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ELECTROCHEMICAL BEHAVIORS OF ELECTRODEPOSITED POLY(N,N-DIMETHYLANILINE). A NEW ORGANIC SEMICONDUCTING ION-EXCHANGE POLYMER

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Poly(N,N-dimethylaniline) film, deposited electrochemically on a Pt surface, is a semiconductor having an anion exchange ability. Electrochemical behaviors of poly(N,N-dimethylaniline) electrodes are remarkably different from those of polyaniline electrodes.

Organic conducting or semiconducting electrodes have a wide field of applications, such as electrochromic display, photoelectric devices, electrocatalysis and energy storage. Polyaniline, polypyrrole and their analogues are typical conducting organic polymers which can be prepared electrochemically.1-3) It is important to synthesize a new conducting polymer which has attractive properties not already known. In this paper, we would like to report the electrochemical preparation and properties of the poly(N,N-dimethylaniline)[PDA] film electrode which shows quite interesting electrochemical behaviors compared to those of other polyaniline[PA].

The PDA film was prepared onto Pt electrodes by continuous potential cycling between -0.2 and 1.0 V (vs. SCE) in 0.1 M H_2SO_4 containing 0.1 M N,N-dimethylaniline (1 M = 1 mol dm^{-3}). After about 300 cycles, the dark green polymer film began to deposit on the Pt surface. The potential cycling was repeated up to 600 cycles.

In contrast to PA, the PDA film electrode does not give any redox wave originating from the redox reaction of film itself. In spite of this, the PDA electrode thus obtained was active towards the electrode reaction of solution species. Figure 1 shows the cyclic voltammogram of catechol on the PDA electrode. Although the reversibility of the redox reaction is somewhat poor compared with naked Pt, the PDA does respond to the catechol/quinone couple. Another characteristics of PDA is that the cathodic current of a redox couple is always suppressed with this electrode (see Fig. 1, full line). A similar behavior was also observed with hydroquinone/benzoquinone and Tl^+/Tl^{3+} couples. The conductivity of PDA was determined to be $5 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$, that is, typical conductivity region of a semiconductor. The suppression of cathodic current may be correlated, at least in part, to the rectification effect of p-type semiconductor.

A PA electrode is active to soluble redox species only in the limited potential range where PA film itself is electroactive.1c) The PDA electrode has no such limitation. The oxidation peak of Br^-, Mn^{2+}, and Tl^+ was clearly observed with the PDA electrode, while the PA electrode was found to be inactive to these species. A nonconducting PA film, which exhibits no redox wave of polymer itself, shows a limited response towards redox reactions of solution species.[1e)] Electrochemical response in that case was observed only for relatively small ions which can penetrate into the polymer film. On the other hand, the PDA electrode was found to be electroactive to all solution species studied regardless of their size and the redox potentials.

A conducting PA electrode is useful only in a limited pH range.[1a,d)] The redox wave of $Fe(CN)_6^{4-}$ is not observed in neutral or alkaline solutions (pH >4). So long as the redox reaction of $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$ couple is concerned, the PDA electrode gave a constant response in the whole pH range studied (pH 1 - 13).

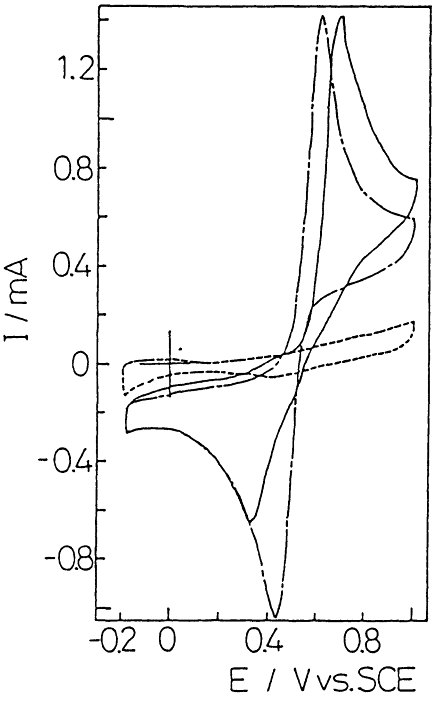

Fig. 1. Cyclic voltammogram (steady-state) of 10 mM catechol on PDA(—) or Pt(—·) electrode in 0.1 M H_2SO_4. Dotted line indicates background current of PDA electrode.

A PA film has cationic sites in acidic solutions due to the protonation of amino nitrogen.[1d)] If the polymerization reaction is assumed to be the head to tail coupling of monomer cation radical, the possible structure of PDA can be expressed as shown in Fig. 2. Therefore PDA is expected to show an anion exchange character regardless of the solution pH. In order to examine this point, the PDA electrode was immersed in neutral 0.1 M $K_3Fe(CN)_6$ solution for one hour, then transfered to 0.1 M H_2SO_4 solution to take voltammograms. The amount of anions taken into the polymer film was determined to be 1.26×10^{-7} mol cm^{-2} by the graphical integration of voltammogram.

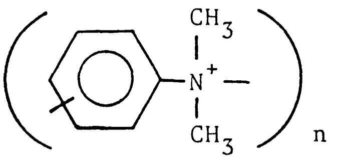

Fig. 2. Possible structure of PDA.

Since the electropolymerized PDA film has unique properties as mentioned above, it will be a promising functional material in the field of electrocatalysis and photoelectrochemistry.

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