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Electrochemical Synthesis of Polyaniline Composite Films in Acetonitrile/Water Medium

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The electroconductive polyacrylonitrile(PAN)/polyaniline composite can be synthesized by the electrochemical polymerization of aniline on the PAN-coated Pt electrode in acetonitrile/water medium. The electrochemical properties of PAN/polyaniline composites were investigated comparing with polyaniline.

Keywords: electroconductive composite; polyaniline; electrochemical synthesis

INTRODUCTION

Polyaniline(PANI) has poor mechanical properties. Thus, the efforts to improve the mechanical properties and broaden the application ranges have been directed to develop composite systems by blending a common polymer with PANI either by solution^[1] or melt process^[2]. But these conventional methods for the preparation of PANI composite are largely limited because PANI degrades before melting and only its limited solubility in organic solvents like N-methylpyrrolidone^[3] and DMSO^[4] has been reported. Thus, the authors have focused on the electrochemical polymerization method for the preparation of polyacrylonitrile(PAN)/PANI composite. For the electrochemical preparation of PAN/PANI composite, aniline, medium, and electrolyte ion should be able to penetrate into PAN, but PAN is very hydrophobic and has very compact structure. Thus, the compact structure of PAN can not be loosened in an electrolytic aqueous medium. In this study the authors investigated the appropriate medium for the preparation of PAN/PANI composite based on the analysis of the electrochemical properties.

EXPERIMENTAL

PAN containing 9.0 % of methylacrylate as a comonomer was obtained from Hanil Synthetic Fiber Co.. GR grade aniline(Aldrich) was purified

by distillation and stored under nitrogen before use. ACS grade acetonitrile(Mallinckrodt) was stirred over CaH_2 for 24 hrs at 83°C and then fractionally distilled under nitrogen atmosphere.

The electrochemical polymerization of aniline onto PAN was performed by EG & G PAR Model 173 Potentiostat connected to an EG & G PAR Model 179 coulometer. Electrochemical polymerization was carried out in a simple cell chamber of 200 ml capacity using a three-electrode system, i.e., a disk-type Pt working electrode(diameter, 1 cm) coated with 2.0 μm -thick PAN film, a plate-type Pt counter electrode(1 cm \times 1 cm), and an aqueous sodium chloride saturated calomel electrode(SSCE) as a reference electrode. The electrolyte solution consists of 0.1 M aniline and 1.0 M sulfuric acid in acetonitrile/water mixture. The potential range for electrochemical polymerization and the scanning rate are $-0.2 \sim 1.0$ V(vs. SSCE) and 50 mV/sec, respectively. The details of the experimental technique are reported in an earlier paper^[5].

RESULTS AND DISCUSSION

For the preparation of PAN/PANI composite film, acetonitrile/water mixture solution was chosen as a medium. The authors have expected the loosening of the compact PAN structure by acetonitrile. Figure 1

shows the first oxidation peak current (I_{pa}) of the 20th cyclic voltammogram according to the content of water on synthesizing pure PANI and PAN/PANI composite in acetonitrile/water medium.

In the case of pure PANI, I_{pa} increases with the content of water in acetonitrile/water medium as we expected. However, in the case of PAN/PANI composite, I_{pa} increases with the content of water, reaches a maximum at 50 % of water, and then decreases. We speculate that this results from the relative competition between the dissociation capacity of electrolyte by water and the swelling capacity of PAN by acetonitrile.

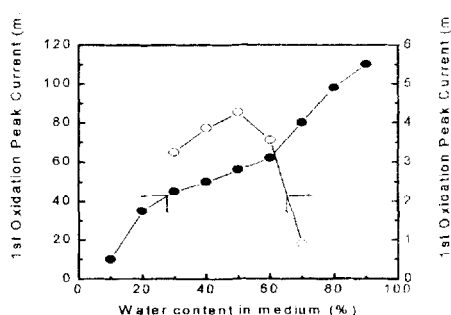


FIGURE 1. Dependence of I_{pa} of pure PANI (●) and PAN/PANI composite (○) on the content of water in acetonitrile/water medium.

Figure 2 shows the peak potential separation, $\Delta E_p (= |E_{pa} - E_{pc}|)$ of the 20th cyclic voltammogram according to the content of water on synthesizing pure PANI and PAN/PANI composite in acetonitrile/water

medium, where E_{pa} and E_{pc} are the first anodic and cathodic peak potential for the oxidation and the reduction reaction, respectively. As the content of water in the medium increases, ΔE_p decreases in both cases. This result may be explained as follows: As the content of water in the medium increases the conductivity of the electrolyte solution increases by the more dissociation of electrolyte and thus the oxidation potential and the reduction potential in the positive direction and the negative direction, respectively, decrease.

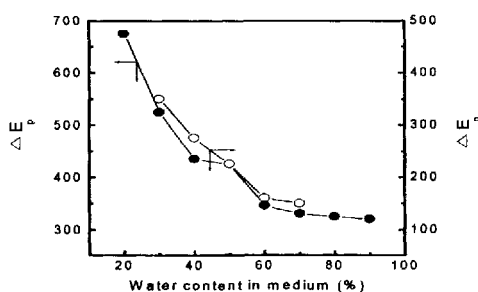


FIGURE 2. Dependence of ΔE_p of pure PANI (●) and PAN/PANI composite (○) on the content of water in acetonitrile/water medium.

Acknowledgements

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