

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.

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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

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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 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.

Electrode 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 a 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

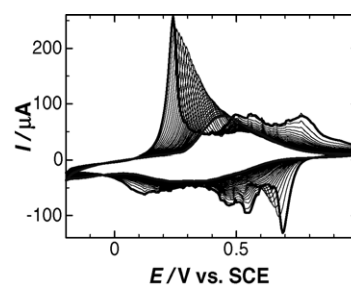


Fig. 1. Cyclic voltammograms of polyaniline-coated electrode in 1.0 M sulfuric acid at multiple scans with the scan rate 0.01 V s^{-1} . The film was generated by potentiostatic polymerization at 1.0 V in 0.1 M aniline + 1.0 M H_2SO_4 for 300 s.

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 I_p , at ca. 0.2 V 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-

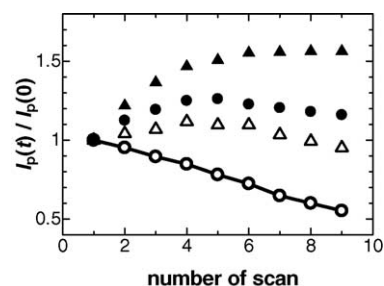


Fig. 2. Variations of the anodic peak currents at ca. 0.2 V for cyclic voltammetry in the potential domain from -0.2 to 1.0 V in solutions including 0.0 M (\circ), 0.005 M (\triangle), 0.01 M (\bullet), 0.03 M aniline (\blacktriangle) + 1.0 M H_2SO_4 . The film was generated by potentiostatic polymerization at 1.0 V in 0.1 M aniline + 1.0 M H_2SO_4 for 300 s.

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