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Stability and Electrochemical Characteristics of Polyaniline Salt Films in 1 N HCl Solution

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Thin films of polyaniline (PANI) salts were *in situ* deposited on a Pt plate during either chemical polymerization or electrochemical polymerization. The oxidation states of the salt films were controlled by the applied DC potential. AC impedance of the Pt/PANI electrode were measured in monomer-free 1 N HCl solution in order to investigate the electrodic properties of the films at the following applied DC potentials: 0, 0.45 and 0.75 V *vs.* SCE. Very small differences in film conductivity according to its oxidation state were observed by analysis of the impedance spectra, the reasons of which are complicated by enriched water content in the film and possible decrease in the film thickness during the measurements. The electrochemical activity of the film/solution interface varied with its oxidation state. Stability of the film in 1 N HCl solution was also evaluated by impedance and cyclic voltammetry measurements.

Introduction

Among organic conducting polymers, polyanilines (PANIs) have been extensively studied as prospective materials for various electrochemical applications such as electrochromic devices, energy storages, photocorrosion protection, and electrochemical sensors.¹⁻⁷ Their electrochemical properties, stability in air, and various processing methods have been also illuminated in the literature.⁸⁻¹² It was reported that electrochemical characteristics of polyaniline films can be effectively investigated by impedance measurements.¹³ Mensfeld *et al.*¹⁴ used impedance spectroscopy (IS) technique to examine the effectiveness of polybutadiene coating on metal surface and showed the applicability of this technique. Pasquali *et al.*¹⁵ also used impedance spectroscopy and cyclic voltammetry to investigate storage characteristics of substituted polyanilines under several different environments. Goldenberg *et al.*¹⁶ compared the electrochemically grown films with the films

prepared by several methods and demonstrated possibility of using a number of simple techniques to produce electroactive thin films of polyanilines.

Even though PANI is referred to as the most stable material within the class of conducting polymers,⁹ only a few studies devoted to stability have been reported.^{15,17,18} Stability in aqueous or organic solutions at open circuit or at given potentials should be thoroughly investigated in order to assess its full applicability in practical uses. Resistance to degradation in sulfuric and organic solutions was reported in the literature,¹⁵ in which unpleasant degradation would be serious problem in its practical applications. In this work, IS technique and cyclic voltammetry were utilized in order to investigate stability in acidic chloride solution and the electrodic properties of PANI salt films at three different oxidation states (emeraldine, pernigraniline, and leucoemeraldine).

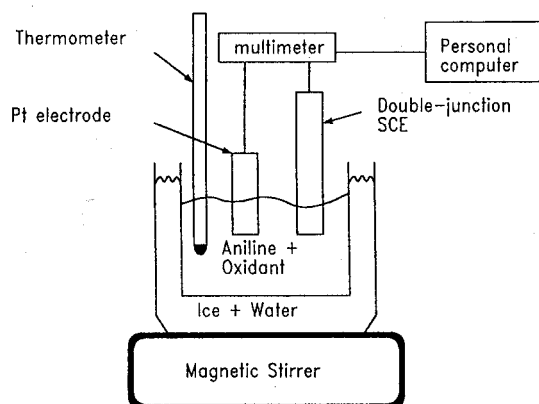


Figure 1. A schematic apparatus for measuring open circuit potential during chemical polymerization.

Experimental

Polyaniline films on a Pt electrode were made by *in situ* deposition either chemically or electrochemically. For direct chemical deposition, 1 N HCl solution containing 0.85 M of aniline monomers and 1 M HCl solution containing 0.2 M ammonium peroxydisulfate 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 as shown in Figure 1. The measurements were repeated at least three times to obtain reproducible data. A magnetic stirrer and a stirring bar were used for continuous stirring the solution during polymerization. The electrodes covered with the polymer films were carefully rinsed with distilled water and 1 N HCl, consecutively, and then stored in 1 N HCl for impedance measurements.

Electrochemical preparation of polyaniline films was carried out by the typical potential sweeping method.¹⁸ 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, $2 \times 5 \times 0.02$ cm³) which was partially immersed in the solution mixture, a counter electrode (Pt plate or wire), and a reference electrode (saturated calomel electrode, SCE). The sweeping range of potential was between 0.4 and 0.75 V (vs. SCE). Potential sweeping was continued for 100 cycles and resulted in a fairly dark green PANI film on the working electrode. The solution was either stirred with magnetic stirrer during potential sweeping, or stagnant. The Pt/PANI electrode was then rinsed with distilled water and 1 N HCl solution.

Electrochemical impedance measurements of the Pt/PANI electrode were carried out in 1 N HCl solution at the different DC potentials of 0.75, 0.45, and 0 V which are representing pernigraniline, emeraldine, and leucoemeraldine, respectively. 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 (~2 hours) at each potential. The amplitude of the applied AC potential was 5 mV and the frequency range was from 10 mHz to 10 kHz. Impedance spectra and cyclic

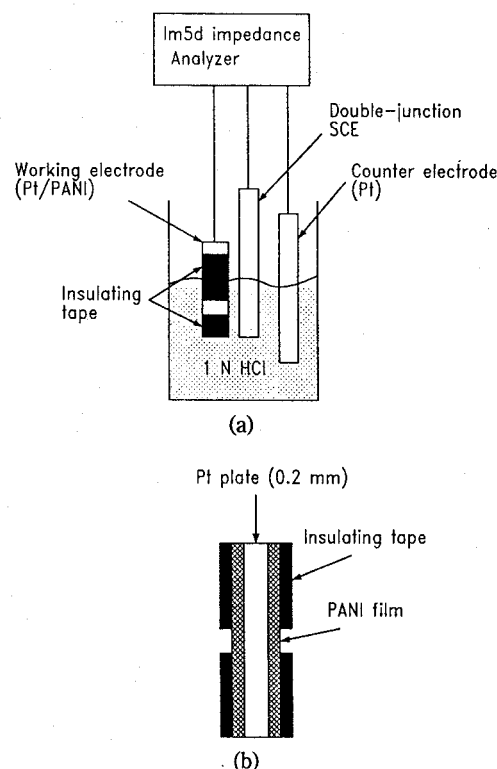


Figure 2. Schematics of (a) an instrumentation for impedance measurements and cyclic voltammetry and (b) the cross section of Pt/PANI electrode.

voltammograms were obtained for the freshly prepared films and the aged films stored in 1 N HCl solution at 0.45 V (vs. SCE) for 7 days. Potential scanning between -0.2 and 0.8 V (vs. SCE) with a scan speed of 50 mV/s was applied to the fresh film in 1 N HCl solution in order to investigate stability of the film in this potential region. Impedance measurements and cyclic voltammetry were also carried out before and after potential scanning. The electrochemical cell and the apparatus are schematically shown in Figure 2.

Results and Discussion

Figure 3 shows variation of the open circuit potentials, E_{oc} (vs. SCE) of the Pt electrode immersed in the solution mixture during chemical polymerization of PANI. Before mixing the solution containing the oxidant, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, the open circuit potential of the Pt electrode was approximately 0.32 V (vs. SCE). 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.^{19,20} At this stage, the color of solution was dark blue, which indicated the pernigraniline salts being formed. 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. However, the blue film on the Pt electrode turned into the green within a few minutes after being stored in aniline-free 1 N HCl solution. This observation

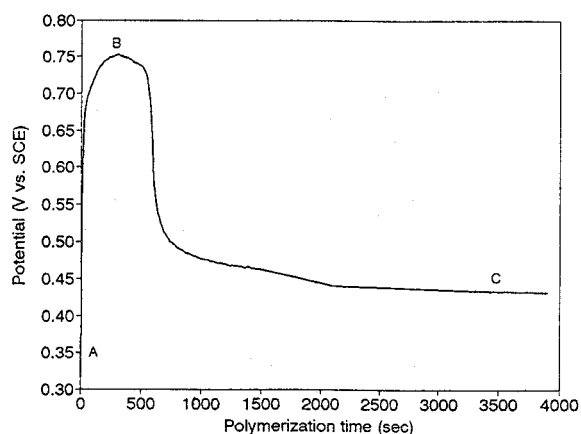


Figure 3. Open circuit potential profile of the Pt electrode during chemical polymerization.

agrees well to the hypothesis²⁰ suggesting that the fully oxidized state (pernigraniline) of polyanilines is initially produced, which is a strong oxidizing agent to oxidatively polymerize any excess aniline to the emeraldine, while it is itself reduced to the half-oxidized state. A subsequently following 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 half oxidized state (emeraldine) of polyanilines was formed. The film formed on the Pt electrode was not uniform and easily removed by hand-scratching. It was carefully rinsed with distilled water and 1 N HCl solution to obtain a very thin uniform film. This film was then used for impedance measurements and cyclic voltammetry.

The film formed by *in situ* electrochemical deposition within the stirred solution was uniformly thick and strongly adhered to the Pt electrode, while the film formed within the stagnant solution was thick and smooth, but the outer layer of the film was easily removed by rinsing with distilled water and the very thin uniform inner layer was remained on the Pt electrode. Stability and the electrodic properties of these two different films were investigated by IS measurements and cyclic voltammetry.

In Figure 4, the solid lines with symbols are the experimental impedance spectra of the fresh Pt/PANI electrode under the different applied potentials, that is, (a) 0.75, (b) 0.45, and (c) 0 V (*vs.* SCE), and dashed lines are the theoretical impedance spectra at the above potentials obtained by fitting the experimental data to the basic equivalent electric circuit. Fitting was carried out by the analysis program installed in IM5d impedance analyser. Table 1 summarized the values of each components in the equivalent circuit. The Pt/PANI electrode was made by the potential sweeping between 0.4–0.75 V with a scan rate of 50 mV/s while stirring the solution. The spectra of other Pt/PANI electrodes prepared by chemical deposition and potential sweeping under the stagnant solution, which were not presented in this paper, showed similar behaviors. It indicates that the films prepared by chemical and the electrochemical processes have quite similar electrochemical properties.²¹ The different ten-

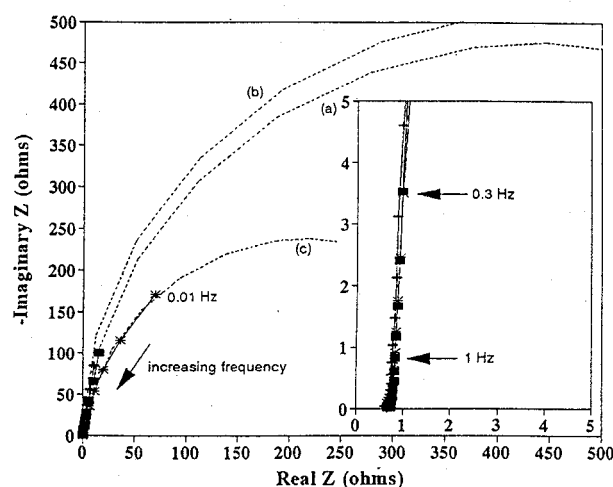


Figure 4. Impedance spectra (solid lines with symbols) of PANI salt film formed by potential sweeping between 0.4 and 0.75 V (*vs.* SCE) with a scan speed of 50 mV/sec at the following applied potential: (a) 0.75 ($\square$), (b) 0.45 ($+$), and (c) 0 ($*$) V (*vs.* SCE). Dashed lines are the theoretical impedance spectra obtained by fitting the experimental data to the basic equivalent electric circuit appeared in Table 1. The solution was stirred during film formation. The figure in the small box shows the impedance spectra of high frequency region.

Table 1. Summary of the values of each component in the basic equivalent circuit^a

Applied potential (V <i>vs.</i> SCE)	R_s (ohm)	R_d (ohm)	C_i (mF)
0.75	0.856	995	144
0.45	0.838	1043	154
	0.865	424	53

^athe basic equivalent circuit

dencies of the impedance spectra may result from the different electrochemical properties of the Pt/PANI interface, PANI film, and PANI/solution interface. The total impedance of the system will be dominated by the largest impedance among these components because of the serial connection of the elements. When the film is conducting, 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 phases.²² The value of this resistance component would depend on interfacial area if adhesiveness between the two phases were considered to be equal. In this work, the interfacial impedance (resistance) between the metal/film can be negligible because uniform and well adhesive polyaniline films on the Pt electrode were formed during *in situ* electrochemical polymerization.

The second component of the total impedance is film resistance. The impedance of the film is expected to vary according to the applied DC potentials since resistivity of the PANI film is changed with its oxidation states. The x-intersections of the spectra (a), (b), and (c) at the high frequency region are all about the same as shown in the small box in Figure 4. The value of x-intersection is the sum of solu-

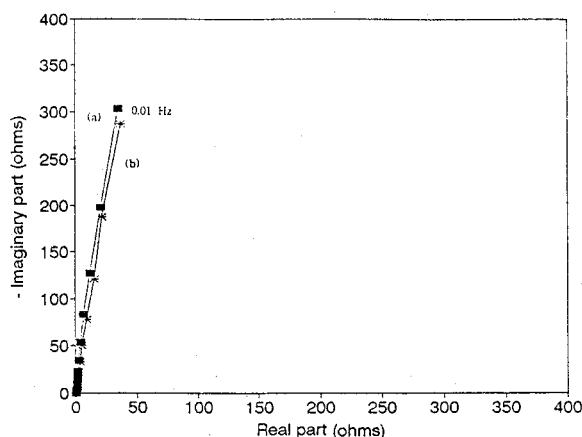


Figure 5. Impedance spectra of (a) the fresh emeraldine salt film, and (b) the film stored in 1 N HCl solution for 7 days at open circuit potential.

tion resistance between the reference and the working electrode, and the film resistance. It indicates that the film does not serve as a pure resistive layer, but is somewhat electrically conducting, and the value of the film resistance is very small. Even though the difference in the magnitude of the resistance among emeraldine, pernigraniline and leucoemeraldine salts would be expected to be greater than 5 order of magnitude for dry materials, the very smaller differences were observed from the impedance spectra and their analysis. This observation could be explained by (1) enriched water content in the film, and (2) possible decrease in film thickness due to degradation of polymer chains at the fully oxidized pernigraniline state. Relationship between film thickness and resistance will be discussed in detail in the later section.

Therefore the remaining part is the film/solution interface. The impedance of the film/solution interface could be contributed by either ion exchange processes (diffusion components) or non-diffusional components. By fitting the experimental data to the theoretical data calculated from the equivalent circuit (Table 1), the spectra in Figure 4 are turned out to be a small portion of semi-circle, which indicates that the impedance of the film/solution interface is dominated by non-diffusional components. A small deviation of the phase angle from 90° was observed for each spectra, which could be explained by structural defects or roughness of the film. The spectrum (a) exhibit a smaller semi-circle than the spectrum (b) and the spectrum (c) showed a smaller semi-circle than the spectra (a) and (b). Extrapolating of the spectra would reveal the spectrum (a) to have the largest charge transfer resistance, R_{ct} , and the spectrum (c) to have the smallest R_{ct} . This was well agreed with the current observed during impedance measurements. A smaller impedance arc and the large current value indicate that the charge transfer resistance of the film/solution interface could depend on the electrochemical activities of the film/solution interface.

Figure 5 shows the impedance spectra of the fresh emeraldine salt film made by potential sweeping between 0.4 and 0.75 V (*vs.* SCE) in the stirred solution and of the aged one which was stored for 7 days in 1 N HCl solution at 0.45 V (*vs.* SCE). The cyclic voltammograms which appeared

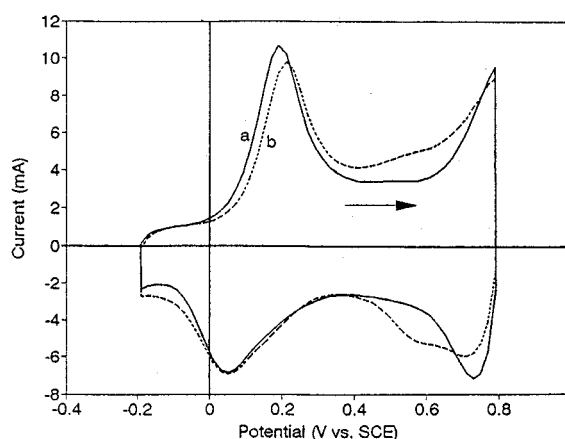


Figure 6. Cyclic voltammograms of (a) the fresh emeraldine salt film, and (b) the film stored in 1 N HCl solution for 7 days at open circuit potential. Potential sweeping between -0.2 and 0.8 V (*vs.* SCE), and a scan speed of 50 mV/sec were applied.

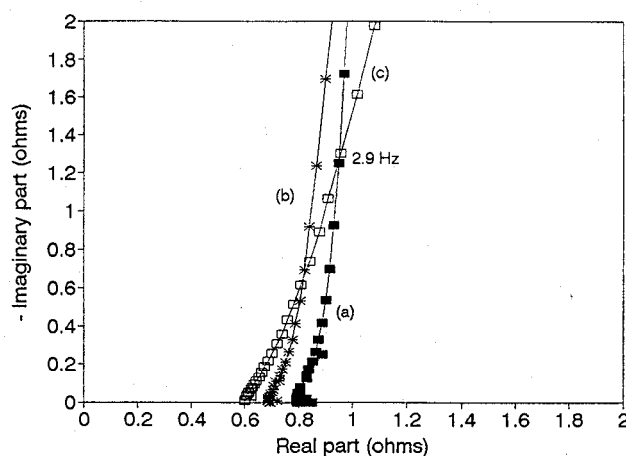


Figure 7. Impedance spectra of (a) the fresh emeraldine salt film, (b) the film after 100 times of potential sweeping between -0.2 and 0.8 V (*vs.* SCE) with a scan speed of 50 mV/sec, and (c) the bare Pt electrode.

in Figure 6 were obtained before impedance measurements. From these figures, no significant degradation was observed. However, after 100 times of potential sweeping between -0.2 and 0.8 V (*vs.* SCE) with a scan rate of 50 mV/sec, the impedance spectra and cyclic voltammograms shown in Figure 7 and 8, respectively, provide the plausible evidences of decrement in its thickness.

In Figure 7, the spectra were obtained at the constant potential of 0.45 V. The impedance spectrum of Figure 7 (c) is for the bare Pt electrode (surface area = 6.0 cm^2) in 1 N HCl solution. The approximate value of x-intersection is ~ 0.6 ohm attributed to solution resistance between the reference electrode and the Pt electrode. The corresponding value for the fresh-prepared Pt/PANI as shown in Figure 7 (a) was ~ 0.8 ohm, while it decreased to ~ 0.7 ohms (Figure 7 (b)) after potential perturbation. Resistance of the film is proportional to its thickness, since $R = \rho l / A$, where ρ is resistivity, l is length (film thickness in this work), and A is surface area. Decreasing of the resistance observed after

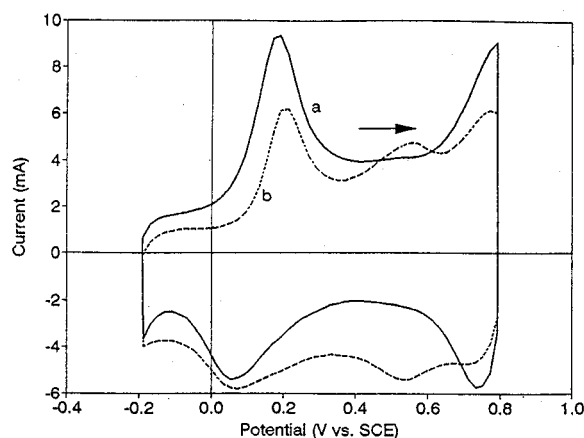


Figure 8. Cyclic voltammograms of (a) the fresh emeraldine salt film, and (b) the film after 100 times of potential sweeping between -0.2 and 0.8 V (*vs.* SCE) with a scan speed of 50 mV/sec.

potential cycling is an obvious evidence for film thinning since A and p are constant. The maximum value in the first oxidation peak of Figure 8 (b), which can determine film thickness of polyaniline,²³ also decreased significantly. However, charge capacity of the film did not decrease proportionally as the film thickness decreased. It might be explained by cross-linking reaction between polymer chains, which was observed in the CV diagram of Figure 8 (b). The peak developed at 0.59 V during potential perturbation was correlated to cross-linking reaction between polyaniline chains.²⁴

Conclusions

The open circuit potential profiles of the Pt/PANIs films during the chemical polymerization demonstrates that the formation of the emeraldine salts are followed by the formation of the pernigraniline salts. Impedance technique was utilized for investigating the electrochemical properties of the Pt/PANI system and distinguished the different oxidation states of the PANI films. The electrochemical properties of the Pt/PANI (chemical deposition) and of the Pt/PANI (electrochemical deposition) were turned out to be the same. It was suggested that the differences in the spectra observed at the different DC potentials would be due to variation of electrochemical activity of the film/solution interfaces with applied DC potential. PANI salt film is not stable under sustaining potential perturbation between -0.2 and 0.8 V (*vs.* SCE), while it is if stored at open circuit potential between 0.4 and 0.5 V (*vs.* SCE).

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