



Investigation on the redox mechanism of polyaniline film in acid solution by in situ rapid-scan time-resolved infrared spectroelectrochemistry



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ABSTRACT

The redox mechanism of polyaniline (PANI) film in acid solution was studied by in situ rapid-scan time-resolved infrared spectroelectrochemistry (RS-TR-FTIRS) method. In the potential rang between -0.29 and 0.91 V, there are four pairs of redox peaks. These four pairs of redox peaks were minutely investigated by cyclic voltammetry (CV) and in-situ infrared spectroelectrochemistry. The results illustrated that the first pair of redox peaks are according to oxidation of the secondary amines in the middle of molecular PANI chain, the second pair of redox peaks are according to oxidation of terminal primary amines, the third pair of redox peaks are according to oxidation of terminal hydroxyl groups, the forth pair of redox peaks are according to oxidation of the polaronic PANI to the bipolaronic PANI. The bipolaronic PANI completely turns to quinoid structure with highly conjugated by deprotonation when the electrode potential was higher than 0.71 V. Meanwhile, the hydrogen bonding between the oxidation products of PANI and water molecules disappeared.

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1. Introduction

Polyaniline has been extensively studied due to its interesting electrical and optical properties [1–10]. It is well known that polyaniline in the emeraldine (half-oxidized) oxidation state can be reversibly switched between electrically insulating and conducting forms [11]. One of the important issues in polyaniline is the charge-transport rate due to diffusion of counterions into/out of the conductive polymer film during redox processes [12]. So it is very important to study the redox mechanisms of polyaniline.

To this end, some studies using polyaniline have been previously accomplished either by classical electrochemical techniques [13] or spectroelectrochemical techniques [3,14–21]. Previous studies indicated that the electrochemical process of PANI may be a two-electron transfer mechanism. According to Gordana Ćirić-Marjanović [16] and Andrea Kellenberger's [21] research, the phenazine rings are considered as a part of the polymer chain. But data is still scarce about the redox mechanism of PANI. As a powerful tool, the infrared (IR) spectroelectrochemistry cyclic voltabsorptometry can track reactant, intermediate, and product simultane-

ously during electrochemical process [22–24]. In this paper, the reactive intermediates, the oxidation products and hydrogen bonds were detected simultaneously by in situ IR spectroelectrochemistry in the dynamic processes of polyaniline on glassy carbon electrode in acid solution for the first time. The dynamic processes of polyaniline on glassy carbon electrode in acid solution were successfully investigated.

2. Experimental

A home-made spectroelectrochemical thin layer cell was used [25,26]. The cell body was made of teflon which allow it be used with a wide variety of solvents. Electrochemical measurements were performed at a standard three-electrode electrochemical cell with electrochemistry workstation CHI 660D (ChenHua Instruments Co., Shanghai, China). A glassy carbon (3 mm in diameter) was employed as the working electrode. The electrode was polished using alumina powder of size $0.3 \mu\text{m}$ to obtain a mirror finish and then clean in an ultrasonic bath in ethanol solution and ultra pure water respectively. The Pt wire and Ag/AgCl were employed respectively as the counter and reference electrode. The Ag/AgCl potential is corrected frequently and all potential reported here vs. normal hydrogen electrode (NHE).

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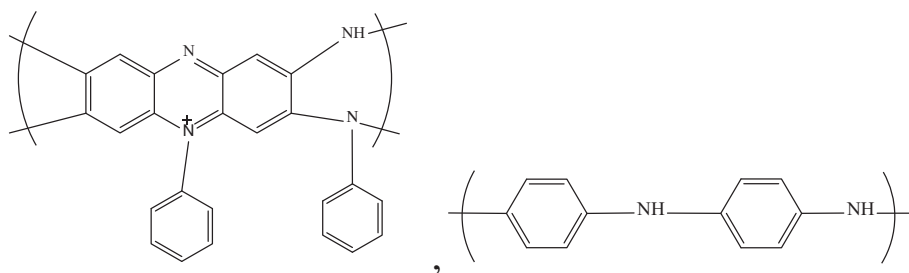
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The electrochemical in situ rapid-scan time-resolved Fourier transform infrared (FTIR) spectrometer included a Nexus 870 FTIR spectrometer (Nicolet) and a smart attenuated total reflection (Spectra-Tech, Inc.) equipped with a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen. Under the rapid-scan mode, up to 70 spectra per second can be collected at a spectral resolution of 16 cm^{-1} .

The resulting spectrum is defined as the potential difference spectrum:

$$\Delta R/R = [R_{(ES)} - R_{(ER)}]/R_{(ER)} \quad (1)$$

$R_{(ER)}$ and $R_{(ER)}$ are single-beam spectra collected at the reference potential ER and at a sample potential ES, respectively.



The chemicals used in the experiments include perchloric acid (super pure grade), aniline (analytical pure grade, Aniline was distilled under reduced pressure.) and distilled water.

The PANI films were grown electrochemically from solutions containing 1.0 M HClO_4 and 0.1 M aniline by cycling the potential from -0.29 to 0.91 V at a scan rate of 10 mV/s . The growth of the polymer film was terminated after 15 complete voltammetric cycles.

3. Results and discussion

The cyclic voltammograms recorded during the PANI films growth are shown in Fig. 1. The deposition current was enhanced in subsequent cycles when growth continues mostly on the polymer surface. The deposition charge as estimated from the

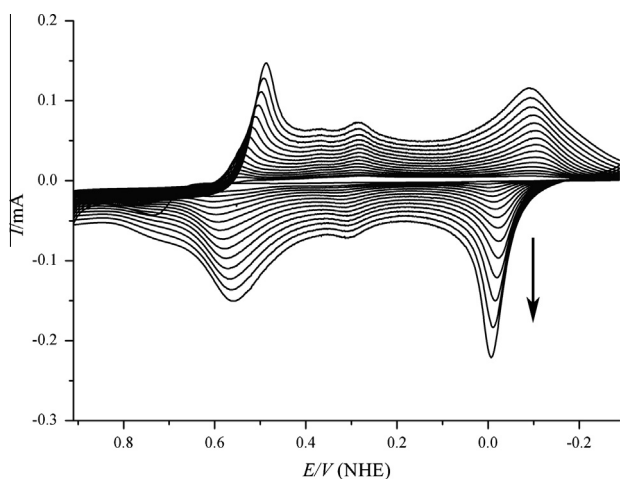


Fig. 1. The cyclic voltammograms (CVs) for the deposition of PANI in aqueous solution of 1.0 M HClO_4 and 0.1 M aniline.

cathodic charge in the voltammogram at the completion of deposition is found to increase with the number of cycles. The film thickness was estimated using the charge associated with proton doping of PANI [27]. Based on our measurements the films are estimated to be approximately $0.99\text{ }\mu\text{m}$ thick.

The PANI films were characterized by means of Fourier transform infrared (Fig. 2). The quinoid and benzoid ring vibrations appear at 1580 and 1498 cm^{-1} respectively. The presence of substituted phenazine structural units, formed by the intramolecular cyclization of branched PANI chains, has been identified by the appearance of characteristic FTIR bands at 1622 cm^{-1} [21]. The structure of PANI is generally represented by the following diagram.

The potential was scanned from -0.29 to 0.11 V and then back to -0.29 V at a scan rate of 5 mV s^{-1} . The electrochemical switching of polyaniline between oxidation states can be readily monitored by cyclic voltammetry as illustrated in Fig. 3(a). The reference spectrum was collected at -0.29 V by co-adding 40 interferograms. The three-dimensional (3D) infrared spectra plots are shown in Fig. 3(b). Fig. 3(c) displays a series of representative bands extracted from Fig. 3(b). Fig. 3(d) shows the derivative cyclic voltabsorption.

There is a pair of redox peaks when the potential was scanned from -0.29 to 0.11 V at 5 mV s^{-1} . According to literature [28], the terminal group of PANI may be hydroxyl or amino groups which are generally represented by the following diagrams.

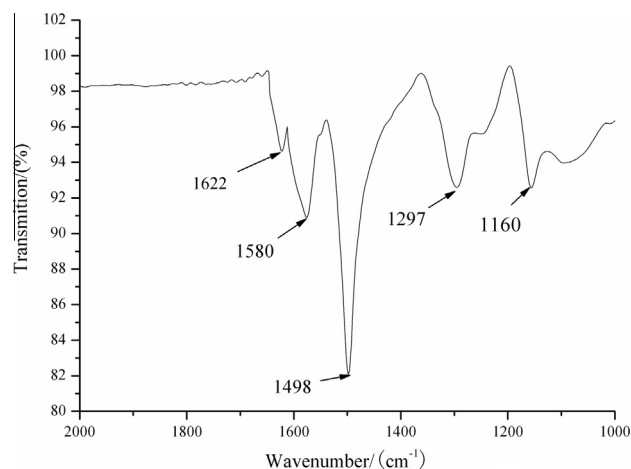


Fig. 2. FTIR spectra of PANI.

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