Electrochemical and Spectroelectrochemical Characterization of Some Polypyrrole/Anthraquinone Sulfonate Films

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We have fabricated composite films of polypyrrole/quinone sulfonate *via* electropolymerization. The FTIR investigation indicated the incorporation of quinone sulfonate in the polypyrrole (PPy) film to compensate for a positive charge in the polymer chain. Further, the elemental analysis of PPy/9,10-anthraquinone-2-sulfonate (AQS⁻) showed that 0.29 of the sulfonate was incorporated per pyrrole unit. Cyclic voltammetric results in dimethylsulfoxide and dimethylformamide solutions showed that the two 1-electron transfer steps could be assigned to the formation of radical dianion (AQS^{2•-}) and trianion (AQS³⁻). The positive shift of the first cathodic peak for the incorporated AQS⁻ indicated a strong interaction between the dianion and the cationic sites of the polymer. The PPy/AQS⁻ film worked as a cation-exchanger at electrode potentials below about -0.3 V *vs.* Ag/AgCl (saturated KCl) because of the creation of the anionic sites of the reduced quinone.

Keywords Polypyrrole, anthraquinone sulfonate sodium salt, cation exchange property

Conducting polymer films incorporating electroactive species have been used for sensor applications, and the redox properties have been utilized in charge-storage devices such as super-capacitors and batteries.¹⁻⁶ The optical properties associated with redox switching in some conducting polymers have been studied for possible use in electrochromic devices with high coloration efficiencies.⁷⁻¹⁴ Polypyrrole (PPy) is one of the most useful conducting materials, since it polymerizes easily, forms a membrane readily and has high conductivity and chemical stability.¹⁵⁻¹⁷ Moreover, since it is easy to combine PPy with other anionic molecules, many functional composites with various properties have been investigated.¹⁸⁻²⁰ Especially, the PPy/quinone film is of analytical importance for the application in electrocatalysis and enzyme sensors.²¹⁻²³

In connection with our study, charge transfer of pyrrole copolymers substituted by anthraquinone, phenothiazine, or anthracene moieties has been reported.²⁴⁻²⁶ The electrical conductance of PPy films doping with various anthraquinone and naphthalene sulfonates appears to be very well correlated to the number of sulfonate groups attached, with the highest conductance attained at one sulfonate group per dopant molecule.²⁷⁻²⁹ Heipel has shown that the electrochemical quartz crystal microbalance (EQCM) technique can be used successfully to examine the doping level and the ion transport rate.³⁰

In this research, we prepared several composite films

consisting of polypyrrole and quinone sulfonates in aqueous solution by using electropolymerization techniques. FTIR spectral measurements and elemental analysis of PPy/9,10-anthraquinone-2-sulfonate (AQS⁻) revealed that the quinone sulfonates were incorporated in the polypyrrole matrix. Cyclic voltammetry and spectroelectrochemistry indicated the formation of di- and trianions of AQS⁻ during the reduction of the film. Further, it was found that the PPy/AQS⁻ could function as a cation-exchanger at electrode potentials below about -0.3 V *vs.* Ag/AgCl.

Experimental

Materials

Pyrrole (Wako Chemicals Co.) was used without further purification. All quinones used here were reagent grade and were purified by vacuum sublimation or recrystallization when impurities were found in voltammograms. Tetraethylammonium perchlorate (TEAP) was dried in a vacuum and stored over P₂O₅. Milli-Q water was used throughout our experiments. Reagent grade dimethylsulfoxide (DMSO) and dimethylformamide (DMF) were used as received from Wako Chemicals.

Equipment and procedures

Glassy carbon (GC) electrodes (Tokai, grade GC-20, diameter 3 mm) were polished with fine alumina (60 µm) and then sonicated for 5 min. Gold plated semi-transparent plastic films (FM-1 Courtaulds Performance Films, USA, 1.75 cm²) were used as

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working electrodes in spectroelectrochemical experiments. All the potentials reported here were referred to an aqueous Ag/AgCl (sat. KCl) electrode. FTIR-spectra were measured with a HORIBA Model FT-710 spectrometer. The spectroelectrochemistry of PPy/AQS⁻ films was studied with a Shimadzu UV1200 spectrometer controlled with an Apple Macintosh computer.

To prepare PPy/Cl⁻, pyrrole (0.5 M) was polymerized under potentiostatic conditions (+0.80 V) in an aqueous solution containing 0.1 M KCl. For preparation of PPy/AQS⁻, an aqueous solution containing pyrrole (0.5 M) and anthraquinone sulfonate (0.1 M) was electrolyzed at +0.80 V. The modified electrodes were then rinsed with water and dried with nitrogen gas before characterization in DMSO or DMF. All experiments were carried out under ambient temperatures (22±1°C), and 0.1 M TEAP DMF or DMSO solutions used for electrochemical measurements were deaerated by passing nitrogen gas through them for about 10 min before measurements.

Results and Discussion

The composition of the film

The FTIR-spectra of AQS⁻, PPy/Cl⁻, and PPy/AQS⁻

Fig. 1 FTIR-absorption spectra of (A) PPy/Cl⁻, (B) Na⁺AQS⁻, and (C) PPy/AQS⁻ diluted with KBr powder.

films (Fig. 1) demonstrated the >C=O stretching vibration for both the authentic AQS⁻ (B) and corresponding film (C) at almost the same frequency (*ca.*1670 cm⁻¹). The spectra are good evidence for the immobilization of AQS⁻ in the PPy film to compensate for the positive charge on the polymer chain. Elemental analysis of the PPy/AQS⁻ film (% found: C, 60.78; H, 3.78; N, 8.27; S, 4.77) indicated that 0.29 of AQS⁻ was doped electrostatically per pyrrole unit, *i.e.* {[-(C₄H₂NH)₃]⁺AQS⁻}_n. It has been pointed out that up to 0.3 AQS⁻ ion can be incorporated per pyrrole unit to balance the positive charge and to preserve local electroneutrality.^{27,31,32}

Electrochemical study

The cyclic voltammogram of 5 mM AQS⁻ dissolved in 0.1 M TEAP-DMF solution (Fig. 2A) displayed classical quinone electrochemistry with two well-defined Nernstian processes (*E*_{1/2}=-0.80 V for AQS⁻/AQS²⁻, and -1.35 V for AQS²⁻/AQS³⁻). Figures 2B and 2C show the cyclic voltammograms of the PPy/Cl⁻ and PPy/AQS⁻ films measured in 0.1 M TEAP-DMF. Peak potentials similar to those in Fig. 2 have also been observ-

Fig. 2 Cyclic voltammograms of (A) dissolved 5 mM AQS⁻, (B) PPy/Cl⁻, and (C) PPy/AQS⁻. The voltammograms were recorded in 0.1 M TEAP-DMF at scan rates of (A and B) 50 mV s⁻¹ and (C) 10 mV s⁻¹ at GC electrodes. Electrodeposition of PPy, +0.8 V for 5 min.

ed in DMSO solutions (Table 1). Although the E° for the second reduction of PPy/AQS⁻ (pc_2) was very close to that for the first reduction of the dissolved quinone, the pc_2 could not be ascribed to the semiquinone formation because of the following reasons. (1) Spectral measurements, as will be discussed later (Fig. 3), demonstrated that the onset of AQS⁻ reduction appeared at about -0.3 V. (2) This mechanism failed to explain the positive shifts of the pc_1 on the addition of Li⁺ ion (see Fig. 4B), if the pc_1 would have arisen solely from the reduction for the cationic sites of PPy. Consequently, it can be concluded that the first and second peaks of PPy/AQS⁻ that appeared at more positive potentials than those for the dissolved quinone are to be assigned to the formation of AQS²⁻ and AQS³⁻. In addition, the peak for AQS²⁻ is merged into that for polypyrrole.

The positive shift for the semiquinone formation indicates that AQS²⁻ was associated with the cationic site of the polymer as follows:

where Py_3 is the repeating unit of PPy consisting of three pyrrole rings, *i.e.* $-(C_4H_2NH)_3-$, and TEA^+ is tetraethylammonium ion inserted from the solution phase. However, polymer reduction should also coincide with Eq. (1), as suggested by the voltammogram (Fig. 2 C).

Ion pairing between anion radical and TEA^+ is usually negligible in aprotic dipolar solvents, and the interaction in the polymer texture was also assumed to be negligible because of the bulky structure of TEA^+ .

The positive shift of the second cathodic peak (pc_2) for PPy/AQS⁻ means that there is still an interaction between the trianion (AQS³⁻) and the polymer cationic charge (Fig. 2 C and Table 1). Figure 2 C suggests that the polymer should be in the reduced and nonionic form at the potentials where the second reduction occurs. However, as will be discussed later, spectroscopic evidence suggested that the polymer still had a substantial amount of the oxidized pyrrole unit, even at these negative potentials, during the measurements (Fig. 3 B). Thus, the unreduced PPy unit can interact with the quinone trianion, shifting the pc_2 to the positive potential:

Similar behavior in the peak potential of the pc_2 has been observed for 9,10-anthraquinone-2,6-disulfonate (Table 1). In contrast to the quinone sulfonates, 2-naphthalene sulfonate and *m*-nitrobenzene sulfonate in films did not exhibit substantial shifts when compared

Table 1 Electrochemical characteristics of polypyrrole/anthraquinone sulfonate composite films on glassy carbon electrodes in 0.1 M TEAP-DMSO

Compound	E_{pc1} / V	E_{pc2} / V
PPy/Cl ⁻	-0.23	N.D.
AQS ⁻	-0.83	-1.40
PPy/AQS ⁻	-0.50	-1.20
AQ(S ⁻) ₂	-0.80	-1.40
PPy/AQ(S ⁻) ₂	-0.65	-1.20
NS ⁻	-2.50	N.D.
PPy/NS ⁻	-2.50	N.D.
MS ⁻	-1.68	N.D.
PPy/MS ⁻	-1.70	N.D.

E_{pc1} and E_{pc2} are the first and second peak potentials referred to Ag/AgCl (sat. KCl). The concentration of the dissolved compounds were 5 mM. Abbreviations: AQS⁻, 9,10-anthraquinone-2-sulfonate; AQ(S⁻)₂, 9,10-anthraquinone-2,6-disulfonate; NS⁻, 2-naphthalene sulfonate; MS⁻, *m*-nitrobenzene sulfonate; N.D., not found.

to the dissolved sulfonates. The results can be explained in terms of the reduction potentials, which are much more negative than those of the quinone sulfonates. At these highly negative potentials, the polymer is reduced almost completely, so very few cationic sites should be available in the film. The potential shifts could also be explained in terms of the Donnan potential, accompanied by the introduction of the film on the electrode. However, this mechanism can be excluded because of the negligible shifts observed for naphthalene and nitrobenzene sulfonates. The positive shifts could also be assigned to trace water in the films, because they were prepared in aqueous solutions. However, this mechanism failed to explain the evidence that the PPy/AQS⁻ films that had been soaked in DMSO or DMF for 24 h gave almost the same potential values as those used without such treatment.

The oxidation peak for the semiquinone did not appear in the cyclic voltammogram of PPy/AQS⁻ as shown by the dashed curve in Fig. 2 C. As will be discussed later, AQS²⁻ is stable enough over periods of spectroscopic measurements, so the disappearance of the oxidation peak should not be due to a follow-up reaction for the semiquinone. Presumably, the anodic peak was merged into the anodic peak of PPy polymer, which appeared above 0 V for the PPy/AQS⁻ film, and the anodic peak at around -0.5 V (pa_2) can be assigned to the oxidation of trianion. Obviously, both the PPy and AQS⁻ show slower electron transfer with the electrode, when made into a composite film. The correlation coefficients between the cathodic peak height and the square root of the scan rate were more than 0.95 over 10 - 100 mV s⁻¹.

Spectroelectrochemistry of PPy/AQS⁻ composite films

The semiquinone radical AQS²⁻ dissolved in 0.1 M TEAP-DMF on an Au semitransparent electrode was purple in color and had a strong absorption band, which

is characteristic of AQS^{2-} , with a maximum at 565 nm. The spectra also indicated that the semiquinone radical was quite stable over periods of spectral measurements. Audebert *et al.* studied the cyclic voltammetry and spectroelectrochemistry of the 6-(pyrrol-1-yl) hexyl-9,10-anthraquinone-2-sulfonate monomer and polymer in 0.1 M LiClO_4 -DMSO.²⁰ The film electropolymerized on an optically transparent electrode exhibited an absorption band at almost the same wavelength as that for the monomer.

Figure 3A shows the potential dependence of absorbance at 565 nm for AQS^- dissolved in 0.1 M TEAP-DMF. The sharp increase in absorbance at -0.7 V is due to the formation of AQS^{2-} radical, and the decrease below -1.0 V can be attributed to the formation of AQS^{3-} , which was yellowish brown in color. Figure 3B illustrates the absorbance-potential curves for the PPy/ Cl^- and PPy/ AQS^- films, and the relative increase for the PPy/ AQS^- film indicates the formation of AQS^{2-} in the film. Here, the decrease in the absorbance of PPy/ Cl^- with a decrease in the potential can be assigned to the reduction of PPy, which agrees with the voltammetric results in Fig. 2B. However, Fig. 3B shows that below the reduction potential (-0.23 V), absorbance of PPy/ Cl^- (b) decreases only gradually with a decrease in the potential and that a substantial number of the cationic (oxidized) sites are still present

at -1.2 V. As a result, the absorbance-potential curve (a) shifted towards more positive potentials than that for the dissolved quinone (A) because of the interaction between the cationic site and AQS^{2-} . The ion pairing with AQS^{3-} is also likely at a potential as negative as -1.2 V, since the reduction of the PPy matrix is often slow.

Cationic exchange in PPy/ AQS^- film

When conducting polymers are reduced to their non-ionic states, large anions doped in the polymers are not ejected completely or at all from polymer texture. As a result, cations in solution are inserted into the texture to compensate for the anionic charges of the dopants, and the polymers behave like cation exchangers. Consequently, a similar property is expected for PPy/ AQS^- , although the cation exchange should be potential dependent because of AQS^- undergoing the redox reactions. In this section, we discuss the exchange properties of the PPy/ AQS^- film and hence ion pairing between AQS^{2-} and Li^+ ion in the film.

Figure 4 illustrates the dependence of voltammetric behavior on the concentration of Li^+ ion for the dissolved AQS^- (A) and PPy/ AQS^- (B), where Li^+ ion was added to examine if there would be some ion pairs formation with the reduced quinone. Ion pairing for many semiquinone systems has been successfully studied by assuming EC mechanisms, and the positive shifts of p_{c1} with an increase in the Li^+ concentration can be analyzed similarly.^{33,34}

Fig. 3 Absorbance vs. potential curves of (A) 5 mM AQS^- dissolved in 0.1 M TEAP-DMF and (B) PPy films monitored at 565 nm on Au plastic film electrodes: In (B), the curves a and b show the absorbance of the PPy/ AQS^- and PPy/ Cl^- films. Since precise control of the film thickness was difficult, the absorbance of two films was normalized to give the same value at 0 V. All the spectra given here are after the base line corrections for the Au-plastic electrodes. Electrodeposition of PPy, $+0.8$ V for 1 min.

where $(\text{Li}^+)_p\text{AQS}^{2-}$ is the ion pair formed in the film and p is the stoichiometric coefficient, and the association of AQS^{2-} with TEA^+ is neglected, as has been assumed in the previous section. The association constant K for Eq. (5) is given as follows:

$$K = \frac{[(\text{Li}^+)_p\text{AQS}^{2-}]}{[\text{Li}^+]^p[\text{AQS}^{2-}]} \quad (6)$$

The shift in the half-wave potential, $\Delta E_{1/2}$ with respect to the ion pair formation can be expressed approximately by the following equation:³³

$$\Delta E_{1/2} = \frac{RT}{F} \ln K + \frac{RT}{F} p \ln C_{\text{Li}^+} \quad (7)$$

where C_{Li^+} is the concentration of Li^+ ion in the bulk solution, $\Delta E_{1/2}$ is the difference in the potential between the PPy/ AQS^- films with and without Li^+ ion, and the other symbols have their standard meanings. Equation (7) predicts that, if there is an ion pair interaction, $E_{1/2}$ will vary linearly with respect to $\log C_{\text{Li}^+}$. The interaction between the Py_3^+ and AQS^{2-} , which coincides with Eq.(5), should have no effect on the potential, as long

Fig. 4 Cyclic voltammograms of (A) 5 mM AQS⁻ dissolved in DMF and (B) the PPY/AQS⁻ film at scan rates of (A) 50 mV s⁻¹ and (B) 10 mV s⁻¹. The Li⁺ ion concentrations are (a) 0.0, (b) 0.05, (c) 0.10, and (d) 0.30 M. The ionic strength was adjusted to 0.30 with TEAP. Electrodeposition of PPY, +0.8 V for 5 min.

as $\Delta E_{1/2}$ is used.

Figure 4 B shows the voltammograms of the PPY/AQS⁻ film at different Li⁺ concentrations. Successive decreases in the currents and positive shifts of the peaks were observed on the addition of Li⁺ ion. When the concentration of Li⁺ ion was increased from 0.0 to 0.30 M, the potential of the first cathodic peak shifted about 200 mV to the positive direction. The shifts confirm the ingress of Li⁺ ion into the film to counterbalance the negative charge arising from the quinone reduction. Therefore, the PPY/AQS⁻ film worked as a cation-exchanger at electrode potentials more negative than the onset potential of the first quinone reduction (ca. -0.3 V vs. Ag/AgCl). The p and K values for the semiquinone dissolved in DMF were evaluated to be 0.93 and 74 M⁻¹ and agreed well with the values that have been reported for the ion pairs of semiquinones in DMF.^{33,34} Although Eq. (7) would not allow the evaluation of the accurate p and K values for PPY/AQS⁻ because of the quasi-reversible nature of electron transfer, we evaluated tentative p and K values of 1.2 and 1.1×10^3 M⁻¹ for the ion pair in the film. The marked increase in the K value on the incorporation, which is also indicated by the comparison of Fig. 4A with Fig. 4B, seems to be more than the experimental uncertainties arising from the slow electron transfer. The reason for the increase of K is not clear, but the formation of a more compact film may be responsible. The polymer texture would become less polar by the formation of the contact ion pairs, leading to a more compact film by

the ejection of dipolar DMF molecules and bulky TEA⁺ ion. The decreases in the currents on the addition of Li⁺ ion might also be explained in terms of the formation of the compacted films arising from ejecting the electrolyte and DMF from the film (Fig. 4B).

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