—Communication—

An Enhanced Anion Doping Process at NBR/Polypyrrole Composite Polymer Electrode

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1 INTRODUCTION

It has already been found that an electrochemical doping-undoping process at a polypyrrole(PPy) electrode is strongly affected by the film morphology¹⁻⁴⁾ and that a diffusion rate of anions within the film can be accelerated by choosing suitable conditions for film formation such as the formation potential^{1,2)} and electrolyte anions³⁾. Recently, a unique preparation of a PPy-based composite polymer⁵⁾ has been attempted as one of the variations of electro-polymerization materials. As a new conducting material composed of PPy and an insulating material, we prepared polypyrrole on Pt substrate which has initially been coated with a nitrile rubber(NBR) insulating film. In the procedure of NBR/PPy film formation, the primarily coated NBR film may play a role of a host polymer which regulates a direction of the growth of the guest or the PPy film. In this communication, we report interesting behavior about a highly accelerated anion doping process at a Pt/NBR/PPy electrode.

2 EXPERIMENTAL

Reagent grade acetonitrile(AN) was used as a solvent without further purification. All the potentials were referred to the Ag/Ag⁺ electrode. Pt/PPy was formed by electro-oxidative polymerization at 0.8V in AN solution containing 0.1 mol dm⁻³ tetra-n-butylammonium perchlorate(TnBAClO₄) and 0.1 mol dm⁻³ pyrrole monomer. For the preparation of Pt/NBR/PPy, the Pt substrate was firstly coated with commercially available NBR prepolymer (ca.2 μm thick) and dried. Then PPy was grown through the NBR film in the same manner as in the case of Pt/PPy film. Film thickness was controlled by the passed charges. Cyclic voltammograms were obtained in 0.1 mol dm⁻³ TnBAClO₄/AN. Frequency dispersions of the electrode impedance were measured from 1.0 Hz to 2.5 kHz by using the FFT impedance method⁶⁾. Apparent diffusion coefficients (D_{app}) were determined from the slope of Cottrell plot obtained by the potential step chronoamperometry⁴⁾.

3 RESULTS AND DISCUSSION

Figure 1 shows typical cyclic voltammograms (20-30th cycles) for the Pt/PPy and Pt/NBR/PPy electrodes with the same formation charges (1.0 C cm⁻²). As can easily be seen, the anodic and cathodic currents for the Pt/NBR/PPy electrode show remarkable increases. Therefore, the anion doping/undoping process at the Pt/NBR/PPy film is considered to be highly accelerated. It

Fig.1 Cyclic voltammograms for a) Pt/PPy and b) Pt/NBR/PPy film electrodes in 0.1 mol dm⁻³ TnBAClO₄/AN at a scan rate of 10 mV s⁻¹. The thickness of NBR film was ca. 2 μm.

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is also observed that the doping charge for the Pt/NBR/PPy electrode far outnumbers the Pt/PPy electrode. The behavior similar to that in Fig.1 was also observed for other Pt/NBR/PPy films of more charged PPy films (2.0, 5.0 and 10 C cm⁻²) formed on the same thickness of NBR films.

Electrode impedance for these electrodes was measured at each anodic peak potential and was demonstrated in Fig.2. The total impedance for the Pt/NBR/PPy electrode is obviously smaller than that for the Pt/PPy electrode. The reaction resistance for the oxidation process would be reflected in the diameters of these semi-circles. The doping process at the Pt/NBR/PPy electrode is considered to be easier than that of the Pt/PPy electrode. The D_{app} values obtained for Pt/PPy and the Pt/NBR/PPy electrodes of 1 C cm⁻² charged films are 5.01×10^{-11} cm² s⁻¹ and 1.04×10^{-10} cm² s⁻¹, respectively. These values together with the results of Cole-Cole plots can support well evidence of an remarkable improvement of the anion doping process at the Pt/NBR/PPy electrode.

Brief images of PPy film growth for Pt/PPy and Pt/NBR/PPy electrodes could be schematically illustrated in Fig.3. The illustrations would better explain the formation procedure of two electrodes. When PPy is formed on a bare Pt substrate, the resulting film will show a random growth. In contrast, for the Pt electrode initially coated with the NBR film, the electrode system is considered to be insulated at first. However, the AN/TnBAClO₄ solution gradually penetrates into NBR film, which forms fine channels through the NBR film at the same time. The PPy film may grow along these channels.

One of the most probable reasons for the improvement would be owing to an easier diffusion in the direction perpendicular to the substrate across such an oriented structure of the PPy film.

Fig.2 Typical Cole-Cole plots for a) Pt/PPy and b) Pt/NBR/PPy film electrodes in 0.1 mol dm⁻³ TnBAClO₄/AN, when the potentials are polarized at peak potentials a) 0.5 V and b) 0.0 V, respectively.

Fig.3 Typical models of the film growth for a) Pt/PPy and b) Pt/NBR/PPy electrodes. The arrows represent the direction of PPy film growth.

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