and PMe_2H_2Q by dissolved oxygen gas, because a sufficient deaeration of an alkaline solution by bubbling nitrogen gas could serve to slow down the rate of lowering of their durabilities. Moreover, even after used successively in an alkaline solution, both $PMeH_2Q$/CFE and PMe_2H_2Q/CFE could be practically restored by electroreduction of the resulting quinone moieties to the hydroquinone ones at −0.5 V (vs. SCE) in a weak acidic buffer solution for ca. 30 min in a nitrogen atmosphere. On the other hand, the PH_2Q/CFE whose response function had been lowered could scarcely be restored by the electroreduction. This poor restoration of PH_2Q/CFE may be attributed to the fact that no substituted quinones are more susceptible to aqueous decomposition caused by attack of hydroxide ion than methyl-substituted quinones in alkaline solution.[13] All of PH_2Q/CFE, $PMeH_2Q$/CFE, and PMe_2H_2Q/CFE prepared under the electrolysis conditions of 1×10^{-4} to ca. 1×10^{-3} mol dm^{-3} in concentration, 20 min to ca. one hour in electrolysis time, and +0.5 to +0.7 V (vs. SCE) in electrolysis potential, exhibited similar excellent Nernstian responses to pH as shown in Table 1 and displayed good durabilities. When mercaptohydroquinones were electrooxidized at higher concentrations or for longer period than have been specified above, PH_2Q/CFE, $PMeH_2Q$/CFE, and PMe_2H_2Q/CFE obtained could not respond well to pH. Moreover, when mercaptohydroquinones were oxidized above +0.8 V (vs. SCE) on CFE, the resulting modified CFE's made no response to pH. We have previously reported that mercaptohydroquinone shows an anodic wave which is probably caused by oxidation of a thiol group, at +0.8 V (vs. SCE) on DC polarogram in a Britton-Robinson buffer solution (pH 6.0) using a glassy carbon electrode.[6] Therefore, the no-response behavior observed probably results from oxidation of sulfide linkage in PH_2Q, $PMeH_2Q$, and PMe_2H_2Q.[14] As has been mentioned above, the PH_2Q/CFE, the $PMeH_2Q$/CFE, and the PMe_2H_2Q/CFE are capable of excellent functioning as pH microsensors and will, therefore, be applicable to various microchemical works.

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