

Comparison of the Growth Process and Electrochemical Properties of Polyaniline Films Prepared by Pulse Potentiostatic and Potentiostatic Method on Titanium Electrode

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Received 28 June 2006; accepted 2 October 2006

DOI 10.1002/app.25770

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polyaniline (PANI) films were deposited on titanium (Ti) electrode in a bath containing 0.3 mol L⁻¹ aniline and 1 mol L⁻¹ HNO₃ by pulse potentiostatic method (PPM) and potentiostatic method (PM). The chronoamperograms during aniline polymerization were recorded, and the morphologies of PANI films prepared with different polymerization periods were examined under scanning electron microscope. The difference between the processes of PANI films growth was studied. The growth processes of PANI films prepared by PPM and PM are divided into two stages. For both PPM and PM, the first stage corresponds to

the formation of a compact granular PANI layer on the surface of Ti electrode. The second stage corresponds to further growth of PANI film on the surface of the compact granular PANI film. However, the PANI films prepared by PPM and PM show different morphologies in this stage. In addition, the electrochemical properties of the PANI films prepared by PPM and PM are obviously different. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 458–463, 2007

Key words: conducting polymers; growth; morphology; pulse potentiostatic method; potentiostatic method

INTRODUCTION

Owing to a great variety of applications in many fields, such as secondary batteries, electrochromic displays, photoelectrochemical devices, sensors, corrosion protections, etc., conducting polymers have received increased research interest.¹ Among the conducting polymers, polyaniline (PANI) has been extensively studied owing to its favorable processibility and relative stability.^{2–8}

PANI can be prepared either chemically or electrochemically. Electrochemical techniques such as potentiostatic method (PM),^{9,10} galvanostatic method,^{11,12} and cyclic voltammetric method^{13,14} are widely employed for electropolymerization of aniline. Modified potentiostatic and galvanostatic methods were reported by some researchers as well. Many reports showed that the morphology and electrochemical performance of PANI were greatly influenced by the electrochemical preparation method. Tsakova and Milchev^{15,16} applied pulse potentiostatic method

(PPM) to the electrodeposition of PANI films for the first time. They found that strong activation of growth of PANI prepared by PPM occurred in comparison with that prepared by PM through examining the ratio of the reduction charge obtained under pulse potentiostatic growth to that obtained under potentiostatic growth. Rajendran et al.¹⁷ have identified the growth equation of PANI, which can interrelate the peak currents of the anodic and cathodic peaks of the PANI film with the PPM preparation parameters. In our previous works,^{18,19} nanofibrous PANI has been prepared on stainless steel (SS) substrate by pulse galvanostatic method (PGM). We found that there exists a corresponding relationship between the preparation method and the electroactivity of the films. The nanofibrous PANI prepared by PGM, when compared with the granular or flake counterparts prepared by galvanostatic method, has a better electrochemical performance mainly because of its larger real surface area and better electronic and ionic conductivity. In spite of the fact that many studies have been reported on the synthesis method of PANI, there is only few on the relationship between growth process and the electrochemical properties of PANI films prepared by different methods.

The objective of the present article was to investigate the difference in the growth of PANI film prepared on titanium (Ti) by PPM and PM and to reveal why PANI films prepared by the two different methods exhibit different electrochemical properties. In

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Contract grant sponsor: The National Natural Science Foundation of China; contract grant number: 50473022.

Contract grant sponsor: Science Project of Hunan Province, China; contract grant number: 05FJ3080.

Contract grant sponsor: Postdoctoral Foundation of Hunan University.

Journal of Applied Polymer Science, Vol. 104, 458–463 (2007)
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this work, we attempted to use scanning electron microscope to study the growth process of PANI films deposited by PPM and PM. And the electrochemical properties of the PANI films prepared by the two methods were also investigated.

EXPERIMENTAL

Aniline was distilled under reduced pressure. Other chemicals used were of analytical grade. All solutions were prepared using double distilled water. All experiments were carried out in a three-compartment electrochemical cell, which contains a platinum wire as counter electrode, a saturated calomel electrode (SCE) as reference electrode, and a titanium disk (1.0 cm^2) electrode as working electrode. The electrolyte used to deposit PANI films was an aqueous solution of 0.3 mol L^{-1} aniline and 1 mol L^{-1} HNO_3 . All potentials were related to that of SCE. Prior to use, the working electrode was polished mechanically with successively finer emery paper (grain size, $5\sim 0.5 \mu\text{m}$) to a smooth finish and then washed with distilled water and etched in diluted HNO_3 .

The pulse procedure used for the electrosynthesis of PANI film is illustrated in Figure 1. The electrosynthesis parameters were as follows: upper potential limit $E_a = 1.0 \text{ V}$, lower potential limit $E_c = 0 \text{ V}$, anodic pulse duration $t_a = 0.8 \text{ s}$, and cathodic pulse duration $t_c = 0.1 \text{ s}$. During the potentiostatic method, the deposition of PANI was carried out at 1.0 V .

After electrosynthesis by PPM or PM, the PANI-film-coated electrode was transferred into another electrochemical cell and was cycled between -0.2 and 0.8 V in a monomer-free background electrolyte. The cyclic voltammogram (CV) was recorded after obtaining a stable CV pattern with minimal changes in peak potential and peak current values. The electrochemical impedance spectroscopy (EIS) was carried out

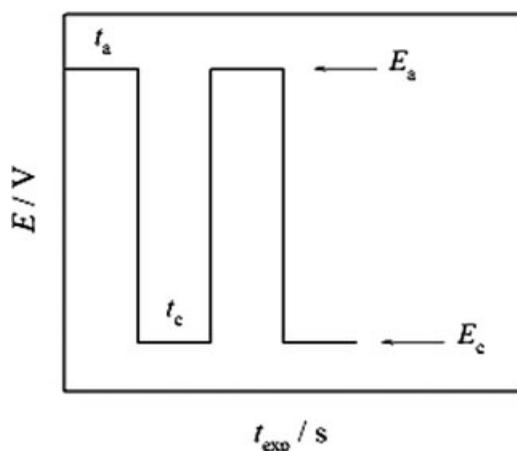


Figure 1 Schematic representation of pulse potentiostatic method.

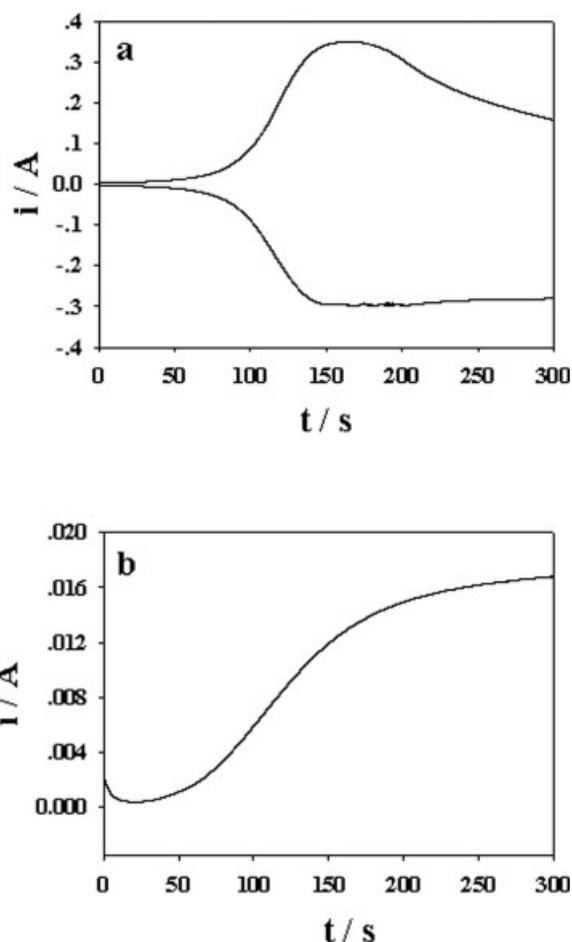


Figure 2 Typical chronoamperograms of aniline polymerization by PPM (a) ($t_{\text{exp}} = 300 \text{ s}$, $t_a = 0.8 \text{ s}$, $t_c = 0.1 \text{ s}$, $E_a = 1.0 \text{ V}$, $E_c = 0 \text{ V}$) and by PM (b) ($E = 1.0 \text{ V}$, $t_{\text{exp}} = 300 \text{ s}$).

with frequencies varying from 10 kHz to 50 mHz and initial potential of 0.1 V .

All electrochemical experiments were performed by a CHI660B electrochemical workstation (Shanghai Chenhua Instrument Factory, China). The morphologies of the PANI films were examined under a JSM-5600LV scanning electron microscope (SEM, JEOL Co., Japan).

RESULTS AND DISCUSSION

The growth of PANI films

Figure 2(a) shows the typical chronoamperogram obtained during the aniline polymerization by PPM. Since the current of PPM is transient current within a period, the y -axis of the chronoamperogram of PPM is composed of the peak current values within each anodic or cathodic duration. It can be seen that the anodic current increases slowly with the increase in the polymerization time (t_{exp}) at the beginning of the polymerization ($t_{\text{exp}} < 80 \text{ s}$). When $t_{\text{exp}} > 80 \text{ s}$, the anodic current increases rapidly and reaches a maximum at 160 s and then decreases slightly with further

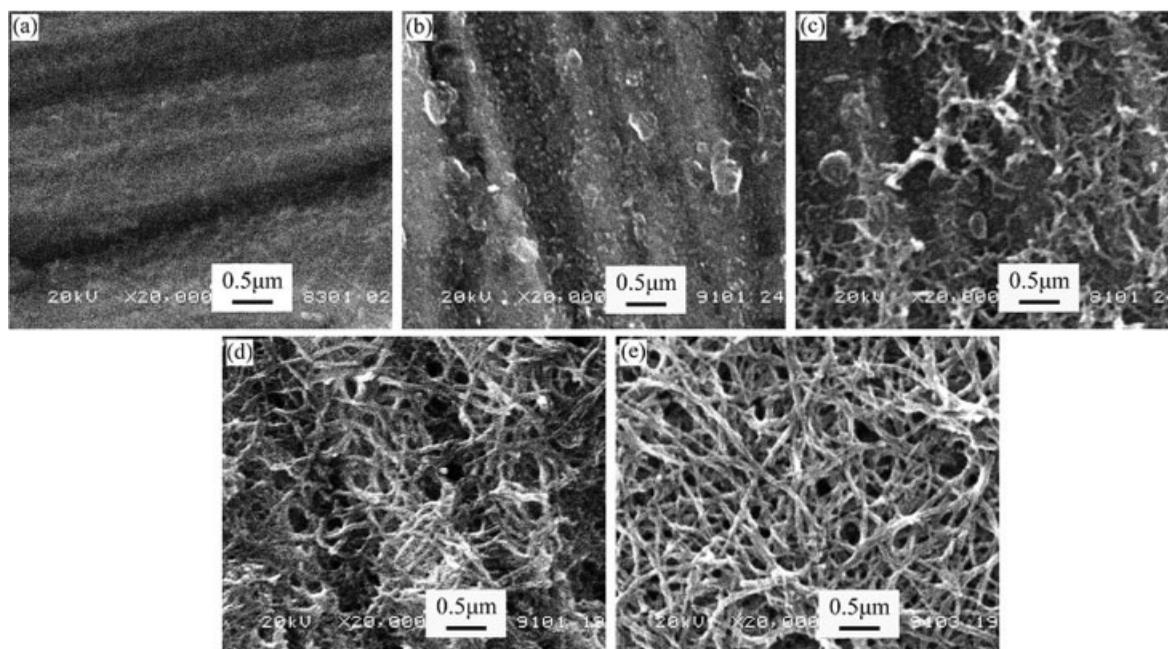


Figure 3 SEM images of the PANI films prepared by PPM with different polymerization time: (a) 40 s; (b) 80 s; (c) 120 s; (d) 160 s; (e) 210 s.

prolonging t_{exp} . Relationship between the cathodic current (corresponding to PANI reduction) and t_{exp} is similar to that between the anodic current and t_{exp} . The typical chronoamperogram of PM is shown in Figure 2(b). It can be observed that the current increases slightly with the increase in t_{exp} at the beginning of the polymerization ($t_{\text{exp}} < 80$ s). And the anodic current increases rapidly during 80–160 s, then it increases slowly when $t_{\text{exp}} > 160$ s.

Comparing Figure 2(a,b), the chronoamperogram of PPM [Fig. 2(a)] consists of two different curves. One is the anodic-current-time curve and the other is the cathodic-current-time curve. But for PM, there is only an anodic-current-time curve. This is due to the difference in schematic diagram of PPM and PM. A constant potential is applied in PM, new layer of PANI film forms continuously, and it is kept in the oxidized state. But for PPM, two potential levels can be controlled to pass the working electrode. When the potential is kept at 1.0 V, the oxidation of aniline to PANI occurs. When the potential changes from 1.0 to 0 V, the polymerization of aniline pauses and the PANI films, which have been formed, reach the reduction state. Thus the reduction current takes place. Moreover, the anodic current of PPM is about 10 times higher than that of PM. The reason may be as follows: For PPM, when the potential changes from 1.0 to 0 V, the cathodic current is caused by the reduction of the formed PANI films. The anodic current can be divided into two parts when the potential changes from 0 to 1.0 V. One is for the polymerization of aniline, and the other is for the oxidation of the

reduced PANI films. Therefore, the anodic current of PPM is much larger than that of PM.

On the basis of the aforementioned discussion, the growth process of PANI prepared by PPM is composed of not only the polymerization of aniline but also the redox process of the PANI films that have been formed during each cycle. However, the growth process of PANI prepared by PM only consists of the polymerization of aniline. Thus, the growth of PANI films prepared by the two methods is obviously different.

As a powerful surface physical technique, SEM is used to provide morphological information of PANI films prepared with different t_{exp} , from which we can know the growth process of PANI films. Figure 3 shows SEM images of the PANI films prepared by PPM with different t_{exp} . As can be seen in Figure 3(a) ($t_{\text{exp}} = 40$ s), Ti electrode is covered by a thin and compact granular PANI film. Because the PANI film is thin, the nicks in the Ti substrate can be observed clearly. From Figure 3(b) ($t_{\text{exp}} = 80$ s), many irregular PANI islands are found to be formed on the surface of the compact PANI film. With the polymerization process going on, the PANI islands begin to branch and form the rudiment of nanofibrous PANI with diameter of about 100 nm [see Fig. 3(c), $t_{\text{exp}} = 120$ s]. When $t_{\text{exp}} = 160$ s, the Ti electrode is covered by a thin layer of nanofibrous PANI and the nicks in the Ti substrate can still be observed [see Fig. 3(d)]. When t_{exp} is further prolonged, the Ti electrode is covered completely by a thick nanofibrous PANI and the nicks in the Ti substrate disappear [see Fig. 3(e), $t_{\text{exp}} = 210$ s].

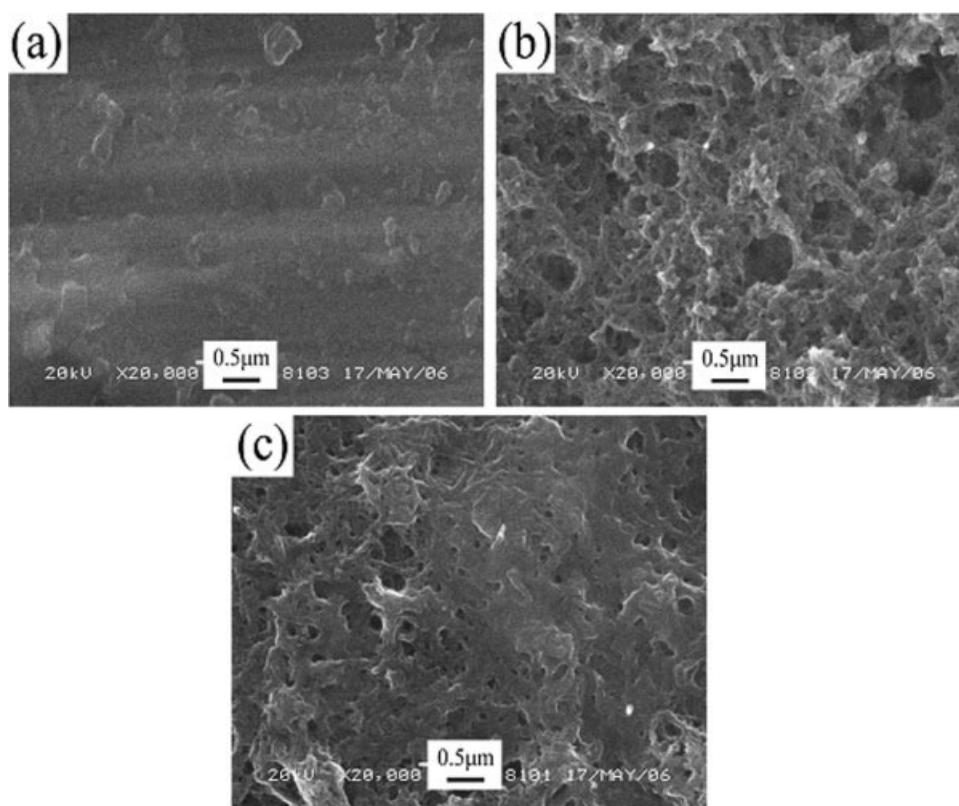


Figure 4 SEM images of the PANI films prepared by PM with different polymerization time: (a) 40 s; (b) 120 s; (c) 210 s.

The fiber has a diameter of 70–100 nm and a length of about 10 μm and the nanofibrous microstructure of PANI films does not change when t_{exp} increases.

SEM images of the PANI films prepared by PM with different t_{exp} are shown in Figure 4. From Figure 4(a) ($t_{\text{exp}} = 40$ s), it can be seen that Ti electrode is covered by a thin and compact granular PANI film. It is very similar to Figure 3(a). From Figure 4(b) ($t_{\text{exp}} = 120$ s), it can be seen that the PANI film exhibits porosity morphology. It is also visible in other researcher's result.²⁰ When the t_{exp} is prolonged further, the porosity of PANI films decreases, and a flake microstructure appears, which can be seen in Figure 4(c).

Comparing the morphologies of PANI shown in Figures 3 and 4, it can be known that the growth processes of PANI films prepared by PPM and PM are divided into two stages. For both PPM and PM, the first stage corresponds to the formation of a compact granular PANI layer on the surface of Ti electrode. The second stage corresponds to further growth of PANI film on the surface of the compact granular PANI film. However, the PANI films prepared by PPM and PM show different morphologies in this stage. For PPM, in the second stage, a nanofibrous PANI layer is formed on the surface of the compact granular PANI layer. For PM, in the second stage, porous PANI film appears and, with further polymerization, the porosity of this film decreases; then a flake layer of PANI

film comes into being. Several possible explanations are considered to understand the difference in growth of PANI deposited by PM and PPM. (i) During PM polymerization, PANI grows continuously. But for PPM, the oxidation of aniline to PANI occurs only in the period of t_{on} and does not occur in t_{off} period. Thus, PANI grows discontinuously during PPM polymerization. (ii) Since the polymerization is uninterrupted, it is possible for the formation of flake microstructure under potentiostatic conditions. On the other hand, this possibility is less under pulse potentiostatic conditions because of interruption of polymerization between consecutive cycles.

The electrochemical properties of PANI films prepared by PPM and PM

Figure 5(a) shows the CV curves measured in 1 mol L^{-1} HNO_3 of PANI films prepared with different t_{exp} by PPM. Three typical oxidation–reduction peaks of PANI can be seen in potential range of -0.2 to 0.8 V. It is clear that the anodic peak current increases with the increase in t_{exp} . This may be due to the increase in the mass of PANI films. And the anodic peak potential is nearly invariant. These results show that the gaps between PANI nanofibers are big enough, allowing the ions transfer freely inside the PANI films, and the transfer resistance of the ions inside the films does

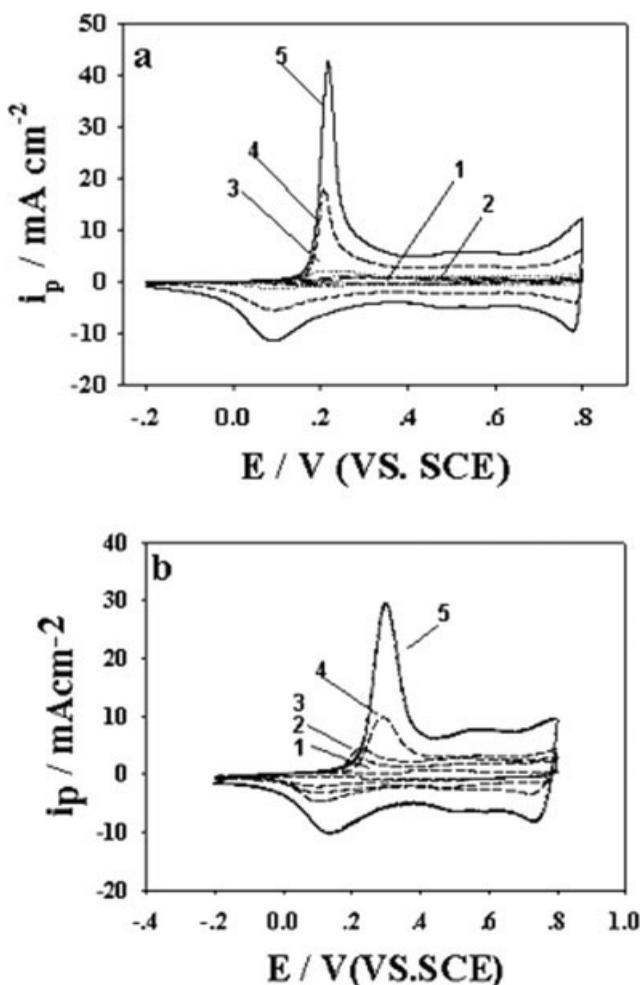


Figure 5 Cyclic voltammograms of PANI films prepared by PPM (a) and PM (b) with different polymerization time. (1) 40 s; (2) 80 s; (3) 120 s; (4) 160 s; (5) 210 s.

not increase when the thickness of PANI films increases. Subsequently, the anodic peak potential is nearly invariant with the increase in t_{exp} . The CV curves of PANI films prepared with different t_{exp} by PM are shown in Figure 5(b). It can be noted that the anodic peak current increases with the prolonging of t_{exp} . Interestingly, the anodic peak potential shifts slowly to the positive direction with the prolonging of t_{exp} . The reason may be suggested as follows: For PM, with the increase in the thickness of PANI films, the porosity decreases and the resistance of ions transfer in the PANI films becomes larger and larger. So the reversibility of the doping–undoping process descends, which results in the positive shift of the anodic peak potential with the prolonging of t_{exp} . Figure 6 shows the dependence of the first anodic peak current density (i_p) of CV curve in 1 mol L⁻¹ HNO₃ of the PANI films prepared by PPM and PM on the scan rate ($v^{1/2}$). A good linear relationship between $v^{1/2}$ and i_p is observed. This suggests that the oxidation of PANI films may be controlled by the diffusion

process.²¹ The peak current density and its increasing rate with $v^{1/2}$ of the PANI films prepared by PPM are higher than those of the PANI films prepared by PM. It also can be considered that the diffusion resistance of the PANI films prepared by PM is larger than that of the PANI films prepared by PPM.

More electrochemical information of the PANI films prepared by PPM and PM was obtained by EIS research. Figure 7(a) shows the impedance spectra of the PANI films in 1 mol L⁻¹ HNO₃ solution (curve 1, PANI films prepared by PPM; curve 2, PANI films prepared by PM). It can be seen that both of the impedance spectra display similar characteristics, a depressed semicircle in the high frequency region and a straight line in the low frequency region, which are typical impedance spectra of polymer film.^{22,23} As reported earlier, the presence of depressed semicircle in the high frequency region is ascribed to the blocking property of electrode, which extremely inhibits the faradic process of the ionic exchange at the polymer/electrolyte interface, while the straight line in the low-frequency region is due to the capacitive characteristics of conducting polymer film.²⁴ Comparing the impedance spectra curve 1 and curve 2, it is found that the diameter of the semicircle in curve 1 declines greatly. The charge transfer resistance (R_{ct}) reduces from 5.3 Ω (PANI film prepared by PM) to 3.2 Ω (PANI film prepared by PPM). This means that the nanofibrous microstructure of PANI films may lead to a faster charge transfer at PANI film/solution interface, compared with the porosity microstructure of PANI films. Additionally, a polarization system was constructed by two same PANI electrodes and CV research was carried out. The CVs in the potential range of 0.20–0.85 V of the PANI films prepared by PPM and PM are shown in Figure 7(b). The CV

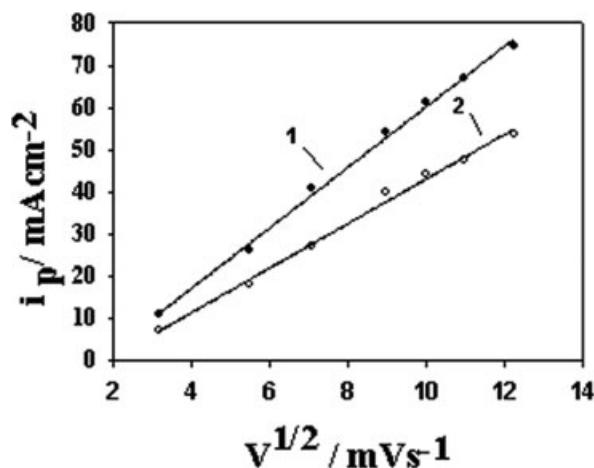


Figure 6 Dependence of the first anodic peak current density of CV curve in 1 mol L⁻¹ HNO₃ of the PANI films prepared by PPM and PM ($t_{\text{exp}} = 210$ s) on the scan rate (curve 1, PANI films prepared by PPM; curve 2, PANI films prepared by PM).

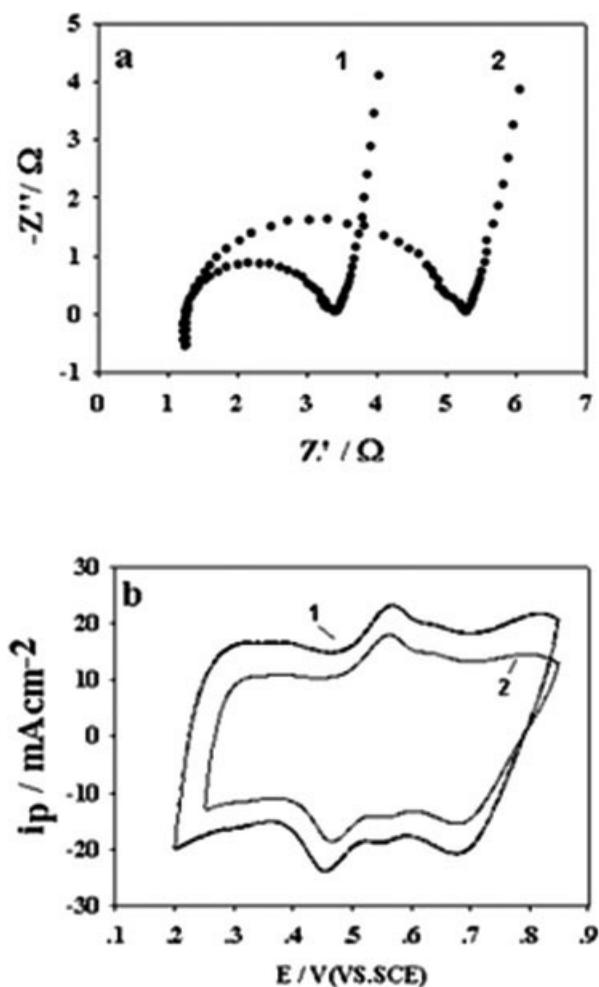


Figure 7 Electrochemical impedance spectroscopy of the PANI films (a) and cyclic voltammograms of two same PANI electrodes (b) prepared by PPM and PM (curve 1, PANI films prepared by PPM; curve 2, PANI films prepared by PM).

curves are nearly rectangular in shape, which presents that the PANI films have good capacitance property. However, the currents of both the anodic and cathodic half-cycles on the PANI films prepared by PPM are larger than those on the PANI films prepared by PM. This indicates that the capacitance of the PANI films prepared by PPM is larger than that of the PANI films prepared by PM.

CONCLUSIONS

PANI was deposited on Ti electrode by PPM and PM. The two chronoamperograms during aniline polymerization were recorded, and the morphologies of PANI films prepared by the two different methods with different polymerization time were examined under scanning electron microscope. The difference between the growth processes of PANI films was studied. For PPM, two different stages of PANI growth were observed: the first corresponds to the

formation of a compact granular PANI layer and the second corresponds to the growth of a nanofibrous PANI layer. And the nanofibrous microstructure of PANI films does not change when t_{exp} increases. For PM also, the PANI growth process consists of two stages. The first one is the same as the first growth stage of PANI prepared by PPM, which is the formation of the compact granular PANI layer. Then porous PANI films appear in the second stage and, with further polymerization, the porosity of these films decreases; then a flake layer of PANI film comes into being. Moreover, CV and electrochemical impedance spectra were used to study the electrochemical properties of PANI films prepared by PPM and PM. The results show that there exists a corresponding relationship between the preparation method of the films and the electroactivity of the films. The charge transfer rate in fibrous PANI prepared by PPM is significantly higher than that in granular one prepared by PM.

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