Simultaneous occurrence of polymerization and decomposition of polyaniline films

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Abstract

A polyaniline film coated on an electrode degrades and loses its thickness at potentials over than 0.7 V versus SCE in acidic solutions, whereas it gains the thickness by polymerization in aniline-including solution at the same potential as in the degradation. A question arises as to whether the polymerization is accompanied with the degradation although the polymerization is obviously an opposite process to the degradation or the decomposition. In order to understand this contradiction, we made chronoamperometry, voltammetry and UV–vis spectrometry for polyaniline films at various concentrations of aniline. It was found that the decomposition occurred simultaneously with the polymerization. Competition between the polymerization and the decomposition varied mainly with concentrations of aniline and potentials, and its conditions were obtained.

Keywords: Conducting polymers, Polyaniline films; Polymerization; Degradation; Competition

1. Introduction

New types of composite polyaniline-coated electrodes have been used for charge storage materials of supercapacitors [1–3] and batteries [4–13]. Since a controlled variable in the energy storage devices is electric current or charge rather than electrode voltage, potentials applied to polyaniline are sometimes out of the limitation of voltage at which polyaniline is degraded by the overoxidation [14–18]. The degradation was recognized early [17,19] and has been explored with several in situ electrochemical techniques [20–32]. The degradation occurs at potentials more than 0.7 V versus SCE to yield soluble benzoquinone [17,20,25,33,34] and quinoneimine end groups [20,25,34]. The potentials for the degradation are close to those of the polymerization (practically 1.0 V versus SCE) in the presence of monomer. The degradation makes the polyaniline film thin owing to formation of dissolved species [25], whereas the polymerization increases the film thickness. Then, a question arises as to whether which process is predominant, the polymerization or the dissolution in the presence of the monomer.

This question has been taken up for the poly(3-methylthiophene) films [35], and the dissolution has been demonstrated to be competed with the polymerization to exhibit steady-state current under conditions of a certain concentration of the monomer and a potential in a stirred solution. The competition condition gives rise to the self-excited current oscillation at potentiostatic electrolysis in a quiescent solution [36]. The oscillation has been explained in terms of the following iterative process: a decrease in the film thickness by the dissolution, an increase in the monomer concentration near the electrode, an increase in the film by the polymerization, a decrease in the monomer concentration and the decrease in the film again. This process is similar to the Lotka–Volterra model [36]. Similar behavior may be observed at polyaniline films. A polyaniline film is synthesized in aqueous solutions, whereas a poly(3-methylthiophene) film is in aprotic organic solvents. Thus, it is predicted that the former is degraded electrochemically to be dissolved less in aqueous solutions than the latter in organic solvents. The polymerization potential domain of the former is narrower than that of the latter. Consequently, the polymerization of
polyaniline may have less influence on the degradation than that of poly(3-methylthiophene). This paper concentrates on obtaining a quantitative relationship between the polymerization and the degradation of polyaniline films in the context of the competition by taking attention to electrolysis time, concentrations of aniline and potentials.

2. Experimentals

2.1. Electrochemistry

For the electrochemical measurements, a standard three-electrode cell was used. The working electrode for measurements of film thickness was a platinum wire 0.1 mm in diameter. The voltammetric working electrode was a platinum disk 1.6 mm in diameter. The counter electrode was a platinum coil, and the reference electrode was a saturated calomel electrode. A twin electrode was fabricated with two platinum wires 0.1 mm in diameter. The wires arranged in parallel were molded with glass by heating, and the tip of the glass was polished until the two platinum disk surfaces were exposed. The potential was controlled with a HECS-318C potentiostat (Huso Electrochemical System) and a dual potentiostat EI-400 FCV (Cypress System), which were controlled with a personal computer through an AD/DA board. A potential-time sequence, including superposition of ac voltage, was controlled with a home-made software. An optical microscope was a VMS-1900 (Scalar) video microscope, connected to a PC using an USB-MPG capture board.

2.2. Chemicals and polymerization

All the chemicals were of analytical grade. Polyaniline films were synthesized electrochemically by applying 1.0 V potentiostatically in 0.1 M + 1.0 M sulfuric acid solution, typically for 30 s, otherwise not mentioned. These films have 20 µm thickness, evaluated from an optical microscope.

2.3. UV spectroscopy

The UV spectrometer used was JASCO V-570. A sample cell was filled with aniline + 1.0 M sulfuric acid, electrochemically dissolved aniline + 1.0 M sulfuric acid, or a solution during the polymerization. The reference cell was filled with 1.0 M sulfuric acid.

3. Results and discussion

3.1. Degradation and dissolution

First, we describe our results of the degradation of polyaniline films, part of which is already known. A cyclic voltammogram of the polyaniline-coated electrode in 1.0 M sulfuric acid, as is shown in Fig. 1, has two main anodic peaks at 0.24 and 0.76 V versus SCE, which correspond to the conversions between leucoemeraldine and emeraldine and between emeraldine and pernigraniline, respectively [37,38]. When the anodic potential limit of the scan was over 1.0 V versus SCE, the iterative scan caused the peak potential at 0.24 V to be shifted in the positive direction and decrease the peak current with the number of scan, as shown by the line in Fig. 2. It tended to and merged with the anodic wave at 0.45 V. These variations have been commonly observed as degradation [14–18]. When the anodic potential limit was less than 0.6 V, neither the positive potential shift nor the decrease in the peak current was observed for a long time potential scan.

We made potentiostatic electrolysis of the polyaniline-coated electrode in the domain from 0.6 to 1.2 V for a given period in 1.0 M sulfuric acid, took voltammograms in the potential domain from −0.2 to 0.5 V immediately after the electrolysis, and then used the anodic peak current in Fig. 2 for a measure of the degradation. This process was iterated until the sum of the electrolysis periods was 10 min. The peak currents decreased with the time and were conspicuous at potentials over 0.7 V. The decrease is obviously ascribed to a loss of leucoemeraldine and emeraldine but does not necessarily mean a loss of film thickness.

There is controversy as for effects of the degradation on the film thickness: the thickness being independent of the degradation [23] or decreasing with the degradation [25]. This effect is important if the polymerization occurs con-
comitantly with the degradation. We obtained time-variation of the thickness of the polyaniline film coated on a platinum wire after applying some voltages to the film in 1.0 M sulfuric acid. The film-coated electrode was taken out from the cell after potential application for a given period and its thickness was evaluated with the optical microscope. The time-variations of the normalized radii of the film, \( \frac{r}{r_0} \), are shown in Fig. 3 for several potential values, where \( r \) and \( r_0 \) are the radii of the polyaniline-coated electrode at the sum of the electrolysis times \( t \), of the polyaniline-coated electrode, and those before the electrolysis, respectively. The area of the film decreased obviously with the electrolysis time, almost being independent of the applied potentials over 0.8 V. Consequently, degraded species is dissolved in the solution to make the film thin. However, it still remains on the electrode, whereas poly(3-methylthiophene) film disappears completely from the electrode [35] .

We used the resistance of the film also as a quantitative measure of a degree of the degradation. The evaluation of the resistance was made at a twin electrode (photograph in the inset of Fig. 4) by applying two voltages with a small difference. Polyaniline was coated electrochemically on the twin electrode (photograph in the inset shows a photograph of the bare surface of the twin electrode).

The accurate applied voltages were \( E_1 = 1.05 \text{V} + E_{ac} \) for electrode (a), \( E_2 = 1.00 \text{V} + E_{ac} \) for electrode (b), \( E_1 = 0.55 \text{V} + E_{ac} \) for electrode (a) and \( E_2 = 0.50 \text{V} + E_{ac} \) for electrode (b), where \( E_{ac} \) is a ac component with 0.01 V amplitude and 1.0 Hz. The time-sequence of the programmed potential is shown at the top of the figure. The inset shows a photograph of the bare surface of the twin electrode.

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The ac-resistance shows the variation similar to the dc-resistance, supporting the increase in the resistance with the electrolysis time. The ac-resistance was smaller than the dc-resistance, probably because of the contribution of the capacitance of polyaniline. Resistivity of the film was estimated to be of the order of $10^{12} \text{cm}^{-1}$ for $R = 10 \text{k}\Omega$, if the film is a rectangle with 20 $\mu$m thickness.

### 3.2. Competition between polymerization and degradation

Thinning of the film by the degradation is phenomenologically opposite to film growth or polymerization. It is predicted that both the degradation and the polymerization occur possibly when potential over 0.8 V is applied to the polyaniline-coated electrode in the solution including aniline. We made cyclic voltammetry of the polyaniline-coated electrode in several concentrations of aniline in upper potential limit 1.0 V. The peak current at 0.2 V increased with the potential scans at high concentrations (e.g., 0.03 M in Fig. 2) of aniline. At low concentrations (e.g., 0.01 M), in contrast, the peak current increased initially because of deposition of polyaniline on the bare electrode and then decreased gradually because of the degradation. Therefore, the degradation occurs concurrently with the polymerization.

Fig. 6 shows UV spectra (a) of the sulfuric solution sampled after the degradation at 1.0 V for 10 min. This is blue-shifted from the spectrum of aniline solution (b) and is more shapeless than the latter. A question is whether spectrum (a) is observed after the polymerization in aniline solution without degrading the film. Spectra were taken for the sulfuric acid solution into which the polyaniline film polymerized in 0.1 M aniline was transferred immediately after the polymerization. Then, no appreciable spectra were observed. The sulfuric acid solution in which the potential scan from −0.20 to 0.60 V (the domain without the degradation) was applied to the polyaniline for several minutes exhibited spectra quite similar to spectrum (a), as shown in curves (c) of Fig. 6. Spectrum (a) was obtained in the absence of aniline, whereas spectrum (c) was in the presence of aniline. The absorbance at 247 nm increased with an increase in the period of the potential application at 1.0 V. Consequently, the degradation occurs during the polymerization. Unfortunately, if the absorption band for (c1–c3) is due to oligomers of oxidized aniline [39], we cannot assign the band to the degradation (a).

Fig. 7 shows chronoamperometric curves of the polyaniline-coated electrode at various aniline concentrations when 1.0 V was applied to the film. The current without aniline decayed to almost zero at 200 s, at which the film became thin. In contrast, the current in the 45 mM aniline solution (curve (a) in Fig. 7) decreased once owing to a capacitive contribution as well as relaxation by mass transport of aniline, and then increased gradually because of the growth of the polyaniline film. The increase in the current suggests the predominance of the polymerization over the degradation, whereas the decrease means the predominance of the degradation over the polymerization. Thus, the steady-state current indicates that the competition occurs between the polymerization and the degradation, as has been discussed in poly(3-thiophene) films [35,36].

We obtained the steady-state conditions from chronoamperometric curves at different concentrations of aniline and at several potentials. Fig. 8 shows variations of the applied potentials with the aniline concentrations for which the time-
derivatives of chronoamperometric curves take a given value close to zero. In the domain lower than the competition (solid) line, the polymerization is predominant over the degradation. The competition potential increases with the increase in the competition concentration. This increase is opposite in sign for poly(3-methylthiophene) films, as is shown as the dashed line in Fig. 8 [36]. According to the conventional electrochemical behavior, an increase in the monomer concentration enhances the polymerization rate or the polymerization current, resulting in electrolysis with more overpotential. This behavior is similar to the variation in Fig. 8, and hence the polymerization occurs with little effects of the degradation in the context of monomer concentration and potential. The other viewpoint in Fig. 8 is that when monomer concentration is increased, for example, from log(c/M) = −1.8 to −1.4 at 1.0 V, the predominant process alters from the degradation to the polymerization at log(c/M) = −1.6. This is also the ordinary behavior. In contrast, poly(3-methylthiophene) films shows the opposite behavior, i.e., the degradation being predominant over the polymerization as monomer concentration increases. Consequently, the increase in the concentration decreases the current. This variation, unfavorable to the polymerization, has caused the self-excited oscillation in the chronoamperometric curves of poly(3-methylthiophene) films [36].

Some experimentalists have experienced that electric noise is often imposed on voltammograms in the potential domain of electric conduction although this phenomenon has rarely been documented [40]. The measurement of the noise may lead to determining the amount of conducting species, i.e., emeraldine, during polymerization. Unfortunately, electric noises varied with circumstances. Thus, we imposed alternating voltage with small amplitude on the dc-voltage. The polymeric film was synthesized in the solution of 0.1 M aniline + 1.0 M sulfuric acid.

The steady-state currents are smaller as the potential is more positive is the potential, the sooner is realized the steady state. The steady-state currents are smaller as the potential is more positive. This potential-dependence of the current looks abnormal from a viewpoint of a Tafel equation for oxidation. This can be explained by the predominance of the degradation over the polymerization when the potential becomes positive (see in Fig. 8 by tracing a vertical line up at a given concentration).

Next our attention is paid to the ac-component in Fig. 9, i.e., the amplitude of the oscillating current, which appears when the film is electrically conductive. The film at 0.75 V keeps conductive until 1000 s. The film at 0.80 V loses conduction over 300 s. No conduction appears at the films over 0.85 V. Therefore, the film polymerized at potentials over 0.85 V must be under the resistive state and may be degraded by the overoxidation.

4. Conclusions

The degradation of polyaniline film brings about dissolution to make the film thin, but leaves the film as resistive skeleton. Therefore, electrochemical machining cannot be applied to polyaniline films, as opposed to poly(3-methylthiophene) films [35]. The polymerization of polyaniline is always accompanied with the degradation because the polymerization potential is closed to the degradation potential. The competition between the polymerization and the degradation is mainly controlled with concentrations of aniline and potentials. The degradation is overwhelmed when aniline concentration is increased and the potential becomes less positive. Once the degradation occurs, the conducting species cannot be restored.

References