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Basic Behaviors and Properties of the Electrodeposited Polyaniline

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Basic behaviors and properties of polyaniline(PA) deposited anodically on platinum electrodes have been studied on the following points. 1) Effect of the mode of electrolysis and supporting electrolytes in the film forming process. 2) Characteristics of charging-discharging processes. 3) Electric conductivity and elemental composition of PA. The different modes of electrolysis do not affect the characteristics of the PA electrode obtained. The growth rate of PA film is 2.7—2.8 times faster in sulfuric acid than in perchloric, nitric or hydrochloric acid. It is indicated that there are two types of doping; one is associated with the acid-base equilibrium between amino or imino group in the film and proton in the solution and the other is associated with the excess charge in the film produced by anodic oxidation. The electric conductivity of PA markedly decreases by the immersion in alkali solutions. The release of doped anion from PA by treating with an alkali solution is confirmed by the elemental analysis. The amount of anions occluded by the electrochemical doping process is determined to be 0.25—0.29 per monomer unit.

Polyaniline (PA) film as a typical electroconductive organic polymer has been first prepared by Diaz and Logan[1] by means of anodic oxidation of aniline in aqueous sulfuric acid. They used platinum as the anode electrode and the polymer film was deposited on it. Recently, Noufi and his coworkers[2] showed that the deposition of PA film is possible onto the surface of several semiconductor electrodes such as Cd-chalcogenides, Si, GaAs, and GaP. Since the latter materials are corrosive in aqueous media, the polymer coating will provide a new mean of the corrosion protection.

In contrast to polypyrrole[3], another representative conducting polymer, studies on polyaniline are very limited and, as far as we are aware, only two papers which are mentioned above have been published in the past. We thus attempted to study the basic characters of polyaniline in more detail.

Experimental

Electrode substrate used was a platinum wire having geometry of 1 mm in diameter and 10 mm in length (S=*ca.* 0.3 cm^2). Only for the determination of doped anions released from the film, a platinum plate having surface area of *ca.* 8 cm^2 was used. Although two types of electrolysis, repeated potential cycling and controlled potential electrolysis, were employed in the film forming process, the most of measurements were made with PA electrode (PAE) prepared by potential cycling. The potential cycling was repeated usually 40 to 50 times in sulfuric acid solutions. Other details of electrochemical measurements are given at appropriate positions in the following description.

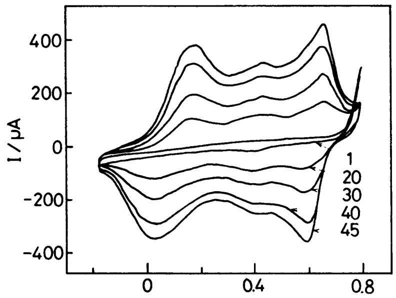


Fig. 1. Change of voltammograms in the preparation of polyaniline film by repeated potential cycling between −0.2 and 0.8 V. Numerical figure attached to each curve indicate number of potential cycle.
Solution: 0.1 M H_2SO_4+0.1 M aniline.
Sweep rate: 100mV·s^{-1}.

Electric conductivity of PA films was measured with the four-probe method described by van der Pauw.[4] Specimens used for the conductivity measurement were prepared by pressing the powdery product obtained by potentiostatic electrolysis.

All the potential values cited in this paper are those referred to a saturated calomel electrode. All experiments were carried out at room temperature.

Results and Discussion

1. Preparation of Polyaniline Film. Polyaniline film electrodes (PAE) were prepared in two different ways, repeated potential cycling and constant potential electrolysis. Figure 1 indicates the cyclic voltammogram observed with a platinum electrode immersed in 0.1 M H_2SO_4 containing 0.1 M aniline (1 M=1 mol dm^{-3}). The redox charge of polyaniline film continued to grow by the repetition of potential cycling. The cathodic charge in Fig. 1 increased linearly with the number of potential cycling. This indicates that the growth of polyaniline film is proportional to the number of potential cycling.

The possibility of preparing the film with constant potential electrolysis was next studied in 0.1 M H_2SO_4

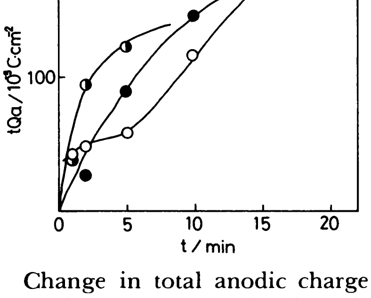


Fig. 2. Change in total anodic charge against the duration of constant potential electrolysis.
Electrode potential: 0.8 [●], 1.0 [○], 1.2 [◑] V.
Solution: 0.1 M H_2SO_4+0.1 M aniline.

containing 0.1 M aniline. The electrolyses were carried out at 0.8, 1.0, and 1.2 V, and the transient current was recorded for each measurement. After finishing the electrolysis, the electrode was subjected to the cathodic potential sweep to determine the charge associated with the redox reaction of the film itself, Qr.

The rate of aniline oxidation is a complicated function of the electrode potential. The total anodic charge, tQa, rapidly and monotonously approached to a saturation value at 0.8 and 1.2 V. Contrarily, at 1.0 V, the tQa-time curve made a step, where tQa almost ceased to increase, and again increased gradually. These are shown in Fig. 2.

Regardless of the electrode potential a tight thin film first appeared on the platinum surface and soon after that a powdery, non-adhesive structure which finally falls down from the electrode grew over the film surface. Inside of this massive structure, the thin film seems to grow progressively as far as tQa continues to increase. In fact, when Qr's were plotted against the time of anodic treatment, the curve forms were entirely similar to those shown in Fig. 2. The cyclic voltammograms exhibited by two PAE's prepared by the constant potential electrolysis and the potential cycling were almost the same and no practical difference was observed.

Although the constant potential electrolysis is complicated by the intervention of the powdery product, it is undoubted that a tight film of definite thickness is also obtained by this method. It should be also noted that by pressing the powdery product we can easily prepare a film or a pellet without spoiling electrode activity.

The effect of supporting electrolytes in the film forming process was studied. PAE was prepared by continuous potential cycling. The increase of doping charge per unit cycle, which is assumed as a measure of the rate of film growth, is listed in Table 1 to see the effect of electrolytes on the rate of film growth. It is indicated that the growth rate of PA film is extraneously faster in sulfuric acid. This may be partly attributed to the bivalency of sulfate anion.

The surface structure of PA film was observed by scanning electron microscopy. It was found that the film prepared in perchloric acid is rather smooth compared to that prepared in sulfuric acid.

2. Charging and Discharging Behavior. In the cyclic voltammograms of PAE in solutions containing no aniline, it is generally observed that the charge consumed in the anodic half cycle is exactly compensated in the succeeding cathodic half cycle. This was also the case, even though aniline was present in the solution, when PA film had already been grown enough after a number of potential cycling (Fig. 1). This indicates that, with a PAE having a thicker film, the film growth is slow enough and the charge consumed for it becomes negligible compared with the charge associated with the redox reaction of the film itself.

TABLE 1. EFFECT OF SUPPORTING ELECTROLYTES IN THE FILM PREPARATION PROCESS

Acid	No. of cycle	Doping charge	Doping charge/cycle
			mC cm^{-2}
0.1 M H_2SO_4	45	6.15	0.137
0.2 M $HClO_4$	80	3.85	0.0481
	135	6.33	0.0469
0.2 M HCl	135	6.30	0.0466
0.2 M HNO_3	200	10.2	0.0510

Potential cycling was repeated between −0.2 and 0.8 V at 0.1 V.s^{-1}.

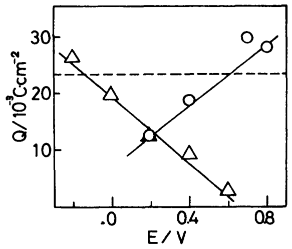


Fig. 3. Redox charge determined by potential step technique as a function of electrode potential.
○: determined from anodic going step from −0.2 V.
△: determined from cathodic going step from 0.8 V.
PAE used for this figure was prepared in 0.1 M H_2SO_4 and measurements were made in aniline free 0.1 H_2SO_4.

In order to see the nature of the charging and discharging reactions of the film more precisely, we employed the potential step technique. Figure 3 shows the results. Anodic charge in this figure was determined from the current decay at a given potential stepped up from the cathodic limiting potential (−0.2 V). Similarly, cathodic charge was determined by stepping down the potential from the anodic limiting potential (0.8 V). It is seen that both the anodic and cathodic charges are linear functions of the electrode potential showing that a PA film has a character of an electric condensor in the sense that the relation Q=CV holds.

Diaz and Logan(1) assumed that the charging-discharging processes of PA are the elimination-addition reactions of proton.

$$(C_6H_5N)_n = (C_6H_4N)_n + nH^+ + ne.$$

There is, however, another possibility of ingress and degress of anionic species in and out of the film as are known with polypyrrole.(3) We shall call this as the doping and undoping reactions.

$$(C_6H_4N)_n + pX^- = (C_6H_4N)_n^{p+}pX^- + pe.$$

In order to confirm the true mechanism, the cathodic dissolution of sulfate anions from the PA film was studied qualitatively. A PAE prepared in sulfuric acid was subjected to the cathodic reduction at −0.2 V in 0.1 M HCl containing $BaCl_2$. By this treatment it was observed that a white cloud grew at the film surface and spread gradually into the solution. The same subject was also studied by using benzenesulfonate as the doping anion. A PAE, which was made free from dopant by cathodic treatment, was oxidized at 0.8 V in 0.1 M benzenesulfonic acid. The PAE thus obtained was washed with water and then reduced at −0.2 V in sulfuric acid for 3 min. The dissolution of benzenesulfonate was confirmed by uv absorption spectra. It is indisputable that benzenesulfonate does dope into the film structue.

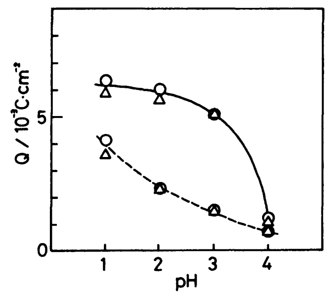


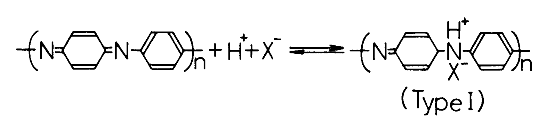
Fig. 4. Effect of the solution pH on the doping capacity.
Full line was obtained with PAE prepared in 0.1 M H_2SO_4 while broken line was obtained with PAE prepared in 0.2 M $HClO_4$.
Δ: anodic charge. O: cathodic charge.

At present, it is not clear whether the charging-discharging process of PAE is of solely doping and undoping reactions. The possibility that the proton elimination mechanism is occurring simultaneously with the doping mechanism cannot be ruled out. Although the detailed mechanism is uncertain, it is undoubted that the doping mechanism is operating during the redox process of PAE. Another information concerning the amount of anions in the polymer structure was also obtained by the elemental analysis of PA, and will be discussed in the succeeding section.

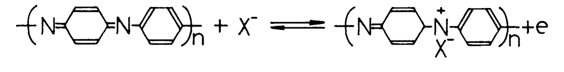
3. *Effect of the Solution pH.* Figure 4 shows the effect of the solution pH on the doping charge of PAE. It is seen that the doping charge decreases with increasing pH and diminishes at about pH=4. Diaz and Logan[1] were aware of this fact and attributed to the difference of nucleophilicity of solvents without any further discussion. This behavior may be related to the acid-base equilibrium of amino or imino nitrogen in the film with proton in the solution. With the increase of the solution pH, the equilibrium will shift towards the deprotonation of amino or imino nitrogen. The deprotonated film seems to lose its electric conductivity. This is the reason why PAE is only active in acidic environments.

In fact, the electric conductivity of a film prepared in H_2SO_4 was decreased from 4.0 $\Omega^{-1}\,cm^{-1}$ (doped state) to 0.26 $\Omega^{-1}\,cm^{-1}$ (undoped state). When, however, the same film was immersed to an alkaline solution (0.1 M NaOH) the conductivity decreased to an unmeasurable value. The release of doped anion from powdery polyaniline by treating with an alkali solution was also confirmed by elemental analysis. Results will be described in detail in the succeeding section.

From the results described above, it can be concluded that there are two types of anions occluded in the film structure; one neutralizes protonic charges associated with the acid-base equilibrium (Type I) and the other compensates the excess plus charges produced by anodic oxidation of film structure (doping process, Type II). The portioning of these two types of anions is an interesting problem to be studied in future studies.



(Type I)



(Type II)

4. *Electric Conductivity.* In aqueous solutions, PAE is electroactive only in acidic environments. In solutions of pH>4, no appreciable charge transfer reaction across the PAE/solution interface takes place. This was attributed to the loss of the electric conductivity of the film due to the deprotonation caused by the acid-base equilibrium. This sort of deactivation will occur only in the surface layer, so long as the time of contact with water is limited.

In order to confirm this view further, a PAE prepared in a sulfuric acid solution was transferred to an acetonitrile solution containing $NaClO_4$ as the supporting electrolyte to take voltammograms. Prior to transferring the electrode, the electrode was rinsed in an aqueous 0.1 M K_2SO_4 solution for 15 min and was washed with water and acetonitrile successively. Voltammograms shown in Fig. 5 were taken periodically as indicated in the figure caption. One can see that the electrode becomes inactive by the water treatment but recovers its activity gradually. Dashed curve in this figure stands for the electrode which has been washed merely with acetonitrile without rinsing in water. The recovery of the electrode activity may be related to the slow diffusion of protons from the inside of the film to its outer surface.

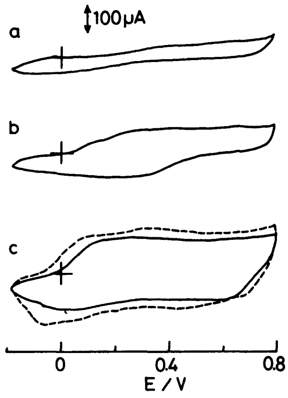


Fig. 5. Recovery of doping capacity during the immersion in acetonitrile.
PAE used was first rinsed in neutral K_2SO_4 solution for 15 min and was transferred into an acetonitrile solution.
a: just after the transfer, b: after 50 min, c: after 2 d. Broken curve was taken by voiding the rinsing in K_2SO_4 solution.

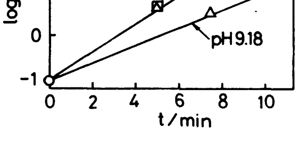


Fig. 6. Change of specific resistance of doped polyaniline with immersing time in alkaline solutions. Full circle indicates undoped polyaniline.

TABLE 2. ELEMENTAL ANALYSIS OF POLYANILINE POWDER PREPARED IN PERCHLORIC ACID
$C_6H_wN_x\, y(\text{dopant})\, z(H_2O)$

Sample	W	X	Type I $y_I(HClO_4)$	Type II $y_{II}(ClO_4^-)$	Z
I(Oxidized form)	3.9_7	0.97	0.85*	0.29	2.35
II(Reduced form)	3.8_8	0.96	0.98	—	1.85
III(Deprotonated form)	4.7_7	0.98	—	0.29	0.16

* Caluculated from the total amount of dopants (y=1.14) and y_{II}.

The change of electric conductivity by the immersion in alkali solutions (pH=9.13 and 11.20) was measured with four probe method.[4] In this experiment PA powder prepared potentiostatically at 0.8 V in perchloric acid was pressed to form a pallet. Logarithum of specific resistance of doped polymer changed almost linearly with the immersion time as shown in Fig. 6. It is thus possible to control the conductivity of PA from conducting to semiconducting states by changing the immersion time and/or pH of the solution.

Full circle located on the ordinate stands for the resistivity of PA which was subjected to a prolonged cathodic undoping. It is worth noting that an appreciable conductivity is still retained by the reduced PA. This indicates that the electric conductivity of the PA film is largely determined by the amount of anions brought into the film by acid-base equilibrium.

5. Elemental Composition of PA. In the preceding section, we concluded that there are two types of dopants in the film; one is to neutralize protonic charges associated with acid-base equilibrium (Type I) and the other is to compensate the positive charges produced by anodic oxidation (Type II). In order to obtain informations concerning the amounts of Type I and Type II dopants the elemental analysis of PA was carried out.

Three kinds of different samples were prepared for this. The first sample was a massive PAE which was prepared by constant potential electrolysis at 0.8 V (Sample I, oxidized form). The same sample was further treated by cathodic reduction at 0 V (Sample II, reduced form). The third sample was basically the same as Sample I but was immersed in a 0.1 M NaOH solution for 2 h (Sample III, deprotonated sample). The amount of anions in Sample III should give the amount of Type II dopant. In all cases, the samples were scratched off from the electrode substrate and they were weighed and subjected to the elemental analysis. Results are summarized in Table 2, where w, x, y, and z are the numerals appearing in the assumed formula $C_6H_wN_x \cdot y(\text{Dopant}) \cdot z(H_2O)$, y_I and y_{II} discriminate the types of dopant.

The y_{II} value can also be determined by calculation if we know the initial weight of a given sample and the charge required for its cathodic reduction. The value thus determined was 0.25 which is in a good agreement with the value determined by elemental analysis, 0.29. The y_I value determined with Sample II should equal to x, if all of the nitrogen atoms of PA participate the acid-base equilibrium. The data confirms this expectation. The existence of water in PA should be correlated with the hydration of doping ions. A drastic change in z value appeared in Sample III may, perhaps, be an indication of that the hydration occurs predominantly to protons rather than anionic species.

The apparent formula of aniline moeity was determined to be C_6H_4N for both oxidized and reduced forms. By considering the amount of Type II doping is 0.25—0.29 per monomer unit, the overall polymerization reaction can be expressed as follows.

$$4n(C_6H_7N) \longrightarrow (C_6H_4N)_n^+ + 12H^+ + 13e.$$

The hydrogen content of the deprotonated sample was somewhat larger than that of oxidized form. The reason is unknown now, but may be partly related to the partial hydrolysis catalyzed by base.

Qualitatively, similar results were obtained for the samples prepared in H_2SO_4. The total amount of dopants (assumed as SO_4^{2-}) was 1.13, 0.81, and 0.16 for oxidized, reduced, and deprotonated samples, respectively. Quantitative discussion is rather difficult because there is a possibility of existing as both monovalent and divalent anions, HSO_4^- and SO_4^{2-} being doped simultaneously.

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