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Electrochemical Studies of Poly(mercaptohydroquinone) and Poly(mercapto-*p*-benzoquinone) Films Prepared by Electropolymerization. III. Basic Behavior and Properties in Aqueous Solutions

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Electrochemical behavior and properties of poly(mercaptohydroquinone)/poly(mercapto-*p*-benzoquinone) (SQ) films prepared on glassy carbon electrodes (GCE) by anodic polymerization of mercaptohydroquinone were examined in detail by cyclic voltammetry. Almost all hydroquinone and/or *p*-benzoquinone moieties in SQ films of less than ca. 100 monolayers are electroactive in acidic and neutral buffer solutions. The formal redox potential (as estimated from anodic and cathodic peak potentials) vs. solution pH plot, the slope of which is −60 mV/pH, suggests that the overall electrode reaction of SQ films is an H^+/e (1:1) reaction. As to the voltammetric behavior of SQ films, the peak current decreased and the peak potential separaxtion (ΔE_p) increased appreciably in unbuffered solutions as compared with those in buffered solutions. The difference of these voltammetric behaviors in unbuffered and buffered solutions increased with increasing pH. Moreover, the peak current increased and ΔE_p decreased with rising solution temperature. These noticeable behaviors observed on SQ films are discussed in connection with the charge-transport mechanism within SQ films. SQ films on GCE showed good durability over a wide potential range from the hydrogen evolution potential to +1.0 V vs. SCE.

Much attention has recently been drawn to the preparation and properties of thin films of polymeric materials covalently bonded to or coated on glassy carbon electrodes (GCE). Especially electroconductive polymers having hydroquinone/quinone moieties are of particular interest as electrocatalysts because they can act as selective chemical oxidants[1,2] and reductants.[3] However, for all electroactive polymers on GCEs having quinone and/or hydroquinone functionalities so far reported, as far as we know, only a few monolayers are electroactive unless small mediator molecules are present that can penetrate the polymer matrix and carry electrons between redox sites.[4]

In a series of our recent papers,[5–8] we have reported of (i) a preparation method of poly(mercaptohydroquinone/mercapto-*p*-benzoquinone)(SQ) films on GCE and on Pt electrode, (ii) applications of SQ film-coated electrodes to various metal sensors and an electrochromic display, and (iii) the electrocatalytic oxidation of NADH to NAD^+. In the present paper, we will report on basic electrochemical behavior and properties of SQ films on a GCE with particular reference to the following points: (i) the redox response behavior of SQ films of ca. 4 to ca. 100 monolayers in thickness, (ii) the influence of solution pH and solution temperature on the charge-transport process within SQ films, and (iii) the applied potential range in which stable voltammetric response is obtained for SQ films on a GCE.

Experimental

Materials and Preparation of SQ Films. Mercaptohydroquinone was synthesized and purified according to the method described in our previous paper.[5] The chemicals used for the synthesis of mercaptohydroquinone were of reagent grade. The other inorganic reagents and ethanol used for rinsing SQ films 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 SQ films. The substrate electrode used was a GCE 3 mm in diameter. SQ films on the GCE were prepared by anodic polymerization of mercaptohydroquinone at a constant potential of +0.5 V vs. a saturated calomel electrode (SCE) in a Britton–Robinson buffer solution (pH 5.0) containing 20 vol% ethanol, as previously described.[5] The surface concentration (Γ^x, where the superscript x stands for x nmol cm^{-2}) of the electroactive sites, i.e., the hydroquinone and/or *p*-benzoquinone moieties, in SQ films was controlled by the amount of charges passed during the electrochemical polymerization and estimated by measuring the area of cyclic voltammograms for the oxidation–reduction reaction of SQ films themselves, obtained at a scan rate of 2 mV s^{-1} in the Britton–Robinson buffer solution.

Apparatus and Procedure. The apparatus used for the preparation of SQ films on the GCE was the same as that used in our previous work.[5] Voltammetric measurements were carried out with a standard three-electrode system consisting of an SQ film-coated GCE working electrode, a Pt plate counter electrode, and an SCE reference electrode having an agar salt bridge of saturated KCl. Cyclic voltammetry was performed by using a potentiostat/galvanostat (Model HA-304, Hokuto Denko Co.). Purified nitrogen gas was bubbled for 30 min to remove dissolved oxygen. Unless otherwise noted, all measurements were run under nitrogen atmosphere at room temperature. All potential values cited in this paper are those referred to the SCE.

Results and Discussion

Cyclic Voltammetric Behavior. Figure 1 shows a typical cyclic voltammogram representing the electrochemical response of an SQ film-coated GCE in the Britton–Robinson buffer solution (pH 6.5) at a scan rate of 50 mV s^{-1}. The SQ film examined has $\Gamma^{10.2}$ corresponding to ca. 17 monolayers based on a close-packed monolayer of ca. 0.6 nmol cm^{-2} for 4-methyl-1,2-benzenediol lying flat on a perfectly flat carbon surface.[2] The voltammetric response remained qualitatively unchanged even after a potential scan cycling of several hours in acidic and neutral buffered aqueous solutions and is similar to that obtained for the ordinary electrode reaction of a solution-phase redox species at an uncoated electrode, that is, the voltammogram has diffusional tails and its shape is unsymmetric as shown in Fig. 1. Cyclic voltammetric behavior at various scan rates in a Britton–Robinson buffer solution of pH 6.0 was examined for SQ film-coated GCEs loaded with three different amounts of Γs, viz., $\Gamma^{2.17}$(=ca. 3.6 monolayers), $\Gamma^{10.2}$, and $\Gamma^{56.0}$(=ca. 93.3 monolayers). The results are summarized in Table 1. For all the three SQ films examined, linear relationships exist between the anodic and cathodic peak currents (i_p^a and i_p^c) and the square root of scan rate ($\sqrt{v}$) on the time scale of 100 mV s^{-1}. At scan rates lower than 50 mV s^{-1}, the anodic and cathodic peak currents are proportional to the Γ values, and the peak separation (ΔE_p) is almost constant irrespective of the film thickness. Thus the amount of the charges consumed in the oxidation–reduction reaction of SQ films are almost proportional to the Γ value. On the other hand, at scan rates higher than 50 mV s^{-1}, the anodic and cathodic peaks were observed to be broader and ΔE_p was increased with increasing scan rate and/or Γ value. These results show that almost all hydroquinone and/or *p*-benzoquinone moieties in SQ films are electroactive even at the scan rate of 50 mV s^{-1} although the charge transport in SQ film was rather slow, and suggest that the electron transfer between the substrate electrode (GCE) and the innermost sublayer of SQ film may be faster than the charge transport within SQ film which may be controlled by electron hopping and/or proton transfer between adjacent electroactive sites, ion migration, polymer motions, or combinations of these actions. From the fact that the SQ film of ca. 100 monolayers may be electroactive on the time scale of 50 mV s^{-1}, SQ film-coated GCEs are superior to other poly(hydroquinone) film-coated electrodes[1–3] in respect of the charge transport within polymer layers.

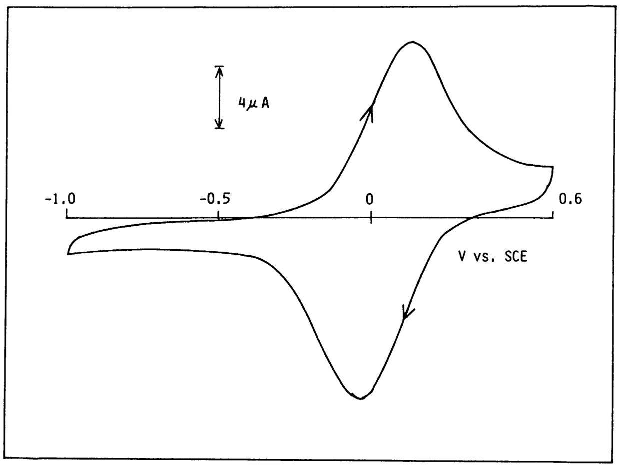


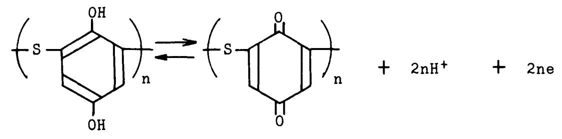
Fig. 1. A typical cyclic voltammogram of SQ film-coated GCE in a Britton–Robinson buffer solution (pH 6.5) at a scan rate of 50 mV s^{-1}. The surface concentration of hydroquinone and/or quinone moieties in SQ film was 10.2 nmol cm^{-2} ($\Gamma^{10.2}$). The arrow indicates the direction of potential scan.

Response in Buffered and/or Unbuffered Solutions. In order to clarify the charge-transport process within SQ film, the pH dependence of cyclic voltammograms of SQ film-coated GCEs was examined over the pH region 2—8 using Britton–Robinson buffer solution. The anodic and cathodic peak potentials (E_p^a and E_p^c) shifted to the negative potential side with increasing pH. E_p^a, E_p^c, and the formal redox potential ($E^{0\prime}$) which is estimated as the average of E_p^a and E_p^c values, are shown in Fig. 2. Over the pH region 2—8, the slope of the $E^{0\prime}$ vs. pH plot is about −60 mV/pH. This result suggests that the overall electrode reaction of SQ film is the H$^+$/e (1:1) reaction in the examined pH region on the time scale examined. On the basis of the fact that SQ film is a hydroquinone/*p*-benzoquinone redox polymer and that the slope of the $E^{0\prime}$ vs. pH plot is ca. −60 mV/pH in the pH range below 8, and with the assumption that the negative logarithm of the first dissociation constant (pK_1) of the hydroquinone moiety in SQ film is from 9 to 10 based on the pK_1

Table 1. Change in Peak Current and Peak Separation of Cyclic Voltammograms of SQ Film-Coated GCEs of Various Values with Scan Rates of Potential Sweeping in a Britton–Robinson Buffer Solution (pH 6.0). Γ Values Were Controlled by the Electrolysis Time of Mercaptohydroquinone

		$\Gamma^{2.17}$			$\Gamma^{10.2}$			$\Gamma^{56.0}$	
Scan rate	i_p^a	i_p^c	ΔE_p	i_p^a	i_p^c	ΔE_p	i_p^a	i_p^c	ΔE_p
mV s^{-1}	μA	μA	mV	μA	μA	mV	μA	μA	mV
10	0.63	0.64	120	2.9	3.0	120	16.0	16.3	130
20	1.20	1.22	130	5.5	5.7	130	28.5	27.5	140
50	2.55	2.70	160	11.5	12.0	170	54.0	56.5	210
100	4.40	4.95	180	18.0	20.5	200	80.0	86.5	270
200	7.60	9.00	210	31.5	34.5	245	134.5	154.0	350

value of hydroquinone (pK_1=9.9), the overall reduction-oxidation reaction of SQ film in aqueous solutions of pH 2 to 8 may be written as



The other pH effects in the buffered solutions on the cyclic voltammograms for SQ film-coated GCEs are summarized in Table 2. The anodic and cathodic peak currents decreased slightly and ΔE_p decreased with increasing pH below 4, while in the pH region higher than 5, both the peak currents increased and ΔE_p decreased with increasing pH. At pH higher than 8, the cyclic voltammograms for SQ films were largely distorted in shape and the integrated current was decreased with increasing pH as shown in Fig. 3, where cyclic voltammograms are illustrated just after 10 cycles since the distortion in shape became more complicated as the potential scan was cycled. Even though the SQ film-coated electrode was transferred to acidic or neutral solution after successive potential sweepings in alkaline solution, the observed distortion remained unchanged. These results show that the distortion in wave shape resulted from some chemical or structural change of SQ film itself because in alkaline aqueous solution *p*-benzoquinone is susceptible to addition of OH^- ion.[9)] Turning to the pH dependence of cyclic voltammograms, very similar behavior is seen to an anthraquinone polymer film reported by Degrand[10)] with respect to the pH dependence of i_p^a, i_p^c, and i_p^a/i_p^c. To date, a similar pH dependence of redox behavior has also been reported with other types of conductive polymers.[11–13)] In order to further detail the pH dependence of the charge transport within SQ films, the cyclic voltammetric

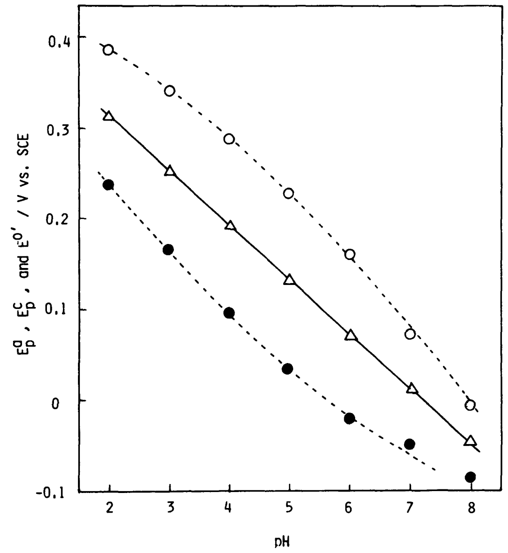


Fig. 2. pH-dependences of the anodic and cathodic peak potentials (E_p^a and E_p^c) and the formal redox potential ($E^{0\prime}$) of the cyclic voltammograms of SQ film-coated GCE using Britton-Robinson buffer solutions. Other experimental conditions are the same as in Fig. 1. ○: E_p^a, ●: E_p^c, △: $E^{0\prime}$.

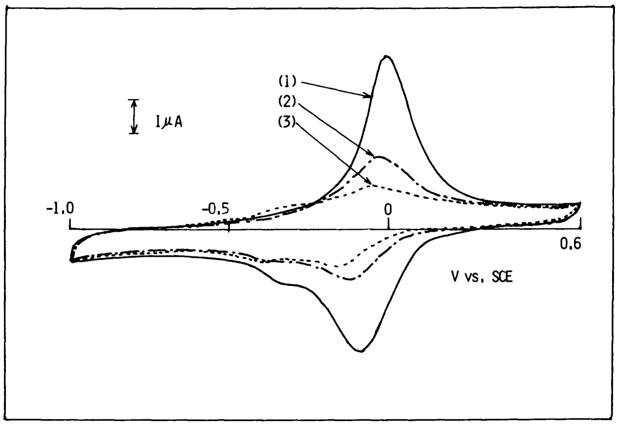


Fig. 3. Wave distortion observed on the cyclic voltammograms for SQ film-coated GCE's of $\Gamma^{13.0}$ just after 10 cycles in alkaline buffer solutions. Scan rate: 50 mV s^{-1}. (1) pH 8.5, (2) pH 9.0, (3) pH 9.5.

Table 2. pH Dependence of the Peak Current and Peak Separation of SQ Film-Coated GCEs Obtained at a Scan Rate of 50 mV s^{-1} in Britton-Robinson Buffer Solutions

pH	i_p^a	i_p^c	i_p^a/i_p^c	ΔE_p	Γ[a)]
	μA	μA		mV	nmol cm^{-2}
2	15.8	18.3	0.86	150	13.4
3	15.5	16.5	0.94	160	13.0
4	14.2	15.0	0.95	190	13.2
5	14.0	14.5	0.97	190	12.5
6	14.3	14.7	0.97	180	12.6
6.5	14.3	15.5	0.99	160	12.9
7	14.6	13.5	1.08	120	12.4
7.5	17.3	15.0	1.15	100	12.6
8	17.5	14.8	1.18	90	12.4

a) All the SQ films examined were prepared on GCEs by a constant-potential electrolysis for 30 min at the same conditions as described in Experimental section.

behavior of SQ film-coated GCEs was examined in unbuffered aqueous solutions since the pH change within SQ films resulting from the oxidation-reduction reaction of SQ films in unbuffered solutions may be more rapid and larger than in buffered solutions. It is, therefore, expected that the charge transport within SQ films will be affected remarkably by this rapid and large pH change. Figure 4 shows cyclic voltammograms for an SQ film-coated GCE having $\Gamma^{13.1}$ (ca. 22.0 monolayers) in unbuffered solutions of various pH values. The wave shapes in the unbuffered solutions differed considerably from those in the buffered solutions. The difference in the wave shapes increased with increasing pH, that is, in the unbuffered solutions the peak current dramatically decreased and ΔE_p remarkably increased with increasing pH, whereas in the buffered solution of pH 5.0 the peak current slightly decreased and ΔE_p slightly increased (see Fig. 2) and at pH 7 two anodic and two cathodic peaks were obscurely observed on the examined time scale. Such voltammetric behavior observed in the unbuffered solutions may be explained as follows: Consider the electro-oxidation process of SQ film (reduced form). The electro-oxidation of one hydroquinone moiety gives one *p*-benzoquinone moiety and two protons over the pH range examined. The numbers of the hydroquinone moieties in the SQ film used were almost equal because the same electrode ($\Gamma^{13.1}$) was used in the examined three cases. The increments of the protons resulting from the electro-oxidation of all the hydroquinone moieties in the SQ film may, therefore, be equal in the three cases. Hence the pH change in the SQ film induced by the electro-oxidation of the film may increase in the order of pH 7>pH 5>pH 3. The pH change in the SQ film results in variation of the redox potential of hydroquinone/*p*-benzoquinone couple in the film. It is clear on the basis of the Nernst equation that the redox potential of hydroquinone/*p*-benzoquinone moieties in SQ films become more negative with increasing pH and more positive with decreasing pH in SQ films. In the case of the oxidation process of SQ films, the decrease in pH within inner layers of SQ films (in the immediate neighborhood of the GCE) may retard the further oxidation of hydroquinone moieties in their outer layers. On the other hand, in the case of the reduction process of SQ films the increase in pH within inner layers may also retard the further reduction of *p*-benzoquinone moieties in outer layers. Judging from their pH dependence described above and their reduction-oxidation behavior in unbuffered solutions, it may safely be said that the propagation of the redox reaction between adjacent hydroquinone/*p*-benzoquinone moieties participates predominantly in the charge-transport process within SQ films on the time scale examined.

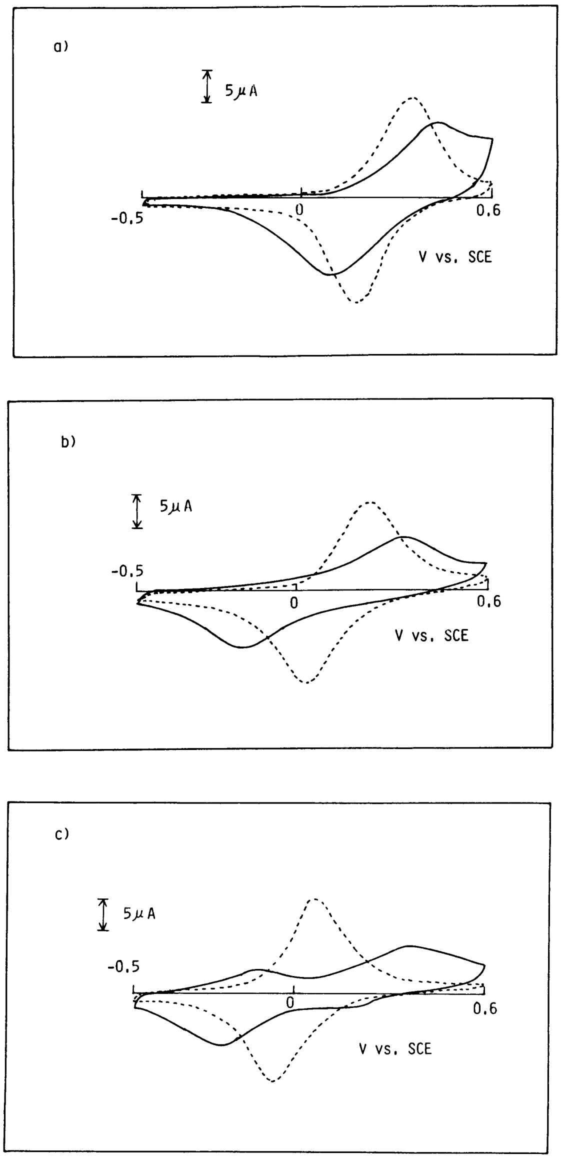


Fig. 4. Comparison between the cyclic voltammograms of SQ film-coated GCE of $\Gamma^{13.1}$ in buffer solutions and those in no buffer solutions. Full lines were obtained in 0.1 mol cm^{-3} KCl solution adjusted to each pH value by addition of an appropriate quantity of dilute HCl or NaOH while broken lines were obtained in Britton–Robinson buffer solutions. Scan rate: 50 mV s^{-1}. a) pH 3.0, b) pH 5.0, c) pH 7.0.

Influence of Temperature. Cyclic voltammetric measurements on the SQ film-coated GCE having $\Gamma^{13.0}$ were carried out over the solution temperatures from 1 to 50 °C. The peak currents increased and ΔE_p decreased with rising temperature, as shown in Fig. 5. The temperature dependence observed is completely reproducible and suggests that the rate of the charge transport through SQ films may be facilitated by rising the temperature. It seems to be a reason for the temperature dependence of the charge transport within SQ films that the rise in temperature makes the segmental polymeric chains in SQ films more mobile

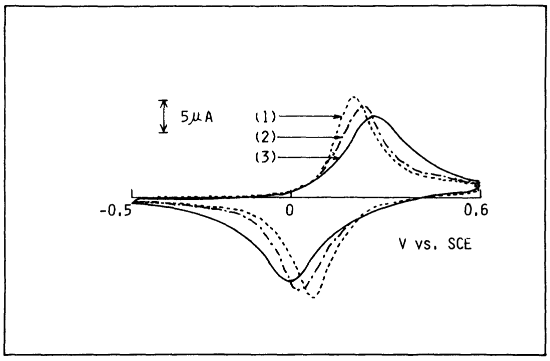


Fig. 5. Temperature-dependence of the cyclic voltammogram of SQ film-coated GCE of $\Gamma^{13.0}$ in the Britton–Robinson buffer solution (pH 5.0). Scan rate: 50 mV s^{-1}. (1) 50 °C, (2)20 °C, (3) 1 °C.

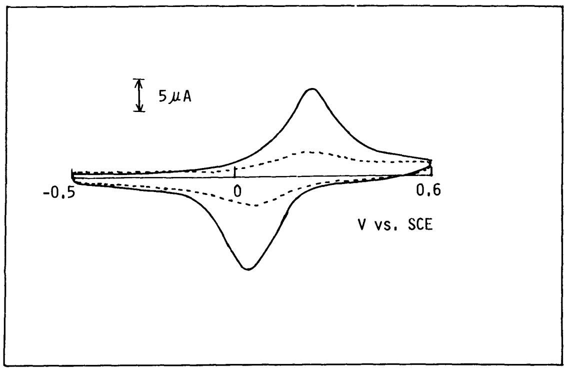


Fig. 7. Change in the cyclic voltammogram of SQ film-coated GCE of $\Gamma^{12.6}$ before and after holding the electrode potential at +1.2 V. Scan rate: 50 mV s^{-1}. ——: 0 min, ---------: 30 min.

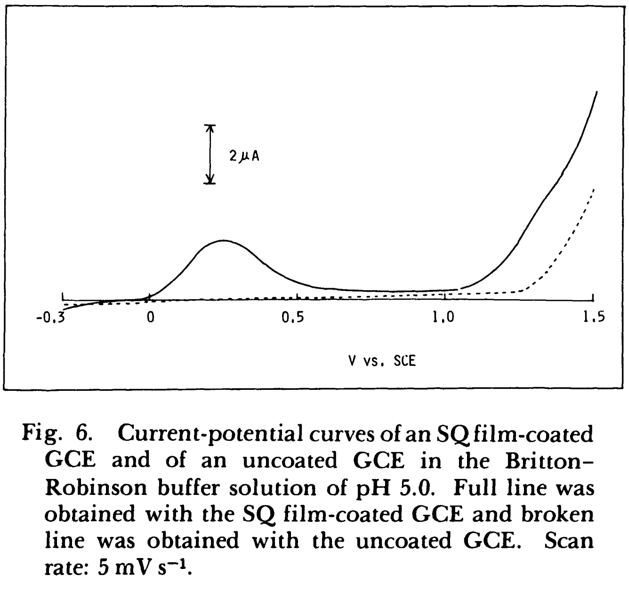


Fig. 6. Current-potential curves of an SQ film-coated GCE and of an uncoated GCE in the Britton–Robinson buffer solution of pH 5.0. Full line was obtained with the SQ film-coated GCE and broken line was obtained with the uncoated GCE. Scan rate: 5 mV s^{-1}.

and that thereby the counter electroactive sites, hydroquinone, and *p*-benzoquinone may be brought more closely together. In addition, the rate of the redox reaction, or the proton migration and electron hopping, between adjacent electroactive sites will also be increased with rising temperature. Thus these two effects are considered to be responsible for the temperature dependence of the charge-transfer rate within SQ films. A similar phenomenon has been reported with a polymerized vinylferrocene.[14)]

Stability to Applied Potential. The stability of SQ films on GCE to applied potential was examined over a wide potential range using a weakly acidic Britton–Robinson buffer solution in which SQ films were very stable as described above. Figure 6 shows anodic voltammograms for an SQ film-coated GCE and an uncoated GCE in the Britton–Robinson buffer solution of pH 5.0. The anodic wave in the potential range of +0.2 to +0.4 V observed on the SQ-coated GCE corresponds to the oxidation reaction of hydroquinone moieties to *p*-benzoquinone ones in the SQ film. At more positive potentials than +1.1 V, appreciable increase in anodic current is observed for the SQ-coated GCE, as compared with the uncoated GCE. This increase in anodic current may probably be caused either by some further oxidation of the oxidized SQ film itself or by an unexpected oxidation of some species in the buffer solution. In order to study this increase in anodic current in more ditail, anodic response for the SQ film was examined after the potential of the SQ-coated GCE had been held for 30 min in the Britton–Robinson buffer solution of pH 5.0 at +1.2 V where the increase in anodic current of the SQ film was observed. As shown in Fig. 7, peak currents significantly decreased while peak potentials remained almost unchanged. A similar decrease in peak current was observed in a potential scanning at 50 mV s^{-1} from −0.5 to +1.2 V in the same buffer solution. The cyclic voltammetric wave caused by the reduction–oxidation reaction of the SQ film got smaller as the potential cycling was repeated and almost disappeared after ca. 100 cycles. These results strongly suggest that the increase in anodic current of the SQ film-coated GCE above +1.1 V may result from some further oxidation of the oxidized SQ film itself, followed by an electrochemical inactivation of the film. At present, the mechanism of the further oxidation reaction is obscure. On the other hand, SQ films on GCE were observed to be very stable for the negative shift up to the potential of hydrogen evolution which depends on the solution pH. Judging from the fact that SQ films, even though of ca. 100 layers in thickness, are stable and conductive over a wide potential range in acidic and neutral aqueous solutions, the SQ film-coated GCE may be used as an excellent dehydrogenating and/or hydrogenating agent because the potential of electroactive sites can be controlled exactly to a desired potential with a potentiostat. We will report elsewhere of the electroreduction of quinones and the electrooxidation of hydroquinones with SQ film-coated GCEs.

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