

# Electropolymerization of aniline in aqueous solutions at pH 2 to 12

XIAO-XIA LIU\*, LING ZHANG, YA-BING LI, LI-JUN BIAN, ZE SU, LI-JUN ZHANG

Department of Chemistry, Northeastern University, Shenyang 110004, People's Republic of China

E-mail: [xxliu@mail.neu.edu.cn](mailto:xxliu@mail.neu.edu.cn)

Electroactive polyaniline (PANI) films were made in aqueous solutions at pH 2 to 12 by means of potential cycling. The protonation degree of oligoanilines and PANI was low in solutions of high pH, resulting in high polymerization efficiency. Fewer PANI hydrolysis products were formed when electropolymerization of aniline was conducted in neutral or slightly basic solutions, providing a synthetic route for PANI with little degradation. FT-IR spectra of PANI made in solutions of different pH displayed main vibrational bands of the polymer, including the characteristic peak of protonated states of PANI. SEM images of films made in neutral or basic solutions showed three-dimensional distributions, which were very different from those made in slightly acidic solutions.

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## 1. Introduction

As a famous conducting polymer, polyaniline (PANI) has been studied extensively concerning its synthesis [1], electroactivity [2] and a great variety of applications in many fields, such as energy storage system, electrochromism, electrocatalysis and etc. [3–7]. Conducting PANI is usually synthesized in acidic solutions and electropolymerization of aniline in neutral or basic aqueous media is very limited [8–12]. We are very interested in the influence of pH value of the solution on electropolymerization of aniline as the reaction media is one of the key factors for the incorporation of some functional materials into conducting polymers, such as enzymes, inorganic particles, and etc. [13, 14]. In this paper, electropolymerization of aniline is performed in aqueous media of different pH from 2 to 12. The PANI films obtained are studied by cyclic voltammetry, FT-IR and SEM investigation.

## 2. Experimental

All chemicals used were of analytical grade and aniline was distilled before use. Solutions were prepared from distilled water. The pH value of the solutions was adjusted by HNO<sub>3</sub> or KOH.

Electrochemical experiments were performed on Princeton Applied Research Model 273A potentiostat/galvanostat. Electropolymerization of aniline was conducted on carbon fibre electrode at ambient temperature. Potentials were measured and reported versus SCE. Prior to electropolymerization, the carbon fibre electrode was cleaned by acetone and distilled

water. Electropolymerization was conducted in solutions of 0.1 mol·l<sup>-1</sup> aniline of different pH containing 0.1 mol·l<sup>-1</sup> KNO<sub>3</sub> as the supporting electrolyte, through 35 successive cyclic voltammetric scans in the potential range from -0.3 to 0.9 V at 50 mV·s<sup>-1</sup>. Electroactivity of PANI was studied in 0.5 mol·l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> by cyclic voltammetry. FT-IR studies were carried out on Perkin-Elmer Spectrum One FT-IR spectrophotometer with KBr pellets. The morphology of PANI films was inspected on SHIMADZU SSX-550 scanning electron microscope.

## 3. Results and discussion

### 3.1. Electropolymerization of aniline

Cyclic voltammograms of electropolymerization of aniline in 0.1 mol·l<sup>-1</sup> aniline solutions of pH < 1 (0.1 mol·l<sup>-1</sup> KNO<sub>3</sub> as the supporting electrolyte) on carbon fibre are very similar to those reported in acidic aqueous solutions [1]. However, when electropolymerization is performed in solutions of pH > 1, the three characteristic redox couples of PANI become ambiguous. Figs 1 and 2 are cyclic voltammograms of electropolymerization of aniline in aqueous solution of pH<sub>synth</sub> = 2.0 and 11.0, respectively. On the second scan, an oxidative peak begins to appear at 0.44 and 0.32 V, respectively in Figs 1 and 2. These peaks should correspond to the oxidation of the dimer of aniline, *p*-aminodiphenylamine (ADPA) produced from the first potential cyclic scan [8]. The comparatively negative peak in the solution of pH<sub>synth</sub> = 11.0 is associated with the low protonation degree of ADPA. This is in accordance with the

\*Author to whom all correspondence should be addressed.

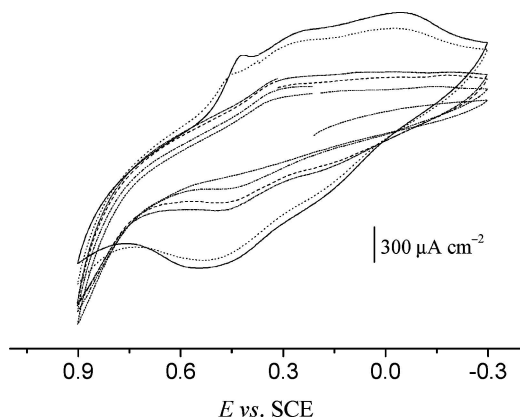


Figure 1 Cyclic voltammograms of PANI film growth from  $0.1 \text{ mol}\cdot\text{l}^{-1}$  aniline solution of  $\text{pH}_{\text{synth}} = 2.0$  (scan rate:  $50 \text{ mV}\cdot\text{s}^{-1}$ ). Dash line: first cycle; dash dot dot line: second cycle; short dash line: fourth cycle; short dash dot line: fifth cycle; dot line: 20th cycle; solid line: 35th cycle.

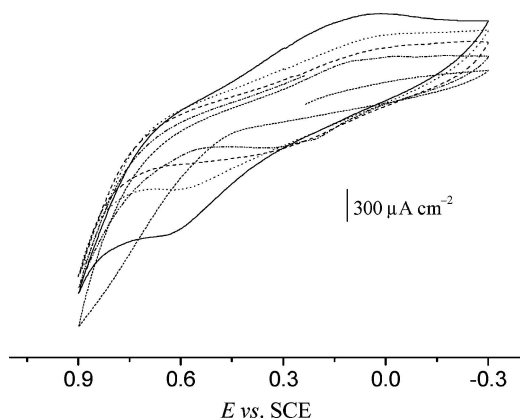


Figure 2 Cyclic voltammograms of PANI film growth from  $0.1 \text{ mol}\cdot\text{l}^{-1}$  aniline solution of  $\text{pH}_{\text{synth}} = 11.0$  (scan rate:  $50 \text{ mV}\cdot\text{s}^{-1}$ ). Dash line: first cycle; dash dot dot line: second cycle; short dash dot line: fifth cycle; dot line: 20th cycle; solid line: 35th cycle.

theoretical calculation result based on Hueckel method by N. Gospodinova, that the oxidation of ADPA and other oligoanilines are easier for the non-protonated ones compared with the protonated ones [15]. The conductivity of the polymer is comparatively low in solutions of high pH, so the potential on the polymer/solution interface is not high enough to oxidize aniline in these reaction media. Therefore the growth of PANI is likely to take place by way of sequential incorporation of aniline ring to the oxidized ADPA and oligoanilines [16]. As potential scan continues, this oxidation peak gradually positively shifts to around 0.6 V on the 35th scan for the polymer chain growth in solutions of  $\text{pH}_{\text{synth}} = 5\text{--}12$ . This implies that PANI may be protonated to the similar degree as electrodeposited in these solutions.

### 3.2. Electroactivity of PANI

After electropolymerization, the electrochemical responds of the PANI films are studied in  $0.5 \text{ mol}\cdot\text{l}^{-1}$   $\text{H}_2\text{SO}_4$  through cyclic voltammetry in the potential range from  $-0.3$  to  $0.6$  V at a scan rate of  $50 \text{ mV}\cdot\text{s}^{-1}$ . The cyclic voltammograms of PANI made in solutions of  $\text{pH}_{\text{synth}} = 2.0$  and  $11.0$  are in Fig. 3. Similar to cyclic voltammograms of PANI made in acidic aqueous solu-

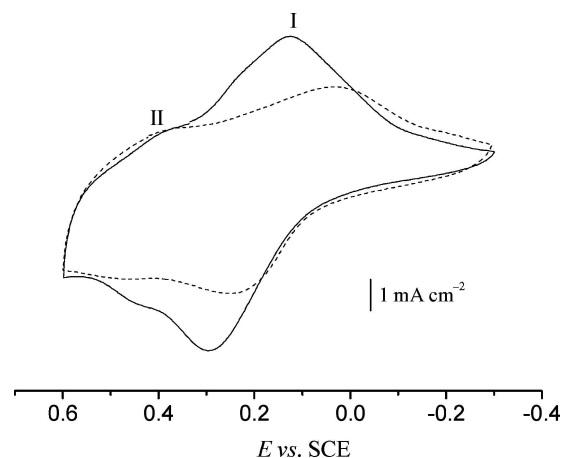


Figure 3 Cyclic voltammograms in  $0.5 \text{ mol}\cdot\text{l}^{-1}$   $\text{H}_2\text{SO}_4$  of PANI films made in solutions of different pH (scan rate:  $50 \text{ mV}\cdot\text{s}^{-1}$ ). Dot line: PANI made in the solution of  $\text{pH}_{\text{synth}} = 2.0$ ; solid line: PANI made in the solution of  $\text{pH}_{\text{synth}} = 11.0$ .

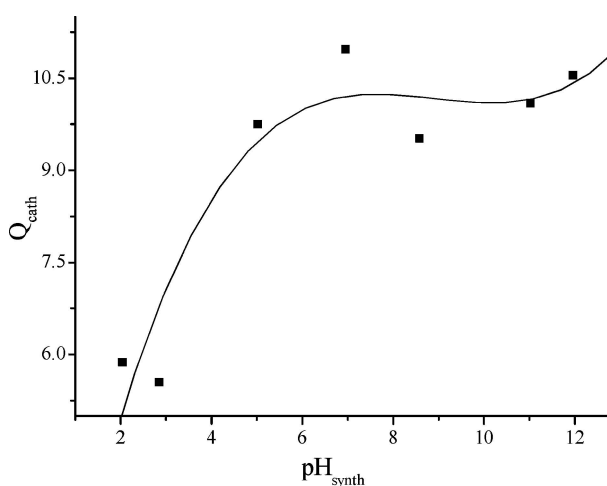


Figure 4 Amount of charge necessary to switch from emeraldine to leucoemeraldine ( $Q_{\text{cath}}$ ) in  $0.5 \text{ mol}\cdot\text{l}^{-1}$   $\text{H}_2\text{SO}_4$  for PANI films made in solutions of different pH.

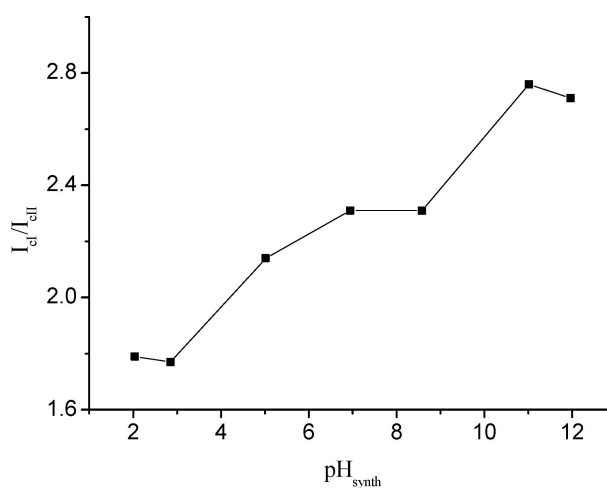


Figure 5 Ratio of the cathodic current of redox couple I to that of II for PANI films made in solutions of different pH.

tions [17], both of the curves display two pairs of redox peak in this potential range. The first redox couple (I) corresponds to the switch of PANI between emeraldine and leucoemeraldine states [2]. While the second one (II) is associated with the hydrolysis products formed during electropolymerization [17, 18]. The potential of redox couple I differs slightly for PANI made in

TABLE I Characteristic frequencies of PANI films.

		Wavenumber $\text{cm}^{-1}$		
Prepared at $\text{pH}_{\text{synth}} 2.0$	Prepared at $\text{pH}_{\text{synth}} 11.0$	Prepared at $\text{pH}_{\text{synth}} 2.0$ then cyclic voltammetried in $0.5 \text{ mol}\cdot\text{l}^{-1} \text{ H}_2\text{SO}_4$	Prepared at $\text{pH}_{\text{synth}} 11.0$ then cyclic voltammetried in $0.5 \text{ mol}\cdot\text{l}^{-1} \text{ H}_2\text{SO}_4$	Band characteristics
1570.1	1635.2	1630.9	1635.1	Nitrogen quinone rings
1481.4	1577.4	1572.0	1572.5	Nitrogen benzoid rings
	1487.7	1473.9	1479.0	Ring C=C vibration typical in <i>para</i> -disubstitued benzens
1384.4	1384.5			$\text{NO}_3^-$ doped in PANI
1307.0	1306.0	1290.0	1301.2	Aromatic C–N stretching indicating secondary aromatic amine group
1239.3	1245.8	1231.6		Characteristic bands of protonated states
1131.5	1127.0	1175.5	1225.3	
		1066.8	1058.8	$\text{SO}_4^{2-}$ doped in PANI

solutions of different pH. This couple appears around 0.17 V for the films made in solutions of  $\text{pH}_{\text{synth}} = 2.0$  and 2.8, while it appears around 0.21 V for the films made in neutral and slightly basic solutions. It was reported that the voltammetric characteristics of this couple were influenced by many factors, including electropolymerization potential, solution composition, and etc. [17, 18]. The current of redox couple I is larger for the films made in basic or neutral solutions than those made in acidic solutions in our experiments. Fig. 4 is the amount of charge  $Q_{\text{cath}}$  necessary to switch from emeraldine state of PANI to leucoemeraldine (calculated by integrating the cathodic part of redox couple I on the voltammograms of PANI in  $0.5 \text{ mol}\cdot\text{l}^{-1} \text{ H}_2\text{SO}_4$ ) for the films made in different solutions. It is obvious

that the efficiency of aniline polymerization is higher in solutions of high pH.

The ratio of the current of redox couple I to that of II is different for the films made in different solutions. Fig. 5 displays the ratio of the cathodic current of redox couple I to that of II. This ratio is higher for the films made in basic or neutral solutions than those made in slightly acidic solutions, indicating that there are less hydrolysis products formed when electropolymerization of aniline are conducted at high pH. Usually accompanying the polymer chain growth in acidic aqueous solutions, polyaniline degradation process occurs. It was reported that the hydrolysis products thus formed were the results of water attack on the polymer in the presence of  $\text{H}^+$  [17, 18]. This process is obstructed

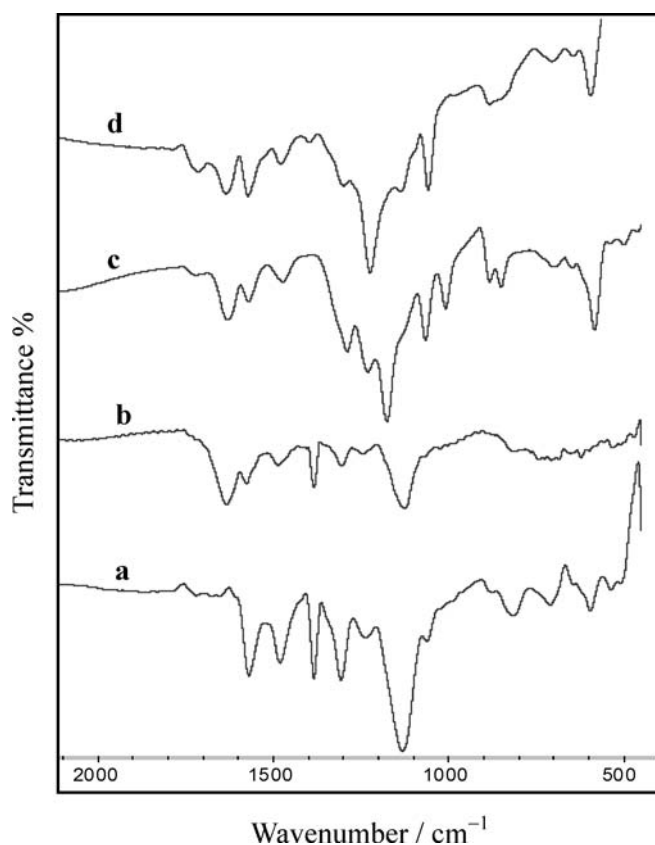


Figure 6 FT-IR spectra of PANI. (a) film made in the solution of  $\text{pH}_{\text{synth}} = 2.0$ ; (b) film made in the solution of  $\text{pH}_{\text{synth}} = 11.0$ ; (c) film cyclic voltammetried in  $\text{H}_2\text{SO}_4$  after being deposited in solution of  $\text{pH}_{\text{synth}} = 2.0$ ; (d) film cyclic voltammetried in  $\text{H}_2\text{SO}_4$  after being deposited in solution of  $\text{pH}_{\text{synth}} = 11.0$ .

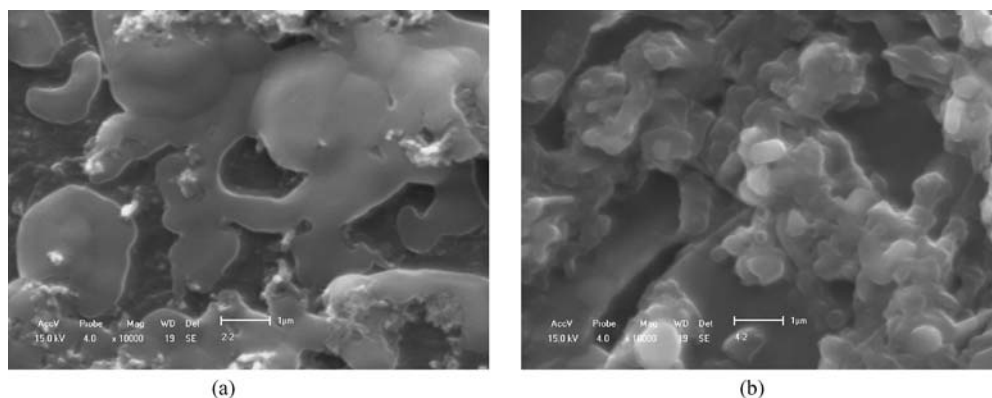


Figure 7 SEM images of PANI film ( $10^4$  times). (a) Made in the solution of  $\text{pH}_{\text{synth}} = 2.0$ ; (b) made in the solution of  $\text{pH}_{\text{synth}} = 11.0$ .

when electropolymerization is conducted in solutions of high pH, in which there is little  $\text{H}^+$  in the solution. So electropolymerization of aniline at high pH provides a method to produce PANI with little degradation.

### 3.3. Characterization of PANI

FT-IR spectra of PANI prepared in solutions of  $\text{pH}_{\text{synth}} = 2.0$  and  $11.0$  containing  $\text{KNO}_3$  as supporting electrolyte are shown in Fig. 6, together with those of the corresponding polymers cyclic voltammetried in solution of  $0.5 \text{ mol}\cdot\text{l}^{-1} \text{ H}_2\text{SO}_4$ . The peak locations related to the corresponding chemical bonds are listed in Table I.

All the spectra display main vibrational bands of PANI. The band at  $1473\text{--}1487 \text{ cm}^{-1}$  is related to ring  $\text{C}=\text{C}$  vibration typical in *para*-disubstituted benzenes [8], indicating polymer chain formation. Bands at  $1570\text{--}1635$  and  $1481\text{--}1577 \text{ cm}^{-1}$  are due to nitrogen quinone and benzoid rings, respectively [19–21]. Bands at  $1290\text{--}1307$  and  $1231\text{--}1245 \text{ cm}^{-1}$  are the  $\text{C}\text{--}\text{N}$  stretch of secondary aromatic amine [19–21]. The characteristic band of protonated PANI appears at  $1127\text{--}1225 \text{ cm}^{-1}$  [19, 20]. The peak at  $1384 \text{ cm}^{-1}$  in spectra of as-deposited polymers is due to  $\text{NO}_3^-$  doped in PANI [22]. After cyclic voltammetried in  $0.5 \text{ mol}\cdot\text{l}^{-1} \text{ H}_2\text{SO}_4$ , this peak is replaced by the absorption of  $\text{SO}_4^{2-}$  at  $1058\text{--}1067 \text{ cm}^{-1}$  [22, 23].

The appearance of the characteristic band of protonated PANI in line b (the spectrum of PANI prepared at  $\text{pH}_{\text{synth}} = 11.0$ ) shows that the polymer is protonated even in the reaction media of  $\text{pH}_{\text{synth}} = 11.0$ . This may be due to proton releasing during polymerization and result in PANI chain growth in this basic media. However, the ratio of intensity of this band to that of nitrogen quinone is smaller in line b compared with the corresponding ratio in line a (the spectrum of PANI prepared at  $\text{pH}_{\text{synth}} = 2.0$ ). And this ratio becomes larger after the polymer being cyclic voltammetried in  $\text{H}_2\text{SO}_4$ .

Fig. 7 shows the SEM images of PANI made in the solution of  $\text{pH}_{\text{synth}} = 2.0$  and  $11.0$ , respectively. The surface of the PANI made at  $\text{pH}_{\text{synth}} = 2.0$  is somewhat flat, while that made at  $\text{pH}_{\text{synth}} = 11.0$  shows a three-dimensional distribution.

### 4. Conclusions

Electropolymerization of aniline in aqueous solutions of  $\text{pH} = 2$  to  $12$  was conducted by means of cyclic

voltammetry. All of the PANI films obtained showed electroactivity after transferred to  $0.5 \text{ mol}\cdot\text{l}^{-1} \text{ H}_2\text{SO}_4$  solution, providing possibility for incorporating other functional materials into PANI film through electrochemical synthesis. The ratio of the cathodic current for the switch between emeraldine and leucoemeraldine state of PANI to the cathodic current of the redox couple of the hydrolysis products was high for the films made at high pH compared with those made in acidic solutions, thus providing a synthetic route to obtain PANI with little degradation. Together with other main vibrational bands of PANI, the characteristic band of protonated PANI appears in all of the FT-IR spectra for the polymers obtained in solutions of different pH from 2 to 12, demonstrating that the polymers are protonated when electrodeposited in these solutions. This may be the reason for aniline to be electropolymerized in aqueous solutions of pH 2 to 12.

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