

Simultaneous polymerization and decomposition of polyaniline films detected by noises

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1. Introduction

Degradation of polyaniline (conducting polymers) occurs at potentials more than 0.7 V vs. SCE to yield soluble benzoquinone and quinoneimine end groups. The potentials for the degradation are close to those of the polymerization (practically 1.0 V vs. SCE) in the presence of monomer. The degradation makes the polyaniline film thin owing to formation of dissolved species 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 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 by use of electric noises as well as ac techniques.

2. Results and Discussion

Chronoamperometry of polyaniline-coated PT electrode was made for 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 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.

We obtained the steady-state conditions from chronoamperometric curves at different concentrations of aniline and at several potentials. Fig.1 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. A viewpoint in Fig.1 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.

The measurement of the noise may lead to determining the amount of conducting species, i.e., emeraldine, during polymerization. We imposed alternating voltage with small amplitude on the dc-voltage for the polymerization. Fig.2 shows chronoamperometric curves of the polyaniline-coated electrode in 0.1 M aniline + 1.0 M sulfuric acid when the

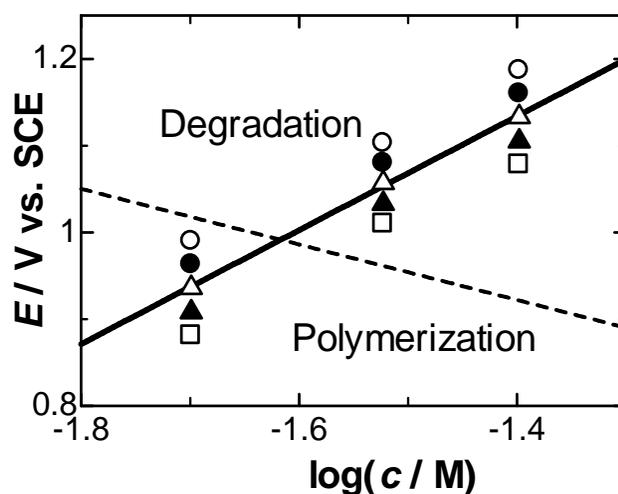


Figure 1. Competition between applied potentials and aniline concentrations for which the time-variations of chronoamperometric curves take $dI/dt =$ (open circles) -0.2 , (filled circles) -0.1 , (open triangles) 0 , (filled triangles) 0.1 and (open squares) $0.2 \mu\text{A s}^{-1}$. The dashed line is the competition line for poly(3-methylthiophene).

alternating voltage with 10 mM amplitude at 1 Hz was superimposed on the dc-voltage. Broad portions on the curves indicate responding ac-currents, which are ascribed to the electric conducting species. We pay attention to the time-variation of dc-component, i.e., taking a center of the broad portions. The current increased 50 s after the potential step, and reached a nearly steady state. The 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.

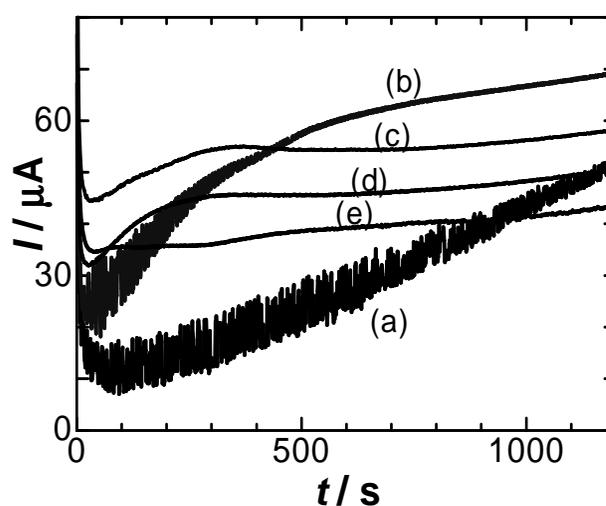


Figure 2. Chronoamperometric curves for the polyaniline-coated electrode in the solution of 0.1 M aniline + 1.0 M sulfuric acid at potentials of (a) 0.75, (b) 0.80, (c) 0.85, (d) 0.90 and (e) 0.95 V vs. SCE. The ac-voltage with 10 mV amplitude at 1 Hz was superimposed on the dc-voltage. The polyaniline film was synthesized in the solution of 0.1 M aniline + 1.0 M sulfuric acid.