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SELECTIVITY OF POLY(ANILINE) FILM-COATED ELECTRODE FOR REDOX REACTIONS OF SPECIES IN SOLUTION

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The polymer films, prepared by the electrochemical polymerization of aniline and its derivatives, were electroactive in an acidic solution. Electrodes coated with these films were possessed of the selectivity for the redox reaction of species in solution.

Polymeric electrode coatings have recently received remarkable attention, since electrodes with polymeric coatings show promise in potential application to electrocatalysis,1) antiphotocorrosion,2) and analytical sensors.3) In previous papers1) we have demonstrated that the metal complexes incorporated into a film, with which the electrode is coated, serve as electron-transfer mediating catalysts to accelerate slow electrode reactions of reactants present in the solution and that the incorporated complexes can catalyze the reduction or oxidation or both.

We wish to report here the selectivity of electrodes coated with polymer films, which are prepared by the electrochemical polymerization2-6) of aniline and its derivatives, for the redox reaction of redox species in solution. The redox species in solution can be oxidized or reduced at the polymer film-coated electrode only in a limited range of potential, where the dissolved species can be thermodynamically oxidized or reduced by the oxidized or reduced form of the polymer films on the electrode surfaces.

The films used were prepared on basal plane pyrolytic graphite (BPG) (Union Carbide Co., Parma, Ohio) (0.17 cm^2) and platinum (0.078 cm^2) electrodes by electrochemical polymerization of aniline and its derivatives (0.1 M, 1 M = 1 mol dm^{-3}) in 0.5 M Na_2SO_4-H_2SO_4 (pH 1.0) solution as described previously.2-6) A charge of 50 mC cm^{-2} was passed to yield a film the thickness of which was ca. 2000 Å. The resulting film for aniline (abbreviated as PAa) on electrodes is chemically stable and has good adhesion to electrode surfaces, and it is electroactive and conducting in a limited range of potential (i.e., ca. -0.1 — +0.7 V vs. a sodium chloride saturated calomel electrode (SSCE)) in an aqueous supporting electrolyte solution (0.2 M CF_3COONa-CF_3COOH (pH 1.0)), as was previously observed by Diaz and Logan6b) and Noufi et al.2b) So far, no attempt of electrochemical and quantitative characterization of electropolymerized films, such as poly(aniline), poly(pyrrole), has been reported.

Figure 1 shows a typical normal pulse voltammogram for the oxidation of the poly(aniline) film on platinum electrode. The S-shaped wave is similar to that obtained for the redox species incorporated into the electroinactive polymer films.7) Plots of anodic limiting currents of such voltammograms against the inverse square root of the sampling time were found to be linear, as expected for the diffusion process obeying the Cottrell equation.$^{7)}$ It was thus confirmed that the process of "diffusion" of electrons within the film can be treated as a semiinfinite diffusion process$^{7)}$ over the time scale used (i.e., 0.5 to 10 ms). The values of an apparent diffusion coefficient (D_{app})$^{7)}$ for the "diffusion" of electrons within the film were estimated to be 10^{-10} to 10^{-8} $cm^2\ s^{-1}$, depending upon the conditions (e.g., the potential and time of electropolymerization, etc.) used for the electrochemical preparation of the films. For example, the value of D_{app} obtained with the film shown in Fig. 1 was 1.2×10^{-10} $cm^2\ s^{-1}$.

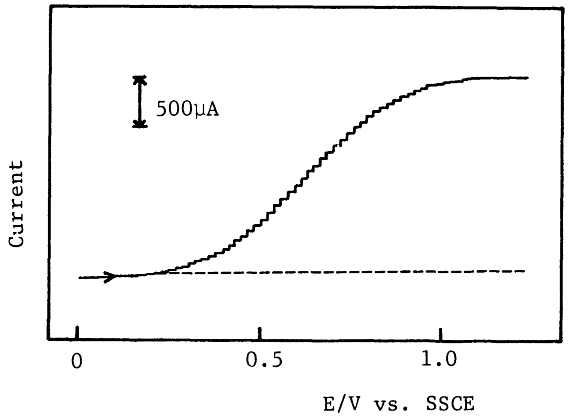

Fig. 1. A typical normal pulse voltammogram for the oxidation of poly(aniline) film on a platinum electrode in 0.2 M CF_3COONa-CF_3COOH (pH 1.0) solution. The concentration of electroactive sites, which was calculated from the total charge required for the complete oxidation of the film (the reduced form), was 9×10^{-7} mol cm^{-2}. Sampling time: 2 ms. Thickness of the film prepared at a constant potential of 1.2 V vs. SSCE: ca. 3600 Å. Dotted line shows a residual current.

Figure 2A shows a typical cyclic voltammogram representing the reversible electrochemical response of the film in an acidic solution. Its electroactivity varied with the pH value of the solution into which the film-coated electrodes were dipped. With an increase in pH, the anodic and cathodic peak potentials shifted to cathodically and at the same time the anodic and cathodic peak currents decreased. For example, the values of the maximum peak current at pH 7 and 10 were about one-seventh and one-fifteenth, respectively, of those at pH 1. Further, the separation between anodic and cathodic peak potentials became larger when the pH value was increased. Such an electrochemical response of the PAa film seems to be associated with a proton addition-elimination reaction.$^{2b)}$ The detailed mechanism of the electrochemical response of the film itself will be described elsewhere.$^{8)}$ Behavior similar to that of PAa film was also observed at poly(N-methylaniline)-, poly(N-ethylaniline)-, poly(2,6-dimethylaniline)-,and poly(2,5-dimethoxyaniline)-coated BPG electrodes.

Figure 2B shows the steady-state current-potential curves for the reduction of $[Ru(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$,and $[IrCl_6]^{2-}$ ions and the oxidation of $[W(CN)_8]^{4-}$, $[Fe(CN)_6]^{4-}$, I^-, $[Ru(CN)_6]^{4-}$,and Br^- ions at both a rotating disk BPG electrode coated with the PAa film and a rotating disk bare BPG electrode. As can readily be seen from this figure, the reduction of $[Fe(CN)_6]^{3-}$ ion and the oxidation of $[W(CN)_8]^{4-}$, $[Fe(CN)_6]^{4-}$,and I^- ions are observed at both PAa-coated and bare electrodes, and the redox potentials and the values of the limiting current of these species at the PAa-coated electrode are almost equal to those at the bare electrode. The redox potentials of these redox couples are within the range of potential in which the PAa film itself is electroactive, and it is thermodynamically possible that these species are oxidized or reduced by the oxidized or reduced form of the PAa film on the BPG electrode. The Levich plots for the reduction of $[Fe(CN)_6]^{3-}$ ion and the oxidation of $[W(CN)_8]^{4-}$, $[Fe(CN)_6]^{4-}$,and I^-

ions at the PAa-coated electrode gave straight lines which coincided with those obtained with the bare BPG electrode. Furthermore, the conventional log-plot[9)] of log $\{i/(i_{lim}-i)\}$ against E (where i_{lim} is the limiting current and i is the current at potential E) gave straight lines with reciprocal slopes of 60-70 mV in agreement with those at the bare electrode. Both the oxidation of $[Fe(CN)_6]^{4-}$ ion and the reduction of $[Fe(CN)_6]^{3-}$ ion can be observed at the PAa-coated electrode. This would be ascribed to the fact that the redox potential of the $[Fe(CN)_6]^{3-/4-}$ couple is within the range of potential where the PAa film is electroactive. Curves 8 of Figure 2B show that the current-potential curve for the reduction of $[IrCl_6]^{2-}$ ion at the coated electrode shifts to a potential more nagative than that at the bare BPG electrode, and that the potential at which the reduction of $[IrCl_6]^{2-}$ ion actually occurs at the film-coated electrode is almost equal to the positive limit of the potential at which the film itself is electroactive. Further, we can see that the reduction of $[Ru(NH_3)_6]^{3+}$ ion and the oxidation of $[Ru(CN)_6]^{4-}$ ion virtually do not occur at the PAa-coated electrode. For this reason, it is thought that the redox potentials of the $[Ru(NH_3)_6]^{3+/2+}$ and $[Ru(CN)_6]^{3-/4-}$ couples are outside the range of potential where the PAa film exhibits electroactivity, so that the reduction of $[Ru(NH_3)_6]^{3+}$ ion and the oxidation of $[Ru(CN)_6]^{4-}$ ion can not be catalyzed by the PAa film on electrode. It has previously been found that only relatively small ions such as H^+ and I^- can partially penetrate into the electroinactive poly(aniline) film which has structure similar to that of the PAa film.[3b)]

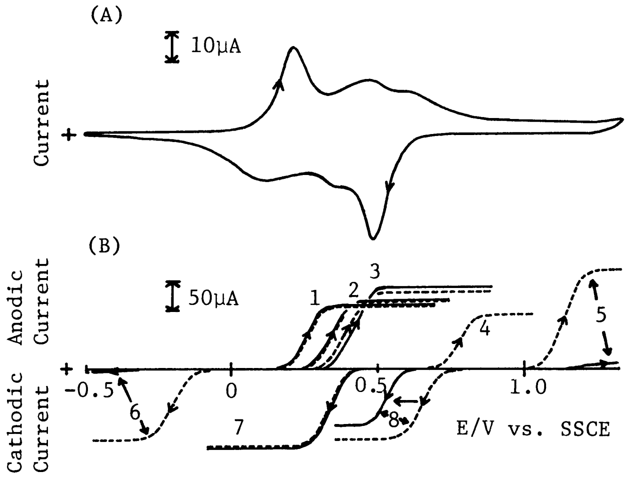

Fig. 2. (A) Cyclic voltammogram showing the electroactivity of poly(aniline) film on the BPG electrode in 0.2 M CF_3COONa-CF_3COOH (pH 1.0) solution. Scan rate: 50 mV s^{-1}. (B) Steady-state current-potential curves for the oxidation or the reduction of various redox species at both bare and poly(aniline)-coated rotating BPG disk electrodes. (——): At a poly(aniline)-coated BPG electrode; (---): at a bare BPG electrode. Oxidation of (1) $[W(CN)_8]^{4-}$, (2) $[Fe(CN)_6]^{4-}$, (3) I^-, (4) $[Ru(CN)_6]^{4-}$, (5) Br^-; Reduction of (6) $[Ru(NH_3)_6]^{3+}$, (7) $[Fe(CN)_6]^{3-}$, (8) $[IrCl_6]^{2-}$. Concentration of the redox species: 2 mM. Supporting electrolyte: 0.2 M CF_3COONa-CF_3COOH (pH 1.0). Rotation rate: 400 rpm. Scan rate: 1-2 mV s^{-1}.

From the above results, we infer that the PAa film-coated electrode possesses the selectivity for the redox reactions of the dissolved redox species which can not penetrate into the PAa film. It is demonstrated that the redox species in a solution can be oxidized or reduced at the PAa film-coated electrode only in a limited range of potential, where the dissolved species can be thermodynamically oxidized or reduced by the oxidized or reduced form of PAa film. That is, the dissolved redox species can be oxidized at the PAa film-coated electrode when their redox potentials are more negative than ca. 0.7 V vs. SSCE and they can be reduced when their redox potentials are more positive than ca. -0.1 V vs. SSCE. The BPG electrodes coated with poly(N-methylaniline), poly(N-ethylaniline), poly(2,-

6-dimethylaniline),and poly(2,5-dimethoxyaniline) films also displayed selectivity for the redox reaction of redox species in solution. We term a polymer film possessing such a property as "redox diode", since the current can flow in a limited range of potential. This property of the polymer films prepared by electrochemical polymerization of aniline and its derivatives as well as the selective permeability of these films to the various redox species dissolved in the solution[3a, 3b] seems to be worthy of remark in the modification of the electrodes by polymeric coatings. The idea presented here can also explain the experimental results of Diaz and Castillo[6a] that the oxidation of ferrocene is readily accomplished on the oxidized poly(pyrrole) film which is electroactive, but the reduction of nitrobenzene is inhibited by the film which is insulating when it is reduced to the neutral form.

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