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Effect of magnetic field on the electrochemical properties of polyaniline films

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ABSTRACT

The polyaniline (PANI) films are prepared on both bare nickel flake and flexible polyethylene terephthalate-indium tin oxide substrates by potantionstatic method in the presence and absence of a constant magnetic field (MF) (0.8T). Based on the cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), Tafel plot and UV-vis spectra, the paper has studied the effect of MF on the electrochemical properties of PANI films, and the result shows that the PANI films prepared in the presence of a constant MF have a higher value of redox-current, better stability, smaller charge transfer resistance, more noble value of the corresponding corrosion potential, and a longer wavelength where the peak of π-polaron transition appears.

KEYWORDS

Polyaniline;
Electrochemical property;
Magnetic field;
Cyclic voltammertry;
Electrochemical impedance spectroscopy.

INTRODUCTION

In the past two decades, conductive polymers received wide concerns in both academia and commerce[1]. Polyaniline (PANI) is one of the most wildly used and studied conductive polymers due to its stability in air and water[2], easy processability and high conductivity[3], which has a broad application in gas and biosensors[4], solar cells[5], rechargeable batteries[6], display devices, and corrosion protection[7].

The effect of magnetic field (MF) on electrochemical reactions received wild concerns in recent years because of their theoretical and practical applications in industry[8,9]. Researchers like White[10] demonstrated that the magnetohydrodynamic (MHD) effect had a significant effect on the rate of electrochemical reactions. MHD effect is a Lorentzian force acting on moving charges (ions) in the presence of MF[11], which leads to the migration of ions, generates solution streaming[11] and induces the orientation of polymer[12]. Some articles concerning the effect of MF on the electrochemistry also found that electropolymerization rate of PANI obviously increased in the presence of MF[13]. These previous studies mainly related to MF effect on open circuit potentials, polarisation resistances, cathodic reduction reactions and anodic dissolution reactions of iron in acidic solutions[14], however, few researches on the effects of MF on electrochemical properties of PANI films have ever been reported, which is the main objective of this research.

The paper has researched the effect of a constant MF (0.8T) on the electrochemical properties of PANI films. The PANI films are characterized by means of cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and Tafel Curves and UV-vis spectra.

EXPERIMENTAL

Materials

Prior to use, distill aniline (99.5%) in vacuum and store in dark. Other reagents including sulfuric acid (H_2SO_4), sulfosalicylic acid (SSA) are also analytical grade reagents. Double distilled water is the required wate throughout the experimental procedures of nickel flakes (NF, R≈10 Ω/sq, Ni % = 99.5 %). Prior to the substrates, clean the nickel flakes by ultrasonic device in 0.1 mol/L H_2SO_4 solution for 2 min and then clean them by distilled water for another 2 min. Put in 0.1 mol/L acetone solution in PET-ITO base to clean for 1 min and then in double distilled water for another 2 min. Dry the substrates in air.

Preparation of PANI films

Prepare PANI films in the presence and absence of a constant MF by a constant potential (1.15V) (WYK-303bB2 DC power, Yangzhou Eastern Group) for 10 min at the room temperature. Take a piece of NF (PET-ITO) as the working electrode, saturated calomel electrode (SCE) as the reference electrode, and stainless steel as the counter electrode respectively. The active area of the working electrode is 2.0×1.0 cm^2 and the solutions applied are 0.35 mol/L aniline, 0.2 mol/L H_2SO_4, and 0.22 mol/L SSA. After deposition, the films should be rinsed with double distilled water. Instill oxygen gas through the electrolyte before electrochemical polymerization to ensure the removal of the rest oxygen. The distance between the working electrode and counter electrode is about 5 cm. The direction of the MF, working electrode, and counter electrode are shown in Figure 1, where X direction indicates the direction of the MF perpendicular to the electric field while the direction of the MF parallel to the electric field is the same as the that of Y.

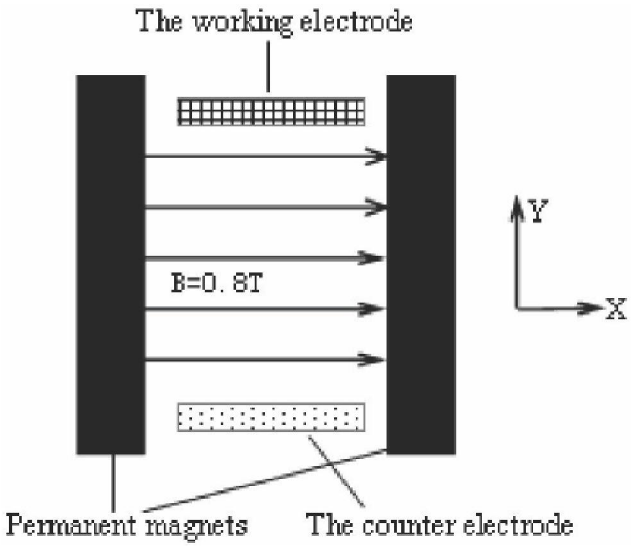

Figure 1 : Schematic illustration of the polymerization cell in the MF.

Characterization of PANI films

The electrochemical properties of PANI films are characterized through CHI660A (Shanghai Calvin China instrument corporation) electrochemical workstation. Use 0.5 mol/L H_2SO_4 electrolyte PANI films as the working electrode, take the stainless steel as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. A UV-Lambda 850 spectrometer (Perkin Elmer Corporation) is used to record the UV-vis spectra of PANI films prepared on PET-ITO substrate.

RESULTS AND DISCUSSIONS

Cyclic voltammetry and stability of PANI films

Figure 2 is the CV picture of PANI film. The operating potential has been scanned from -0.2 V to 0.9 V with a scan rate of 0.03 v/s. The PANI films are prepared on NF substrates in the MF perpendicular to the electric field (curve (a)), parallel to the electric field (curve (b)) and in the absence of a constant MF (curve (c)), respectively. It can be seen from Figure 2 that the curve shapes are quite similar and almost share the same peak potentials. This shows that the peak potentials of the PANI film have hardly been influenced by the MF. However, the peak current in curve (a) is the highest while the lowest one is in curve (c). For example, the first anodic peak current in curve (a) and (b) is 46.99 mA and 38.41 mA respectively; while it is 36.72 mA in curve (c); the second anodic peak current in curve (a) and (b) are 32.71 mA and 29.34 mA; while it is 22.39 mA in curve (c), with the results shown in TABLE 1. It is well known that organic polymers have anisotropic diamagnetic susceptibility[12], hence they have been oriented in the MF. The MF coupled with the electric field can generate Lorentz force, which enhances mass transfer and makes the PANI chains more regularly, thus further facilitate the charge transfer[13]. The Lorentz force will be the largest in the MF perpendicular to the electric field[11]. This is the reason why the peak currents in curve (a) are higher than those in curve (b) and are the lowest in curve (c).

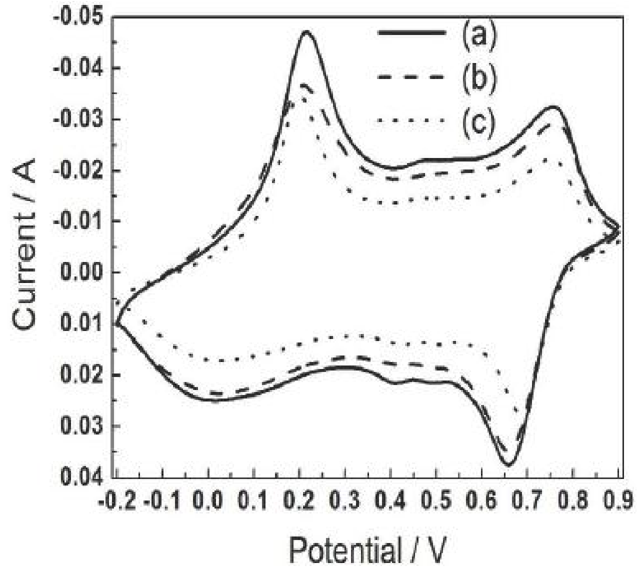

Figure 2 : Cyclic voltammetry of the PANI films in 0.5 mol/L H_2SO_4 between -0.2 and 0.9 V at a scan rate of 30 mV/s. (a) the MF perpendicular to the electric field; (b) the MF parallel to the electric field; (c) absence of a MF.

TABLE 1 : The first and second anodic peak current of the PANI films

Condition	The first anodic peak current/mA	The second anodic peak current/mA
Absenceof the MF	36.72	22.39
MF parallel to the electric field	38.41	29.34
MF perpendicular to the electric field	46.99	32.71

Electrochemical stability is a very important parameter in practical applications. Figure 3 shows the relation between the first anodic peak of PANI and the relative currents among which in curve (a) PANI films are prepared perpendicular to the electric field, those in curve (b) are parallel to the electric field and curve (c) is prepared in the absence of a constant MF. I_r is the ratio of the initial anodic current to the anodic current of a certain cycle. It can be seen from curve (b) and (c) that the two curve shapes are very similar, while in curve (a) I_r shows a significant decay. Thus, the PANI films prepared in the MF and perpendicular to the electric field have a higher electrochemical stability than those in the MF parallel to the electric field and in the absence of the MF. The reason may consist in that the applied MF perpendicular to the electric field deforms the conformation of PANI chains and makes it become more regularly.

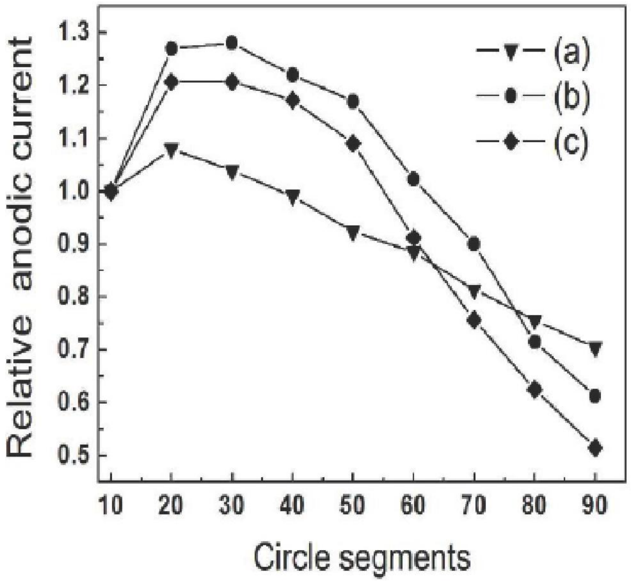

Figure 3 : Dependence of the relative current of the first anodic peak on the numbers of the cycles, The PANI films prepared in (a) the MF perpendicular to the electric field; (b) the MF parallel to the electric field; (c) absence of a MF.

Figure 4 shows the dependence of the first anodic peak current (i_p) in CV curves on the square root of the scan rate ($V^{1/2}$) of PANI films, which are prepared in MF perpendicular to the electric field (curve (a)), parallel to the electric field (curve (b)) and in the absence of MF (curve (c)). The results indicate that i_p increases proportionally according to the $V^{1/2}$, which suggests that the rate of the charge transfer in the system is mainly affected by diffusion process[15]. In addition, the slightly larger slopes in curve (a) and (b) suggest that the diffusion constant of the PANI films prepared in the presence of a constant MF may be larger than those prepared in the absence of a constant MF. Moreover, the slope in curve (a) is the largest among the three slopes.

It also can be considered in another way that the diffusion resistance of the PANI films prepared in the absence of a constant MF is larger than those prepared in the presence of a constant MF. This may be due to the MF orientation effect that makes PANI chains more regularly[12], thus the electron transfer becomes easier.

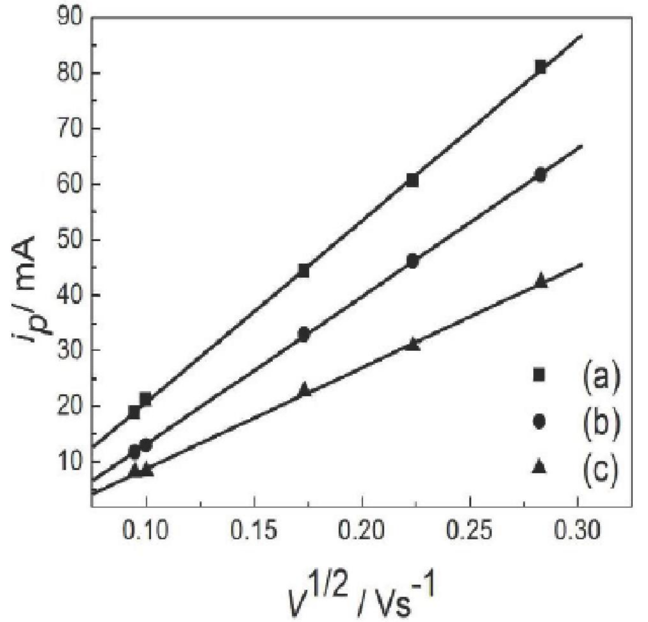

Figure 4 : Dependence of the first anodic peak current of CV curves on square root of the scan rate in 0.5 mol/L H_2SO_4 of the PANI films prepared on NF substrate. (a) the MF perpendicular to the electric field; (b) the MF parallel to the electric field; (c) absence of the MF.

The EIS of PANI films

More electrochemical information of the PANI films has been obtained by EIS research. Figure 5 shows the impedance spectra of the PANI films in 0.01 mol/L H_2SO_4 solution, with the frequency ranging from 0.1 Hz to 10^5 Hz. The PANI films are prepared on PET-ITO substrates in the MF perpendicular to the electric field (curve (a)), parallel to the electric field (curve (b)) and in the absence of a constant MF (curve (c), respectively. It can be seen that the three impedance spectra share similar characteristics, form a depressed semicircle in the high frequency region and a straight line in the low frequency region. Generally speaking, the depressed semicircle in the high frequency region is ascribed to the membrane resistance of electrode; the straight line in the low frequency region is due to the capacitive characteristics of conductive polymer film. Compare with the impedance spectra, it has been found that the diameters in curve (a) and (b) are much smaller than those in the curve (c), and the diameter in curve (a) is the smallest. This indicates that the PANI films prepared in the presence of a constant MF show a lower electrochemical charge transfer resistance than those in the absence of a constant MF. When the MF is perpendicular to the electric field, the PANI films present the lowest electrochemical charge transfer resistance. For example, the charge transference resistance in curve (a) and (b) is 241.5 Ω and 258.6 Ω respectively; while it is 298.9 Ω in curve (c). In other words, the PANI films prepared in the presence of a constant MF exhibit higher electronic conductivity and lower charge transfer resistance than those in the absence of a constant MF. This also may be attributed to the orientation effect of the MF on PANI molecules[12], resulting in easier charge transference and dopant doping, which is corresponding with Figure 2.

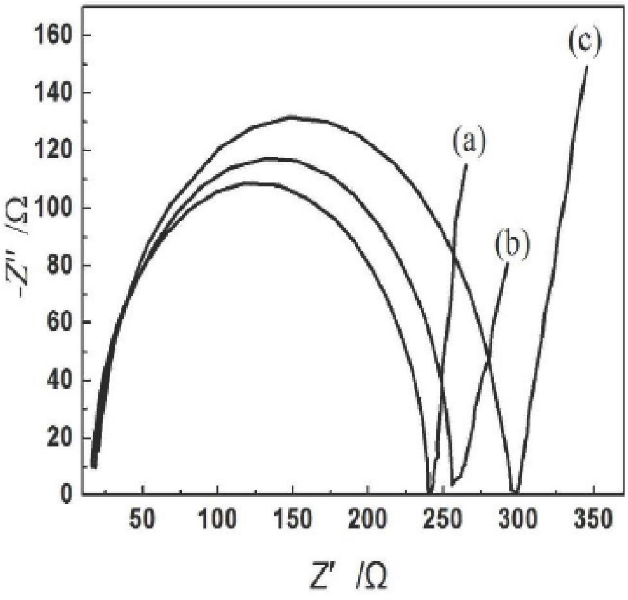

Figure 5 : Electrochemical impedance spectroscopy of the PANI films in 0.01 mol/L H_2SO_4. The films were prepared on PET/ITO substrates in (a) the MF perpendicular to the electric field; (b) the MF parallel to the electric field; (c) absence of the MF. Frequency scan range is from 0.1 to 105 Hz.

Tafel curves

Figure 6 shows the Tafel curves of bare NF (curve (a)) and PANI coated NF in the absence of MF (curve (b)), in addition, the MF is parallel to the electric field (curve (c)) and perpendicular to the electric field (curve (d)). The corresponding corrosion potentials (E_{corr}) are listed in TABLE 2. It shows that the E_{corr} shift to a more noble value in the MF and the most positive E_{corr} value is observed in the PANI coated NF perpendicular to the electric field. The common explanation of this phenomenon is the MHD effect driven by the Lorentz force, which forms a highly conjugate π system in the PANI molecular.

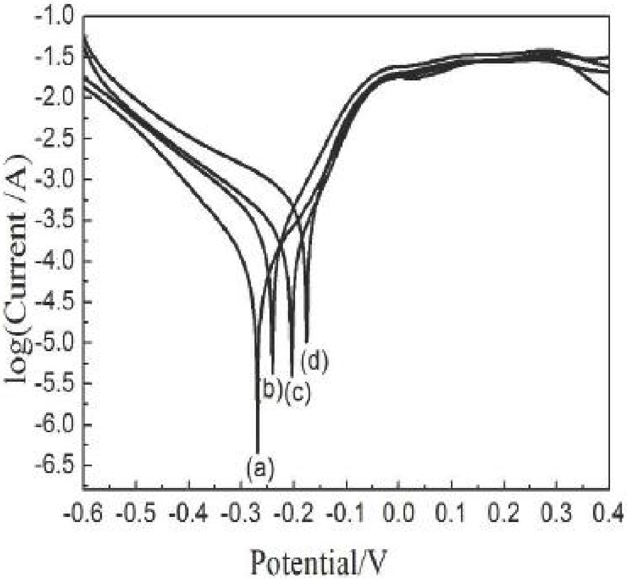

Figure 6 : Tafel plots in 0.5 mol/L H_2SO_4 solution, the PANI films were prepared on (a) bare nickel flakes electrode; (b) absence of the MF; (c) the MF parallel to the electric field; (d) the MF perpendicular to the electric field.

TABLE 2 : The corrosion potentials of PANI films prepared in different conditions.

Substrate	E_{corr}/mV
Bare NF	-271.3
PANI coated NF (0T)	-241.8
PANI coated NF (the MF parallel to the electric field)	-206.5
PANI coated NF (the MF perpendicular to the electric field)	-174.1

UV–vis spectra of the PANI films

Figure 7 shows the typical UV-vis spectrum of the PANI films prepared in PET-ITO substrates, which are in the absence (curve (c)) of a constant MF and the MF perpendicular to the electric field (curve (a)) as well as parallel to the electric field (curve (b)), respectively. It can be seen from Figure 7 that all the samples have four absorption bands. The characteristic peaks of the PANI films appear at about 361 nm due to π-π* transition of the benzenoid ring; at about 436 nm and 805 nm due to polaron-π* and π-polaron band transition[16]. It is interesting to note that the absorption peak resulted from π-polaron transition of the PANI films prepared in the presence of a MF (curve (a)) and (b) appear at a longer wavelength, compared with that of the PANI film prepared in the absence of a MF (curve (c)), which is 841 and 817 nm respectively, as shown in TABLE 3. Nevertheless, the wavelengths at about 361 nm and 436 nm resulted from π-π* and polaron-π* transitions remain unchanged, which suggests that the effects of orientation by MF lead to a regular growth of the PANI films, inducing the enhancement of conjugated effect and interaction of PANI chains[17]. The decreasing band gap energy makes this transition easier.

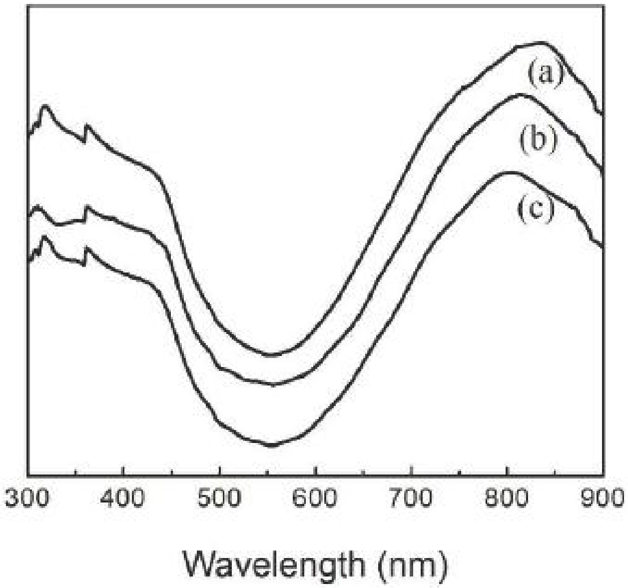

Figure 7 : Shows the UV–vis spectrum of the PANI films prepared on PET/ITO substrates; (a) the MF perpendicular to the electric field; (b) the MF parallel to the electric field; (c) absence of a MF.

TABLE 3 : The wavelength of absorption peak due to π-polaron of the PANI films

Condition	Shift of wavelengths of absorption peak due to π-polaron /nm
PANI film prepared in absence of the MF	805
PANI film in the MF parallel to the electric field	817
PANI film in the MF perpendicular to the electric field	841

CONCLUSIONS

The electrochemical properties of the PANI films prepared in the absence and presence of a constant MF have been researched by CV, EIS, Tafel curves and UV-vis spectra. Some interesting results have been obtained: (i) The CV diagram of the PANI films indicates that the peak currents of the PANI films prepared in the presence of a constant MF has a higher redox peak current value and better stability. The anodic peak current of the PANI films prepared in the MF perpendicular to the electric field is the highest (46.99 mA). (ii) The EIS of the PANI films prepared in the presence of a constant MF shows smaller charge transfer resistance, which are 241.5 Ω and 258.6 Ω, compared with the PANI films prepared in the absence of a constant MF. (iii) The Tafel curves show that the corrosion potential shifts to a more noble value in the presence of a constant MF, the most positive E_{corr} value is -174.1 mV in the MF perpendicular to the electric field. (iv) The UV-vis spectra indicate that the peak of π-polaron transition appears at a longer wavelength, that is, 817 nm and 841 nm in the presence of a constant MF.

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