Bull. Chem. Soc. Jpn., ***64,*** *505—509 (1991)*

Electrochemical Studies of Poly(mercaptohydroquinone) and Poly(mercapto-*p*-benzoquinone) Films Prepared by Electrochemical Polymerization. V. Spectroelectrochemistry of Ten pH Indicators in the Film

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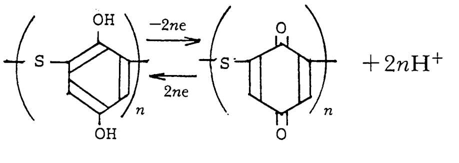
(Received July 26, 1990)

The electroconductive, almost colorless and transparent poly(mercaptohydroquinone/mercapto-*p*-benzoquinone) film, prepared by electropolymerization of mercaptohydroquinone on an SnO_2/glass electrode, was impregnated with a pH indicator. The film exhibited a clear electrochromic behavior arising from proton release/consumption within the film by electrooxidation/reduction, as verified by spectroelectrochemical measurements. For ten different pH indicators examined, such a color change could be well repeated over a long-term continuous experiment by use of potential steps.

There has been considerable interest in examining transition metal oxides,[1] conductive polymer films prepared by electropolymerization,[2] and electrochromic active sites introdueed in polymers as the basis for electrochromic displays.[3] The spectroelectrochemical response observed with these materials comes directly from the coloration of their electrochemically reduced or oxidised form. As described in a series of papers,[4] poly(mercaptohydroquinone) ($\mathrm{SQ_{Red}}$) and poly(mercapto-*p*-benzoquinone) ($\mathrm{SQ_{Ox}}$) are electroconductive and almost transparent films. These redox polymers (SQ, standing for $\mathrm{SQ_{Red}}$ and/or $\mathrm{SQ_{Ox}}$) exhibit no change in the shape of the cyclic voltammogram over more than 1000 times repetitive potential scannings from +0.7 V vs. a saturated calomel electrode (SCE) to the H_2 evolution potential. The oxidation-reduction equilibrium between $\mathrm{SQ_{Ox}}$ and $\mathrm{SQ_{Red}}$ is represented by the following scheme.



Hence, the pH value in an SQ film in contact with an aqueous solution will be decreased by oxidation, while increased by reduction of the film. When a pH indicator is incorporated into the polymer film, the film will exhibit a color change characteristic of the pH indicator by oxidation-reduction of the film. Spectroelectrochemical properties of phenolphthalein, a typical pH indicator, incorporated within the SQ film on a transparent electrode (SnO_2/glass) was briefly reported in a previous paper,[5] where phenolphthalein showed a distinct color change between red by reduction and transparent by oxidation of the film. Here we describe spectroelectrochemical behaviors of ten different pH indicators incorporated within the polymer film and the characteristics of the electrochromic electrodes thus prepared.

Experimental

Chemicals and Preparation of SQ Films. Mercaptohydroquinone was synthesized and purified according to the method described in our previous papers.[6] All of the pH indicators and inorganic reagents used here were of reagent grade and used without further purification. Deionized water was used for preparation of solutions and rinsing the SQ film. The substrate electrode was an SnO_2/glass plate (Taiyo Yuden Co.). The SnO_2/glass plate was washed with acetone and rinsed with water. The SnO_2/glass plate was coated with an SQ film by anodic polymerization of 10 mM (1 M=1 mol dm^{-3}) mercaptohydroquinone at a potential of +0.7 V vs. SCE in a Britton-Robinson buffer solution of pH 7.0 containing 20% volume fraction ethanol in an N_2-atmosphere at room temperature.

Apparatus and Procedure. Potentiostatic electrolysis and cyclic voltammetry were performed with a Toho Technical Research potentiostat/galvanostat Model 2020. The

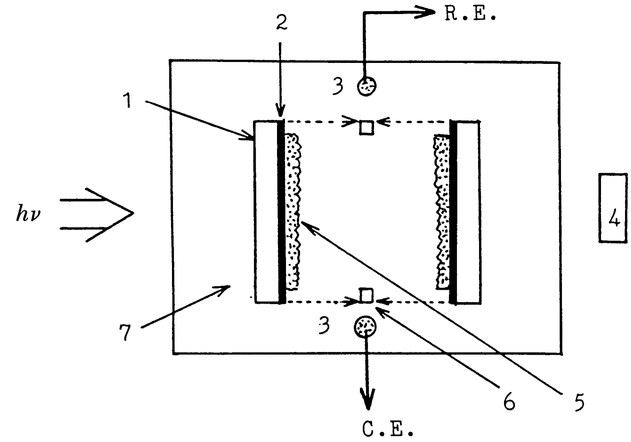


Fig. 1. Schematic view of the experimental arrangement for transmission spectroelectrochemical measurements.
1: Substrate glass, 2: SnO_2, 3: Salt bridge, 4: Detector, 5: pH indicator-impregnated SQ film, 6: Silicone rubber, 7: Supporting electrolyte solution.

electrode surface was examined with a JEOL scanning electron microscope (SEM) Model JSM-35C. Spectroelectrochemical study of the pH indicator-impregnated electrodes was done with a three-electrode system consisting of an SCE reference electrode, a Pt wire counter electrode, and an electrochromic working electrode placed in a Shimadzu spectrophotometer Model UV-240. The electrochromic working electrode consisted of a pair of pH indicator-impregnated electrodes held together face to face via two 0.5-mm thick silicone rubber spacers as shown in Fig. 1.

Incorporation of pH Indicators. Incorporation of pH indicators into the SQ films was carried out by three different methods: (1) electropolymerization of mercaptohydroquinone in a Britton-Robinson buffer solution containing 50% volume fraction of ethanol, saturated with the pH indicator, (2) dipping of the SQ film-coated SnO_2/glass electrode in an ethanol solution saturated with the pH indicator for ca. 20 h, and (3) spray of an ethanol solution containing the pH indicator on the SQ film-coated electrode. The electrochromic cells prepared by methods (1) and (2) were inferior to the cell prepared by method (3) with regard to the optical density, which depends the amount of the pH indicator incorporated within the SQ film, for all of the pH indicators examined. Moreover, the electrochromic cell prepared by method (3) exhibited good reproducibility in color change when the SQ film was repetitively oxidized/reduced. In view of this, the electrochromic cell used in this work was prepared by method (3). The SQ_{ox} film prepared on an SnO_2/glass electrode was rinsed with methanol, washed with water, and then air-dried. A small amount (ca. 0.05 cm^3) of an ethanol solution containing 10% volume fraction of water and 2% mass fraction of a pH indicator was sprayed on a dried SQ film of 1 cm^2 in area. A pH indicator-impregnated SnO_2/glass electrode was then soaked in a 1 M KCl aqueous solution adjusted to a pH value slightly lower than the value where the indicator changes the color, by adding a small amount of an HCl and/or KOH aqueous solution, and used immediately as an electrochromic working electrode. The 1 M KCl solution thus conditioned was also used as the supporting electrolyte solution. The pH value of the 1 M KCl solution adjusted to each of the pH indicators is denoted by "pH in cell" in the last column of Table 1.

Results and Discussion

Properties of SQ Films on SnO_2/Glass. Figure 2 shows the relationship between the time of electrooxidation of mercaptohydroquinone and the amount of the SQ film formed on the SnO_2/glass electrode, calculated from their cyclic voltammograms (CV). The amount of the SQ film increased linearly with the electrolysis time up to 40 min. However, the SQ film became colored in dark yellow by electrolysis for more than ca. 20 min. Therefore, all the SQ films used in this work were prepared by 20-min electrooxidation. A typical CV of the resulting SQ film on an SnO_2/glass electrode is shown in Fig. 3. A pair of broad anodic and cathodic waves arising from reduction-oxidation of the SQ film were observed with peaks at

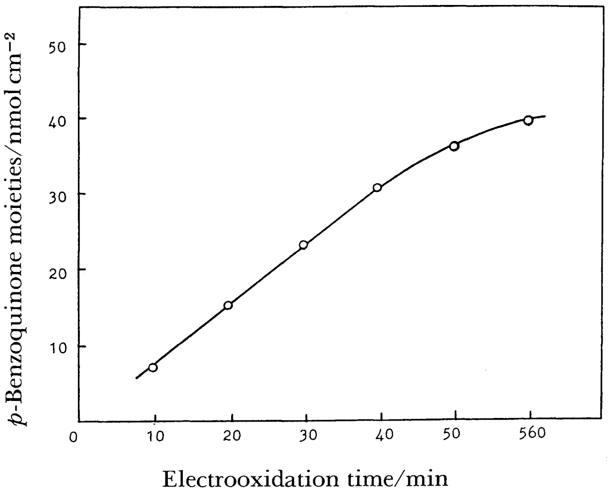


Fig. 2. Increase in the amount of quinone moieties in the SQ film on SnO_2/glass electrode with the lapse of electrooxidation time. The electrooxidation was carried out by anodic oxidation (+0.7 V vs. SCE) of 10 mM mercaptohydroquinone using Britton-Robinson buffer solution (20 vol% EtOH) in N_2 atmosphere.

Table 1. Electrochromic Characteristics of pH Indicator-Impregnated SQ Films Prepared on SnO_2/Glass Electrode[a]

pH indicator	Color change(pH)	Response time	pH in cell
	Acid color Basic color	s	
Bromophenol Blue[b]	Yellow(3.0) ⟷ Blue(4.6)	5—7	2.9
Bromocresol Green[b]	Yellow(3.8) ⟷ Green(5.4)	3—4	3.6
p-Nitrophenol	Colorless(5.0) ⟷ Yellow(7.6)	2—3	4.8
Bromothymol Blue	Yellow(6.0) ⟷ Blue(7.6)	2—3	5.8
Indooxine	Red(6.0) ⟷ Blue(8.0)	2—3	5.8
Quinoline Blue	Colorless(6.6) ⟷ Blue(8.6)	<2	6.4
Phenol Red[b]	Yellow(6.8) ⟷ Red(8.4)	3—4	6.6
o-Cresolphthalein	Colorless(8.2) ⟷ Red(9.8)	<2	8.0
Phenolphthalein	Colorless(8.3) ⟷ Red(10.0)	<2	8.0
Thymolphthalein	Colorless(9.4) ⟷ Blue(10.6)	4—5	9.0

a) All data are average of 10 or more experiments. b) Potential stepping was carried out between −0.5 V and 0.7 V vs. SCE.

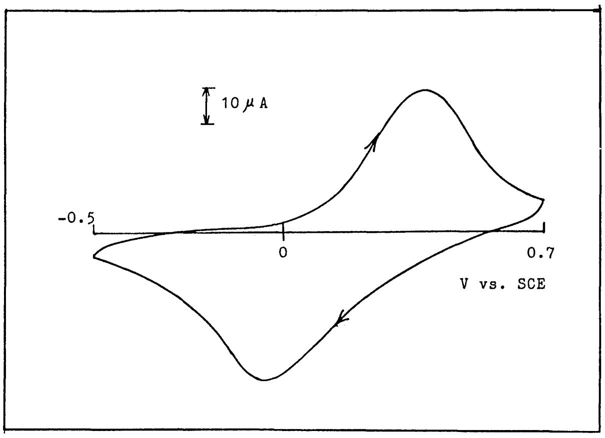


Fig. 3. Cyclic voltammogram of the SQ film prepared on SnO_2/glass electrode (1 cm^2 in area) in Britton-Robinson buffer solution (pH 5.0). The sample electrode was prepared under the same conditions as in Fig. 2.
Electrolysis time: 20 min, Sweep rate: 2 mV s^{-1}.

0.38 V and −0.05 V vs. SCE, respectively. The surface concentration of hydroquinone and/or *p*-benzoquinone moieties was calculated to be ca. 15.6 nmol cm^{-2}. This indicates that in an aqueous solution with a pH value at which one hydroquinone moiety releases two protons via a two-electron reaction, complete oxidation of SQ_{Red} to SQ_{Ox} may increase the amount of proton by 31.2 nmol, while on complete reduction of SQ_{Ox} to SQ_{Red} the same amount of proton may be lost per one sheet of electrode. Hence, in an electrochromic working electrode of 0.5 mm in thickness and 1 cm^3 in area (0.05 cm^3 in volume), the increase and/or decrease in the amount of hydrogen ion is twice this value because two sheets of working electrodes were used. Examination of the SQ film by SEM revealed that the dried film prepared by 20-min electrooxidation of mercaptohydroquinone (Fig. 4(b)) covered the whole surface of the SnO_2/glass electrode, though the film was rougher than that on a glassy carbon electrode.[7] The film thickness was estimated to be 1—2 μm and even after repeated water washings no appreciable morphological change was observed.

Spectroelectrochemical Properties. Figure 5 depicts the absorption spectrum of a colored *o*-Cresolphthalein-impregnated SnO_2/glass electrode when SQ_{Ox} was reduced to SQ_{Red} at −0.7 V, with the dashed curve showing the spectrum of an SnO_2/glass electrode coated with SQ_{Red} alone. In addition, the inset gives a typical absorption spectrum of a colored *o*-Cresolphthalein alkaline solution. The absorption maximum at 565 nm observed for the colored working electrode is in good agreement with that of colored *o*-Cresolphthalein in an alkaline solution. This indicates that the coloration observed on the working electrode is obviously due to that of *o*-Cresolphthalein within the SQ_{Red} film. When the potential of the colored working electrode was stepped to +0.7 V where SQ_{Red} was oxidized to SQ_{Ox}, the absorption spectrum based on the coloration rapidly disappeared. This spectral change was easily observed visually, namely the working electrode became red in a few seconds when reduced and colorless when oxidised. Then the potential was changed by use of square voltage pulses, and both the optical response at 565 nm and the current response were recorded. The result is illustrated in Fig. 6. The time course of absorvance response was almost the same for anodic and cathodic potential steps even after 10 min of the repetitive potential steps. But a small amount of the colored indicator was observed to seep out of the gap between the two sheets of SnO_2/glass electrodes into the solution bulk when the potential step had been continued for more than ca. 10 min.

Similar spectroelectrochemical behaviors were

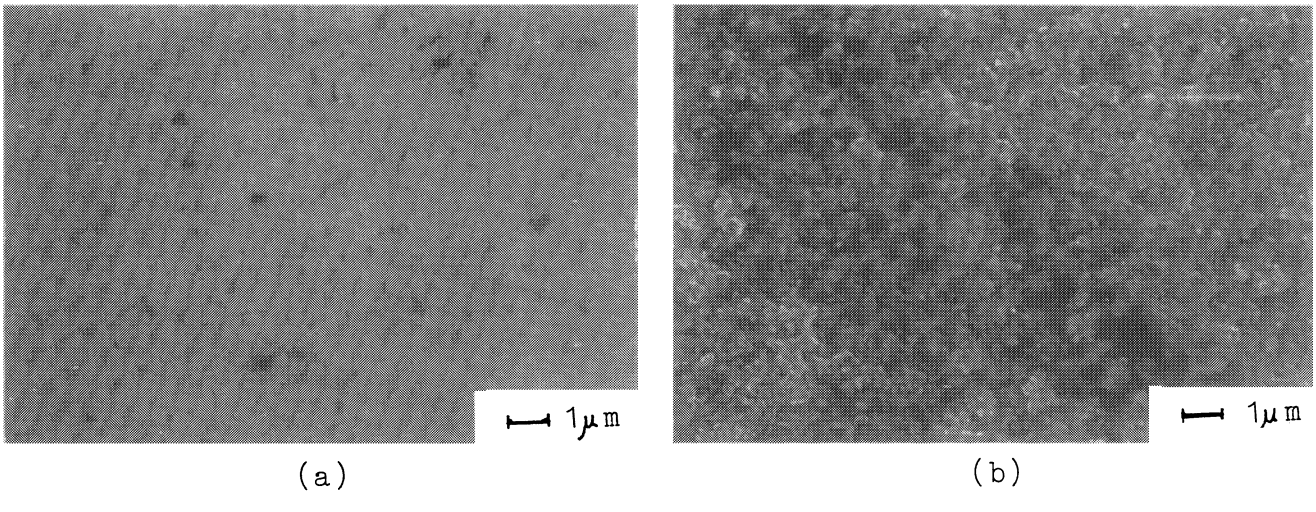


Fig. 4. SEM photograph of the bare surface (a) and the SQ film-coated surface (b) of SnO_2/glass electrode. The SQ film-coated electrode was prepared under the same conditions as in Fig. 3.

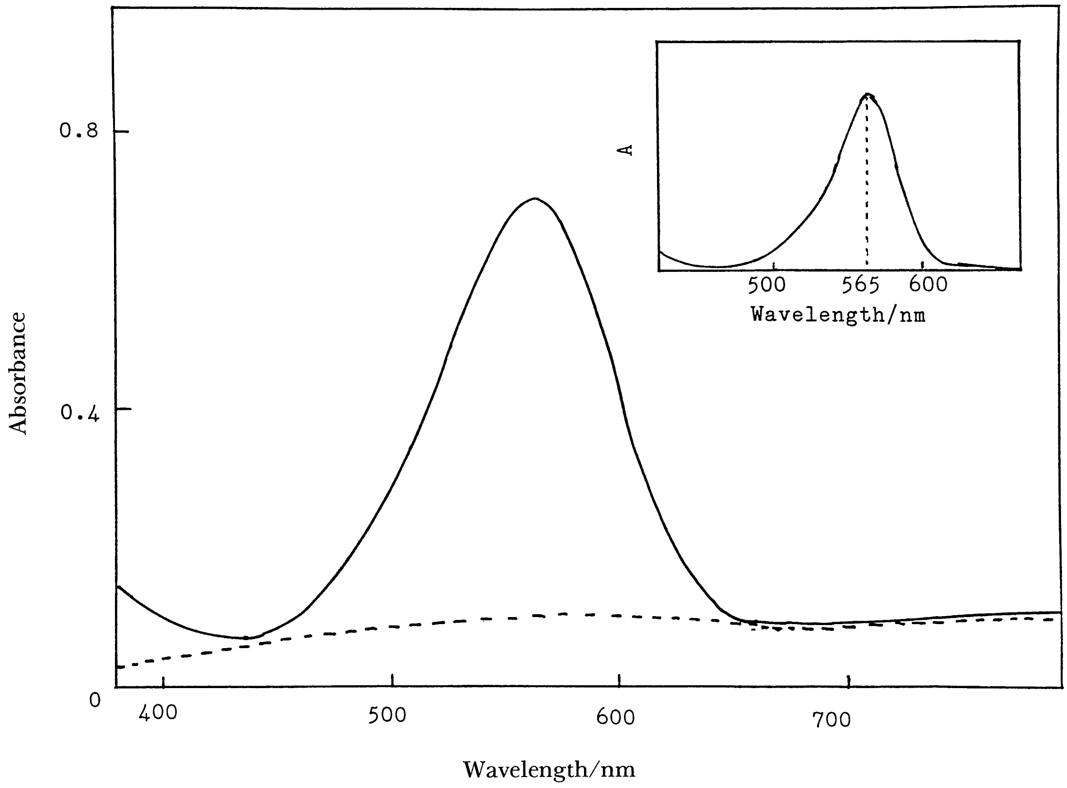


Fig. 5. Absorption spectrum of colored *o*-cresolphthalein incorporated within SQ_{Red} film on SnO_2/glass electrode (solid curve). Dashed curve represents the absorption spectrum of the SQ_{Red} film alone on SnO_2/glass electrode. Inset shows the absorption spectrum of a colored *o*-cresolphthalein alkaline solution.

observed for the other indicators incorporated within the SQ film. Their spectroelectrochemical properties are given in Table 1. Most of the pH indicators examined here exhibited their characteritic color change within ca. 5 s by a potential step of the working electrode. Almost no decrease in optical density of the colored working electrode was observed at least within 10-min run of repetitive potential steps. Moreover, the shaped CV of the SQ film on the SnO_2/glass electrode remained unchanged even after a long-term run of repetitious potential steps. This demonstrates that neither the hydroquinone nor *p*-benzoquinone moiety in the SQ film reacts with the pH indicators examined here. A slight seepage of the colored pH indicator as in the case of *o*-Cresolphthalein was observed in every case.

Bromophenol Blue, Bromocresol Green, and Phemol Red underwent electrochemical reduction in a potential range from −0.7 V to −0.5 V. Therefore, for these indicators the potential of the working electrode was stepped between −0.5 V and +0.7 V. The positive shift in the negative-end potential from −0.7 V to −0.5 V tended to lengthen the response time of the color change at basic pH's. This tendency is reasonable since the response speed of the color change may depend on the rate of reduction-oxidation of the SQ film. Bromophenol Blue which

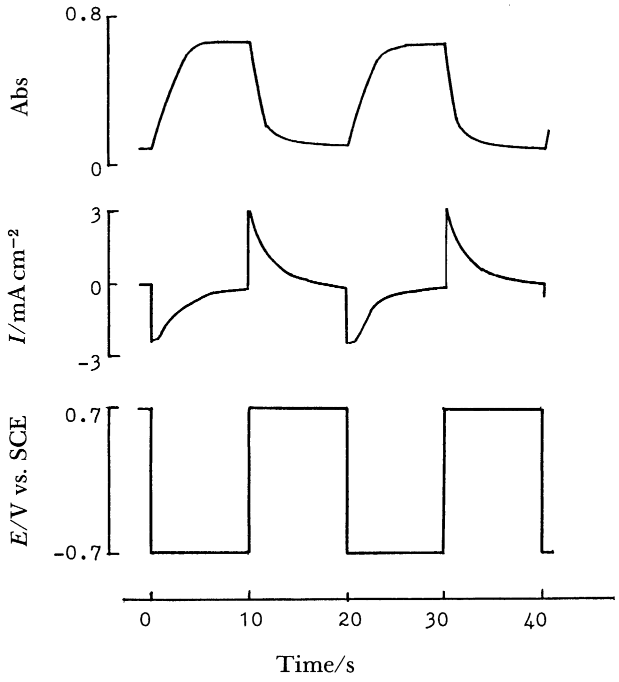


Fig. 6. Response of absorbance and current to a square voltage pulse for the *o*-cresolphthalein-impregnated SQ film (prepared on SnO_2/glass electrode under the same conditions as in Fig. 3) measured in a supporting electrolyte solution of pH 8.0 (see Table 1).

exhibits a color change in the lowest pH range among the pH indicators listed in Table 1, required the longest time for the color change. Thymol Blue, which should change color from red to yellow by a pH range from 1.2 to 2.8, showed no color change even when the potential was stepped between −0.7 V and +0.8 V vs. SCE. Hence Thymol Blue was omitted from Table 1. Judging from the estimate that the decrease in the amount of H^+ ion in the working electrode by reduction of SQ_{Ox} to SQ_{Red} is 62.4 nmol (see above), the phenomena observed for these two pH indicators may be rationalized. In line with this, a slower response in color change was observed also for Thymolphthalein, which should change color in a relatively strong alkaline range, namely between pH 9.4 and 10.6. In a previous work,[8)] we found that an SQ_{Red}-coated carbon electrode showed pH response with a slope of ca. −59 mV/pH over a pH range from 1.8 to 8.5, and with a slope of ca. −30 mV/pH above pH 10. This indicates that the pK_1 of the hydroquinone moiety in the SQ film is nearly 8.5. Hence, the slow response of the color change for Thymolphthalein is understandable in this content.

The present results demonstrate that ten different pH indicators incorporated within the SQ film on an SnO_2/glass electrode show well-repetitive characteristic color changes by potential steps. In addition, the pH indicators suitable for use in the electrochromic cell employed here should change color in a pH range from 3 to 10, should not be electrochemically active over a potential range where the SQ film is oxidised or reduced, and should not chemically react with either SQ_{Red} or SQ_{Ox}.

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