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# Photocurrent Response of Polyaniline Film Electrode

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The photoelectrochemical behavior of polyaniline (PA) film was investigated in acidic aqueous solutions. In the presence of $NO_3^-$ in the solutions, a large cathodic photocurrent was observed at lower potentials than 0.1 V vs. Ag/AgCl. The dependence of the current quantum efficiency at −0.1 V on the wavelength of light indicated that the photocurrent was due to the absorption of ultraviolet light by the reduced film of PA. The variations in potential and spectrum of the reduced film under open-circuit conditions confirmed the transformation of PA from a reduced state to a radical cation state with the ultraviolet irradiation. In conclusion, the cathodic photocurrent at −0.1 V could result from the photo-induced oxidation of the reduced PA film by $NO_3^-$. A film resistance-potential relationship was examined in connection with the pH dependence of the photoresponse of PA. The potential giving a minimum resistance at a given pH shifted to lower potentials with increasing pH. It can be presumed that a maximum in the photocurrent–pH curve arises from the increase in the ease of oxidation of the reduced film with an increase in pH.

Electrical conducting polymers have received considerable attention because of their possible applications to organic batteries, sensors, electrochromic devices, and semiconductor devices.[1—3]

Unlike most conducting polymers, polyaniline (PA) films are readily prepared by the electrochemical oxidation of aniline in acidic aqueous media.[4] It is now well established that the structure of PA is composed of repeating imino-1,4-phenylene units.[5,6] The electrical resistance of the PA film shows unique dependence on its oxidation state.[7] Fundamentally interesting properties of PA are related to its novel conductor–insulator transitions induced by electrochemical doping–undoping and by the change in pH. The good stability of PA in a conducting state in air and water makes it an attractive new electronic material. The photocharacteristics of the PA-electrolyte junction have recently been examined because of its usefulness as a photoactive material of low cost and large area solar cells.[8,9]

In order to develop more effective surface films for conducting polymer-based photovoltaic cells and electrocatalysis, it is necessary to have a detailed knowledge of the basic photoelectrochemical properties of polymer electrodes. In this paper, we describe our studies on the photoresponse of PA film electrodes in aqueous solutions. A mechanism for the generation of cathodic photocurrent at its reduced state is also presented.

## Experimental

**Materials.** Aniline was purified by vacuum distillation over the zinc dust and stored in the dark under a nitrogen atmosphere. The sulfuric acid (Kanto Chemicals, UGR) was used as received and $Na_2SO_4$ used after recrystallization. All electrolyte solutions were prepared with doubly-distilled water.

**Apparatus and Procedures.** The PA films were formed on Pt or ITO glass (1 $cm^2$) by the electrochemical oxidation of aniline in 0.5 M $H_2SO_4$ solution ($M = mol\,dm^{-3}$). The potential of the working electrode was cycled between −0.1 and 0.8 V vs. Ag/AgCl at a scan rate of 100 $mV\,s^{-1}$ for 100—200 cycles. The polymer films were grown to a total charge of ca. 40 $mC\,cm^{-2}$ (oxidation to 0.4 V) for many measurements. According to the empirical equation relating film thickness to the height of cyclic voltammogram peak,[4] this charge corresponded to a film thickness of 0.6 µm. Electrochemical experiments were carried out in a one-compartment, three-electrode Pyrex glass cell at room temperature. An Ag/AgCl/KCl electrode and a large Pt gauze (>10 $cm^2$) were used as the reference and counter electrodes, respectively. All solutions were purged with nitrogen gas prior to and during the electrochemical measurements. Light from an Ushio UXL-500D xenon lamp was passed through a suitable color filter: a band pass filter (Toshiba UV-D35) and a long wavelength pass filter (L-42). The irradiation with light of specific wavelengths was performed with a interference filter of bandwidth 20 nm (IF-BPF, IF-W). The intensity of the monochromatic light was measured with a calibrated thermopile (Scientech 365). Photocurrents were recorded on a Yokogawa 3056 pen recorder under potentiostatic conditions. In situ measurements of film resistances were carried out with the electrodes of two-band type.[10] Two Pt bands separated from each other by 100 µm were prepared by sputtering ca. 40 nm thick Pt film onto the surface of glass substrates. Aniline were electropolymerized on the two-band electrode until the polymer eventually bridged the gap between two Pt bands. After the two-band electrode was potentiostatically reduced, the resistance between two Pt bands was measured with a YHP 4261A LCR meter. Absorption spectra were measured on a Hitachi U-3210 UV-visible spectrophotometer.

## Results and Discussion

Figure 1 shows a typical cyclic voltammogram of the PA film electrode in 0.5 M $H_2SO_4$. It has two pairs of oxidation–reduction peaks. The half-wave potential $E_{1/2}$ of the first redox process was 0.17 V and the one of the second redox process 0.8 V. It is well known that PA is reversibly doped into three states.[5,11] The oxidation states of PA can be divided by the above $E_{1/2}$ values.

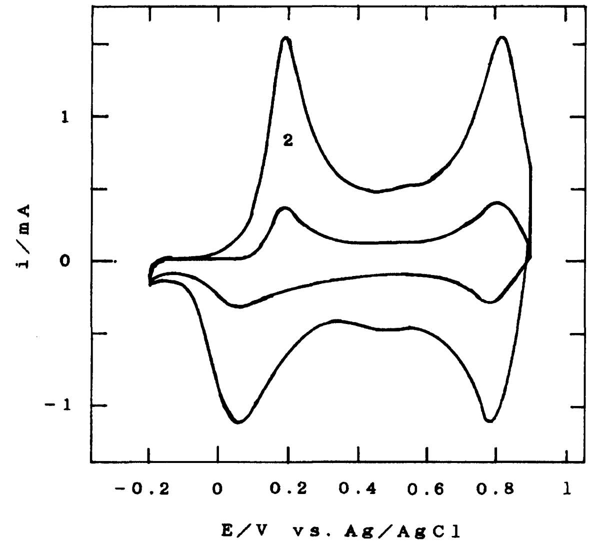

Fig. 1. Typical cyclic voltammograms of PA electrode at a scanning rate of 100 $mV\,s^{-1}$ in 0.5 M $H_2SO_4$. The films were grown by potential cycling method, 1 : 50 cycles, 2 : 100 cycles.

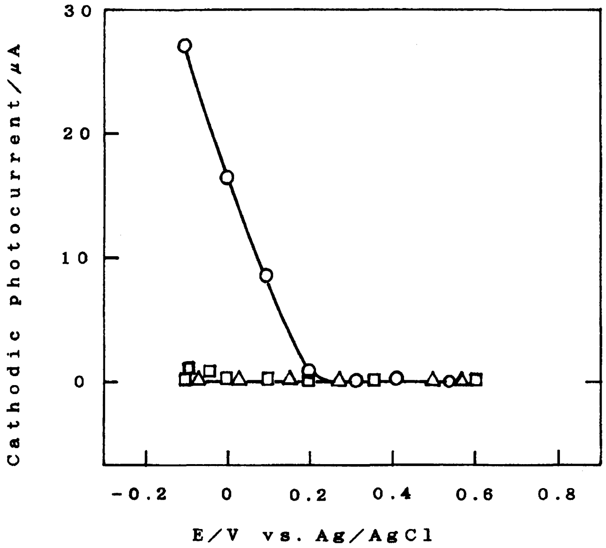

Fig. 2. Photocurrents of PA electrode at different applied potentials in 0.5 M $H_2SO_4$. □: under ultraviolet irradiation. ○: in the presence of 0.05 M $NaNO_3$ under ultraviolet irradiation. △: in the presence of 0.05 M $NaNO_3$ under visible irradiation.

The colorless film reduced at lower potentials than 0 V is called a reduced state hereafter, and the green and blue films in the potential range 0.2—0.7 V called the partially oxidized state whose absorption spectra have the peaks at 420—440 nm and at >800 nm. The peaks in the visible region have been assigned to the radical cation produced in the PA matrix.[12] The violet film oxidized at higher potentials than 0.8 V is called the fully oxidized state which slowly degradates in water. The photoresponses of PA in the reduced state and in the partially oxidized state were examined in 0.5 M $H_2SO_4$.

**Photoresponse of the Partially Oxidized Film.** The photocurrents of the PA electrode are presented in Fig. 2 as a function of applied potential. At higher potentials than 0.2 V, appreciable photoeffect was, on the whole, not induced. In the presence of hydrazine in the solution, a slight anodic photocurrent was observed at 0.3 V under the irradiation with visible light (>420 nm) although a large anodic current flowed in the dark. Under open-circuit conditions in the dark, the potential of the partially oxidized film slowly moved to the lower potentials corresponding to the reduced state. The reduction of the radical cation form by hydrazine (its standard potential is −0.44 V)[13] was confirmed by the color change of the film. These results indicated that the anodic dark current at 0.3 V flowed through electron transfer reactions 1 and 2.

$$4P^{\bullet +} + N_2H_5^{+} \longrightarrow 4P + N_2 + 5H^{+} \tag{1}$$

$$P \longrightarrow P^{\bullet +} + e \tag{2}$$

where P is the reduced form of aniline unit $[-C_6H_4-NH-]$ and $P^{\bullet +}$ is its radical cation form $[-C_6H_4-\overset{\bullet +}{N}H-]$. The total reaction at the electrode was equal to the electrochemical oxidation of hydrazine. The visible irradiation could only slightly accelerate reaction 1, while no photoeffect was induced in the presence of the weak donors such as 1-allylthiourea, triethanolamine, oxalic acid, formic acid, triethylamine, and $Sn^{2+}$.

**Photoresponse of the Reduced Film.** As shown in Fig. 2, a large cathodic photocurrent was observed at lower potentials than 0.1 V under ultraviolet irradiation (310—390 nm) in the presence of $NO_3^-$ in the solution, while no photocurrent was observed under visible irradiation. The cathodic photocurrent at −0.1 V increased with an increase in the concentration of $NO_3^-$ (0—0.1 M), with tendency to approach a maximum. Figure 3 shows the dependence of the apparent current quantum efficiency at −0.1 V on the wavelength of the irradiated light. The apparent current quantum efficiency was calculated from the number of photons incident on the electrode (no absorptance of the film was taken into account). The abrupt rise in the current quantum efficiency at wavelengths below 380 nm indicated that the cathodic photocurrent was due to the absorption of ultraviolet light by the reduced film, because this film exhibited the absorption maximum at 330 nm assigned to a $\pi$–$\pi^*$ transition of the aromatic structure. The peak showed a red shift from that (290 nm) for aniline. The edge of the absorption peak gave a value of 3.3 eV to the band gap of PA, which agreed with the wavelength at rise of the current quantum efficiency. Shown in Fig. 4 are the variations in open-circuit potentials of the reduced film with time. In the presence of $NO_3^-$, the open-circuit potential rapidly moved to higher potentials under irradiation. A final potential of around 0.2 V corresponded to the potential of the radical cation state. This variation in potential was also

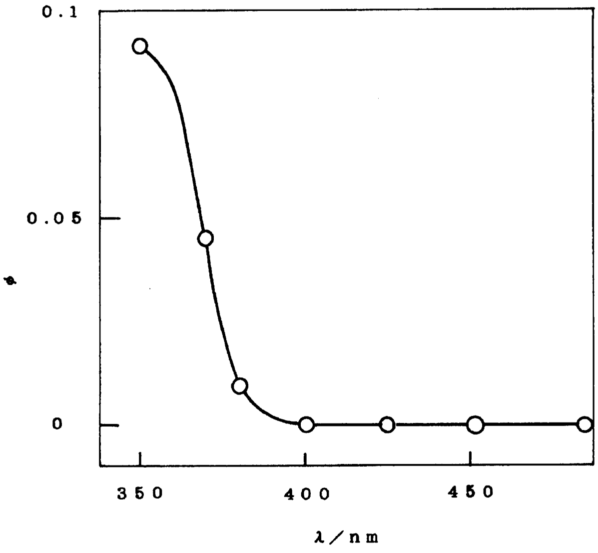

Fig. 3. Dependence of apparent current quantum efficiency at −0.1 V on wavelength of irradiated light. A 0.5 M $H_2SO_4$ solution containing 0.05 M $NaNO_3$.

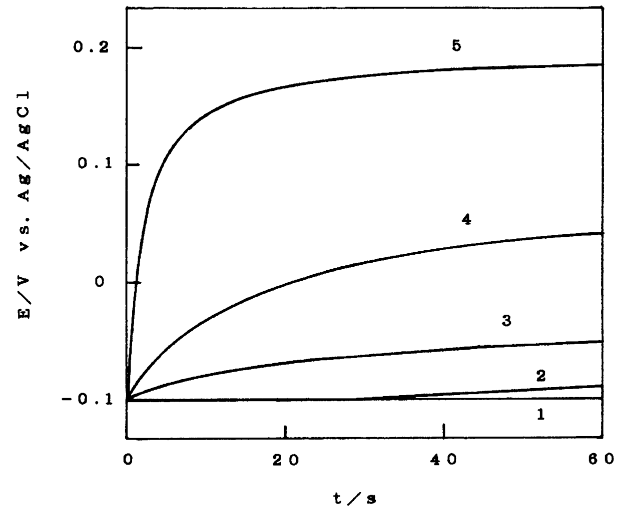

Fig. 4. Variations in open-circuit potentials of the reduced film with time in 0.5 M $H_2SO_4$. Curve 1: in the dark, 2: under ultraviolet irradiation, 3: in the presence of 0.05 M $NaNO_3$ in the dark, 4: in air and the dark, 5: in the presence of 0.05 M $NaNO_3$ under ultraviolet irradiation.

observed somewhat in the dark, and was more rapid in the presence of $O_2$ in the electrolyte. These results suggest that PA in the reduced state is photooxidized by $NO_3^-$.

$$P \xrightarrow[NO_3^-]{\text{light}} P^{\cdot +} + e \qquad (3)$$

This inference was supported by the change in spectrum of the reduced film with the ultraviolet irradiation. Figure 5 shows the change in absorptance at 430 nm, which is the wavelength at absorption maximum of PA in the radical cation state. The absorptance at 430 nm rapidly increased with the light irradiation, with simultaneous decrease in absorptance at 330 nm. This increase in absorptance exhibited the transformation of PA from the reduced state into the radical cation state.

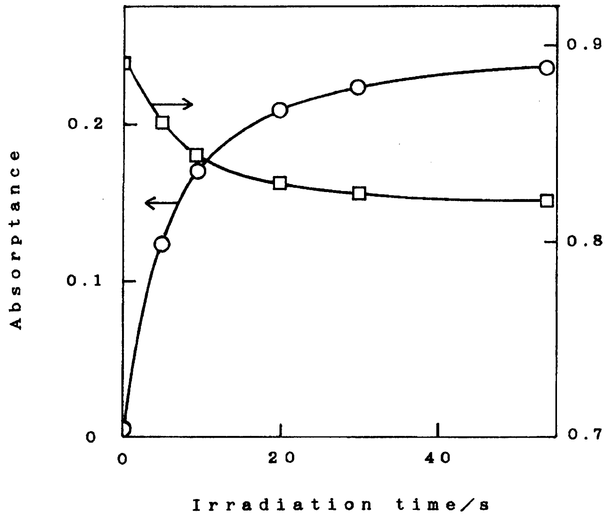

Fig. 5. Change in absorptance of the reduced film with light irradiation in a 0.5 M $H_2SO_4$ solution containing 0.05 M $NaNO_3$. Wavelength; ○: 430 nm, □: 330 nm.

The above photoeffect was not due to the Schottky barrier at the polymer–solution interface, because the reduction of $H^+$ occurred in the dark at lower potentials than −0.25 V. The Faradiac charge transfer must be negligible at the low potentials, if the rectifying barrier is formed on the surface of PA. The variation in film resistance with pH of the solution indicated that proton went into and out of the film (as will be shown later). Therefore, the film may probably contain water among fibrils or proton migrate through the polymer by acid-dissociating reaction 4 of the amino groups, even though PA is p-semiconducting on account of its small ionization energy.[3]

$$[-C_6H_4-NH_2{}^+-] \longrightarrow [-C_6H_4-NH-] + H^+ \qquad (4)$$

The above results led to the conclusion that the cathodic photocurrent at the reduced state resulted from photo-induced electron transfer reaction a in Fig. 6. Reaction (b) which photoinitiated at the Pt–polymer interface could not occur at the reduced state, because no anodic photocurrent was observed in the presence of the above donors at any thickness of the film.

The relationship between the photoresponse of the reduced film and pH of solutions was interest in connection with the dependence of the electrochemical activity of PA on pH. Since the potential giving the colorless film varied with pH, we first examined the relationship between the potential producing the reduced state and pH. The $E_{1/2}$ of the first redox process was determined at a slow scan rate (5 mV $s^{-1}$) owing to lower conductivities of PA in less acidic solutions. The obtained $E_{1/2}$ values shifted to lower potentials with increasing pH at

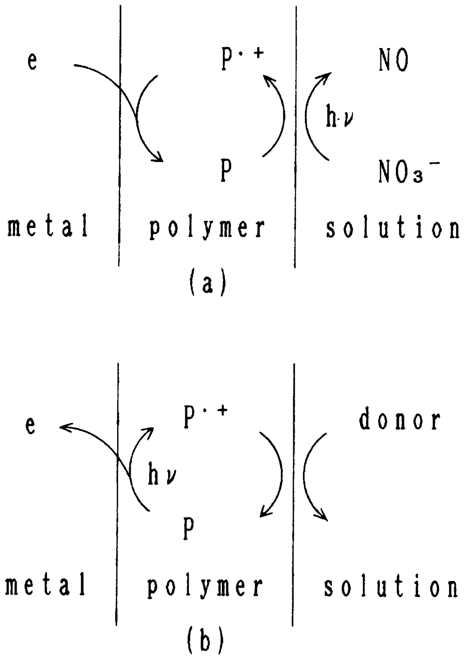

Fig. 6. Reaction scheme for generation of photocurrent at the reduced state.

pH below 1, while the values were nearly independent of pH in the range of pH 1—3. This dependence was in agreement with the result of Huang et al.[5] Since the p$K_a$ value of reaction 4 was estimated to be 0—1 from that of diphenylamine,[14] the above pH dependence of $E_{1/2}$ could be interpreted in terms of reactions 5 and 6.

$$[\text{-C}_6\text{H}_4\text{-NH}_2{}^+\text{-}] \longrightarrow [\text{-C}_6\text{H}_4\text{-}\overset{\cdot +}{\text{N}}\text{H-}] + \text{H}^+ + \text{e} \quad \text{at pH} < 1 \qquad (5)$$

$$[\text{-C}_6\text{H}_4\text{-NH-}] \longrightarrow [\text{-C}_6\text{H}_4\text{-}\overset{\cdot +}{\text{N}}\text{H-}] + \text{e} \quad \text{at pH 1—3} \qquad (6)$$

However, the values of $E_{1/2}$ could not be determined at pH above 3, because the cyclic voltammograms gave no distinct redox peak in this pH region owing to poor conductivities of PA. Therefore, we determined whether the polymer was in the reduced state or not from the film resistance–potential relationship. Figure 7 shows the film resistances obtained after the attainment of equilibrium. The resistance–potential curves have revealed that both the reduced state and the fully oxidized state are insulators, and the partially oxidized state is conductive in acidic solutions. The latter property can be ascribed to the formation of polaron (mobile radical cation) bands in the energy gap. The logarithm of minimum value of the film resistance at a given pH was approximately proportional to pH, which indicated that the conductivities of PA could vary with the acid-dissociating equilibrium of amino groups of the polymer. We should notice that the partially oxidized state comprised various forms of aniline unit such as $[\text{-C}_6\text{H}_4\text{-NH}_2^+\text{-}]$, $[\text{-C}_6\text{H}_4\text{-NH-}]$, $[\text{-C}_6\text{H}_4\text{-}\overset{\cdot +}{\text{N}}\text{H-}]$, and $[\text{-C}_6\text{H}_4\text{-}\overset{\cdot}{\text{N}}\text{-}]$, since the average oxidation number of aniline unit was estimated to be 0.5 at 0.4 V from the charge required to oxidize the fully reduced film. In neutral solutions, PA became no longer conductive in any potential. Figure 7 also indicates that the potential giving the minimum resistance at a given pH gradually shifted to lower potentials with increasing pH.

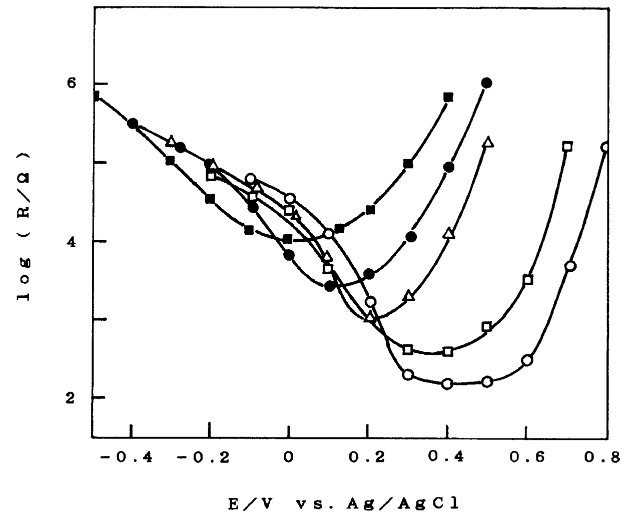

Fig. 7. Relationship between film resistance and electrode potential at different pH's. pH; ○: 1.25, □: 2.30, △: 4.20, ●: 5.85, ■: 8.30.

Figure 8 shows the pH dependence of cathodic photocurrents at the potential giving a high film resistance, that is, at the reduced state. The photocurrent–pH curve had a maximum at pH 1.5—2. This was not in accord with the expectation that the reduction of $NO_3^-$ should easily occur in more acidic solutions.

$$\text{NO}_3{}^- + 2\text{H}^+ + \text{e} \longrightarrow 1/2\text{N}_2\text{O}_4 + \text{H}_2\text{O} \qquad (7)$$

$$\text{NO}_3{}^- + 3\text{H}^+ + 2\text{e} \longrightarrow \text{HNO}_2 + \text{H}_2\text{O} \qquad (8)$$

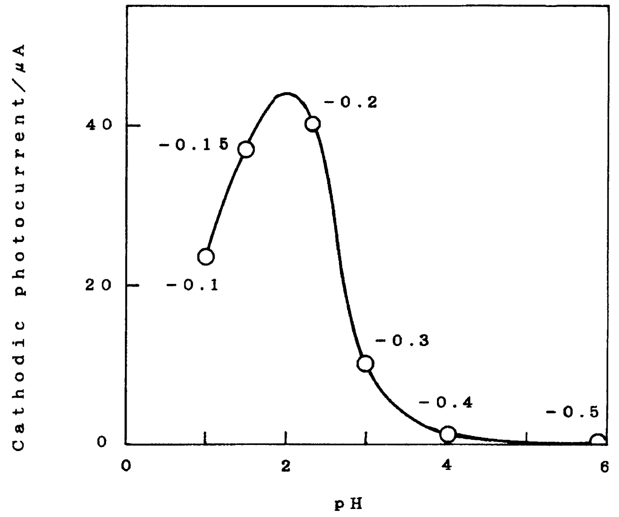

Fig. 8. The pH dependence of cathodic photocurrents at the reduced state in 0.5 M $Na_2SO_4$ solutions containing 0.05 M $NaNO_3$. Numerical values in the figure show the potentials at which photocurrents were measured.

$$NO_3^- + 4H^+ + 3e \longrightarrow NO + 2H_2O \qquad (9)$$

According to the reaction scheme in Fig. 6, it is possible that the photocurrent depends on the rate of charge transport in the polymer. However, there was little difference in film resistances between pH 1 and 2 at the potential producing the reduced state. It was recognized that the conductivity of the polymer or the mobility of radical cations in the polymer was not a rate-controlling factor, since larger photocurrents were observed at the lower potentials giving higher film resistances. Figure 7 suggested that the ease of oxidation of the reduced film might increase with an increase in pH, although the pH shift of the potential giving a minimum resistance was not always consistent with the data of the cyclic voltammetry. A possible explanation for the appearance of a maximum in the photocurrent–pH curve could be a balance of the pH dependences of two quantities: (1) the ease and/or rate of the oxidation of PA, and (2) the reduction of $NO_3^-$. In order to get a better understanding of this concern, the electrochemical kinetics of the PA electrode needs to be investigated further.

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