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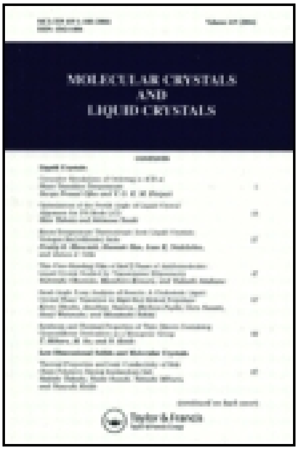

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Electrochemical Impedance Spectroscopy (Eis) Study of the Various Oxidation States of Polyaniline Films in 1 N HCl Solution

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ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) STUDY OF THE VARIOUS OXIDATION STATES OF POLYANILINE FILMS IN 1 N HCl SOLUTION.

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Abstract Pt electrodes filmed with polyanilines were prepared by *in situ* either chemical or electrochemical deposition. The open circuit potentials of the electrodes were recorded during the chemical polymerization. The observed potential profiles were thought to be closely related to the oxidation states of the films deposited on the electrode. The electrochemical deposition of the films on the Pt electrode was carried out in 1 N HCl solution containing a small amount of aniline monomers. The oxidation states of the PANI films were controlled by the applied DC potential and impedance measurements of the Pt/PANI systems were made. Analyses of the spectra were given by comparison the tendencies of the spectra obtained by the controlled DC potentials.

INTRODUCTION

Recently, polyanilines have been extensively studied as a substitute for metals due to their conductivity, relatively high stability, and various processing methods[1-3]. Electrochemical characteristics of polyaniline films can be effectively investigated by impedance measurements of the film[4,5]. Mensfeld et al.[4] used this measurements to examine the effectiveness of polybutadiene coating on metal surface and showed the applicability of this technique. Juttner[5] introduced impedance measurements in order to study uniformity of organic coating on metal surfaces and their corrosion characteristics. Pasquali et al.[6] also used impedance spectroscopy and cyclic voltammetry to investigate storage characteristics of polyanilines under several different environments.

This work uses impedance technique to distinguish the difference in electrochemical properties of the various oxidation states of the polyaniline films and demonstrates that EIS measurements could be a useful tool for the study of conducting polymer films.

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EXPERIMENTAL

For the chemical polymerization, 1 N HCl solution containing ~ 0.85 M of aniline monomers and 1 M HCl solution containing 0.20 M ammonium peroxisulfate were separately prepared and cooled down to 0 °C. Each solution of 50 mL was equally mixed in the reaction vessel and variation of the open circuit potential E_{oc} (vs. SCE) of the Pt electrode was recorded by a personal computer connected to a Keithley 2001 multimeter. The open circuit potential was also monitored during the chemical synthesis of the other polyaniline derivative, polymethylaniline and polyethylaniline.

Electrochemical preparation of polyaniline films was carried out by the typical potential sweeping method[1,7]. The electrolyte was made by mixing 95 mL of 1 N HCl solution and 5.0 mL of aniline monomers. The electrochemical cell consists of three electrodes, that is, a working electrode (Pt plate, 2 x 5 x 0.015 cm^3) which was partly immersed in the solution mixture, a counter electrode (Pt wire), and a reference electrode (Saturated Calomel Electrode, SCE). The potential sweeping was terminated after applying at least 100 cycles (~ 30 min sweeping).

Electrochemical impedance measurements were carried out at the three different DC potentials (0.75, 0.43, and 0.0 V) in 1 N HCl solution. In order to obtain the impedance spectra of the fully oxidized and the fully reduced polyaniline film, the measurements were carried out after waiting a sufficient time (~ 30 min) at a given potential. The amplitude of the applied AC potential was 5 mV and the frequency range is from 10 mHz to 10 kHz. Impedance measurements and the electrochemical polymerization using the potential sweepings except the open circuit measurements were carried out with Im5d impedance analyzer (Zahner Co.).

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RESULTS AND DISCUSSION

Fig. 1 shows variation of the open circuit potentials of the Pt electrode immersed in the solution mixture during the chemical polymerization of PANIs (polyaniline and polymethylaniline). Before mixing the solution containing the oxidant, the open circuit potential of the Pt electrode was approximately 0.32 and 0.24 V for polyaniline and polymethylaniline, respectively. For polyaniline, the open circuit potential increased to ~ 0.7 V within a minute after adding the oxidant solution. The maximum open circuit potential of 0.75 V was then observed at the region B, ~ 300 sec after the polymerization. This value is quite similar to the value of the second $E_{1/2}$ found in the cyclic voltammogram of Pt/PANI system in 1 N HCl solution[8,9]. When the electrode was taken off from the solution at this region, it was observed that the Pt electrode was covered with the dark blue thin films, indicating the pernigraniline salt. However, the blue film on the Pt electrode turned into the green within a few minutes after being stored in the aniline-free 1 N HCl solution. This observations agree well to the hypothesis[9] suggesting that the highest oxidation state of polyanilines is initially produced, while it is itself reduced to the half-oxidized state. A subsequently following

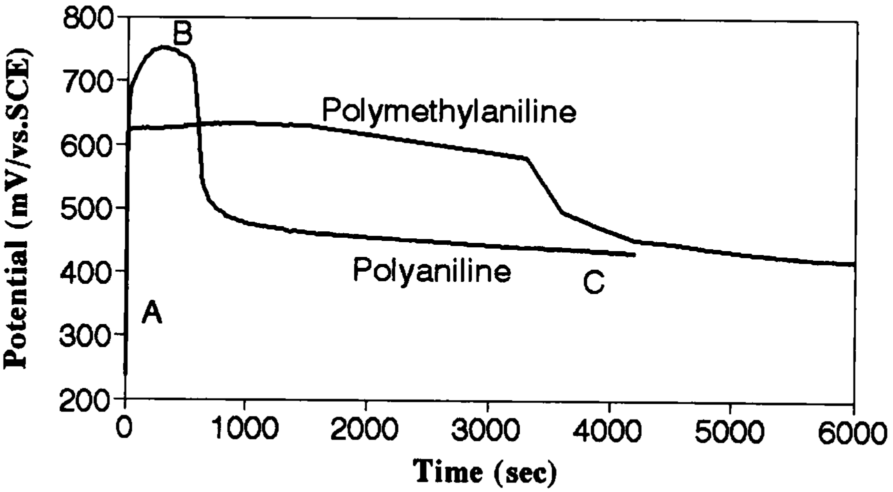

FIGURE 1 Variation of the open circuit potential of the Pt electrode during the chemical polymerization of PANI.

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rapid decrease of the potential around 600 sec indicated that the polyaniline adsorbed on the Pt electrode was then reduced to the emeraldine oxidation state. After a rapid decrease, the potential decreased very slowly to reach at around 0.43 V. At the region C, the most stable emeraldine salts were formed. For polymethylaniline, the open circuit potential was initially observed at 0.24 V before mixing the oxidant solution and increased to ~ 0.62 V immediately after adding the oxidant solution. The potential then slowly reached to the maximum potential of ~ 0.63 V and stayed there for almost 1 hr. The lowered maximum potential (0.63 V *vs.* 0.75 V) and the longer period staying at the maximum (60 min *vs.* 5 min) may indicate that the highest oxidation state of polymethylaniline is more stable than that of polyaniline. Finally, it decreased to 0.43 V and the synthesis was terminated after 6000 sec. In the case of polyethylaniline which is not shown in Fig. 1, the maximum potential was also observed at 0.63 V, but the period staying at the maximum increased to ~ 2 hrs. It can be deduced from these observation that the stability of the oxidation state of polyanilines would depend on the properties of the functional groups attached on the polymer main chains.

The electrochemical synthesis of PANI by potential sweeping between - 0.2 and 0.7 V with the scan rate of 50 mV/sec produced the polyaniline films on both of the Pt electrodes (the working and the counter electrode). Actually, thicker films were formed on the counter electrode. To prevent film formation on the counter electrode, potential sweeping was narrowed between 0.4 and 0.75 V with variation of the scan speed and a number of cycles increased to at least 200. This resulted in the fairly thick green film on the working electrode.

Fig. 2 shows the impedance spectra of the Pt/PANI electrodes under the different applied potentials, that is, 0.75, 0.43, and 0 V (*vs.* SCE). The Pt/PANI electrodes were made by the potential sweeping between 0.4 - 0.75 V with the scan rate of 50 mV/s. The spectra of the other Pt/PANI electrodes prepared by chemical deposition, which were not shown in this paper, showed similar behaviors. This observation is consistant with the evidences found by Chinn et al.[10]. The different tendencies of the impedance spectra, (a), (b), and (c) resulted from the different electrochemical properties of the Pt/PANI interface, PANI film, and PANI/solution interface. In most cases, the impedance of the metal/film interface is likely to appear as a small frequency-independent resistance due to the transfer of electrons between the two phase[11]. The impedance of the film is expected to vary according to the applied DC potentials since the electrochemical properties of the PANI film is changed by its oxidation states. The impedance of the film/solution interface could be contributed by either ion exchange processes (diffusion components) or nondiffusional components. The total impedance of the system will be dominated by the largest impedance because of the serial connection of the elements.

The x-intersections of the spectra (a), (b), and (c) at the high frequency region are all the same. It indicates that the impedance of the metal/film interface is a minor component and the film does serve as a conductive layer. Therefore, the remaining part is the film/solution interface. The spectra in Fig. 2 exhibits a portion of semi circle in the frequency region (from 0.01 Hz to 10 kHz), which indicates that the impedance of the film/solution is dominated by nondiffusional components. The spectra (a) exhibit a smaller semi circle than the spectra (b) and the spectra (c) showed a smaller semi circle than the spectra (a) and (b). The observed values of the external DC current when applied the potentials of 0.43, 0.75 and 0.0 V were less than 10, ~ 200, and ~ - 400 μA, respectively. A smaller impedance arc and the large current value indicate that the

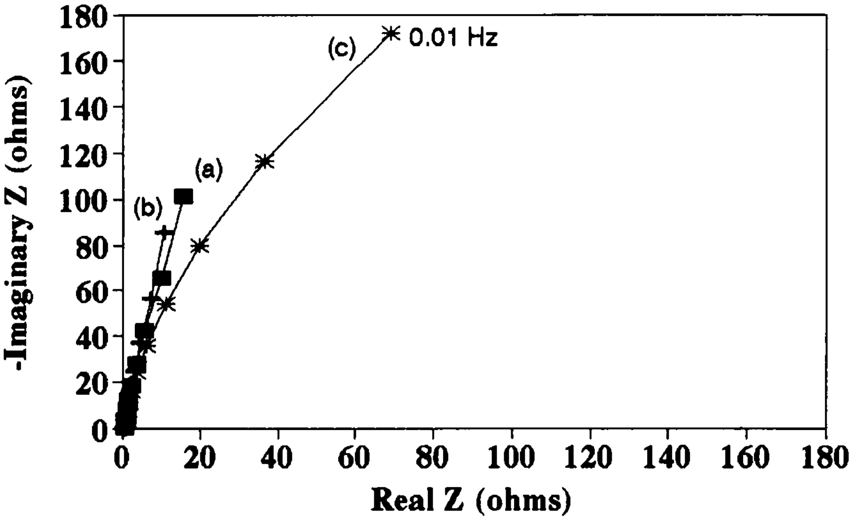

FIGURE 2 Impedance spectra of the Pt/PANI electrode at the following DC potentials: (a) 0.75 V, (b) 0.43 V, and (c) 0.0 V (*vs.* SCE).

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charge transfer resistance of the film/solution interface could depend on the film conductivity.

SUMMARY

The E_{oc} profiles demonstrates that the formation of the emeraldine salts are followed by the formation of the pernigranilie salts and that the stability of the pernigraniline salts may depend on the functional groups attached to the polymer main chain. Impedance technique was utilized for investigating the electrochemical properties of the Pt/PANI system and distinguished the different oxidation states of the PANI films.

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