Electrochemical and Raman spectroscopic study of polyaniline; influence of the potential on the degradation of polyaniline

Abstract The polymerization of aniline has been studied employing in-situ electrochemical and Raman spectroscopical techniques. Aniline was polymerized by cyclic voltammetry on a Pt surface in sulfuric acid solutions of aniline. The Raman bands were assigned for degradation products of the overoxidized form of polyaniline. A discussion of the degradation mechanism is given.

Key words Polyaniline · Electropolymerization · Cyclic voltammetry · Polyaniline degradation · Raman spectroscopy

Introduction

Conducting polymers, especially polyaniline (PANI), were investigated as promising material for the development of organic semiconductors, colour displays, corrosion inhibitors, energy storage devices, rechargeable polymer batteries and opto-electronic devices.

PANI can be prepared chemically or electrochemically by oxidative polymerization. The electrooxidative polymerization method has been preferentially used for the preparation of PANI films, because the deposition of the films can easily be controlled by electrochemical techniques. The morphology of electrochemically prepared PANI depends strongly on the experimental conditions: supporting electrolyte, solvent, current density, potential, nature of electrodes, agitation, temperature etc. The growth rate of a PANI film is apparently dependent on the type of supporting electrolyte in the order: $H_2SO_4 \gg HCl \approx HNO_3 \gg HClO_4$ [1]. This effect is often referred to as “anion effects” [2]. The anion effects are also observed in the electrochemical degradation of PANI film [3]. The rate of polymer overoxidation at relatively high electrode potentials is significantly dependent upon the nature of the anions incorporated in the positively charged polymer [4]. The aniline oxidation reaction is pH dependent in solution of pH<2 in which protonated aniline species react. The oxidation is accompanied by the loss of protons. At higher pH values, non-protonated aniline species participate in the oxidation reaction, which is not pH dependent [5]. The temperature dependence of the polyaniline film voltammetric response in aqueous media has shown that the peak position of the second redox process is affected strongly by the temperature [6]. The film is more stable at low temperatures, probably because of the decrease of the rate of hydrolysis of the quinoid imine structures.

Previous electrochemical studies have shown that, of the electrochemical techniques, cyclic voltammetry (CV) is particularly useful for elucidating basic aspects of the polymer growth and the redox mechanism [7, 8].

In spite of many investigations, there has been a certain controversy regarding the degradation mechanism of PANI [9–11]. So far, few papers have been published dealing with the use of Raman spectroscopy to investigate the dependence of the PANI degradation mechanism on the applied potential [12, 13]. The lack of investigations of the degradation mechanism by Raman spectroscopy is explained by the strong absorption of Raman scattered light from overoxidized PANI. In the overoxidized form of the PANI film, degradation products, which have a weak adhesion and begin to peel off from the electrode surface, are precipitated.

In this paper we describe results of experiments of PANI redox reactions and structure, especially for higher anodic potentials (>0.26 V vs Hg/Hg$_2$SO$_4$ · 0.5 M H$_2$SO$_4$) (overoxidized PANI). In-situ measure-
ments are obviously preferable because of questions regarding the integrity of the film after removal from solution; however, very few such studies have been made [14, 15], and none of the overoxidized form and the degradation products. After many (CV) cycles we have succeeded in monitoring Raman bands of degradation products mixed with the oxidized form.

Experimental

Electrodes

The working electrode was made from a 10-mm diameter Pt disc sealed in glass and placed in the spectroelectrochemical cell with a three-electrode configuration. Before each measurement the Pt electrode was polished with different grades of diamond sprays (3, 1 and 0.5 µm). Then, the Pt electrode was cleaned in an ultrasonic bath and rinsed with ethanol. After each measurement the formed film was chemically dissolved in concentrated HNO₃. The counter electrode was a Pt coil with a large surface housed in a separate compartment of the spectroelectrochemical cell. The Hg/Hg₂SO₄ 0.5 M H₂SO₄ was used as a reference electrode. All potentials presented in this work refer to this reference electrode.

Spectroelectrochemical cell

The spectroelectrochemical cell was a quartz tube built with three compartments for electrochemical measurements and adopted for simultaneous Raman spectroscopical measurements. The position of the working electrode in a quartz tube could be moved until maximum signal intensity was achieved. The solution in the cell was purged with argon for 15 min prior to the experiments.

Solutions

Aniline (Merck p.a.) was distilled under reduced pressure and kept refrigerated under argon. Sulfuric acid (Merck p.a. 96%) was used as received. Aqueous solutions of 1.0 M H₂SO₄ and 0.1 M C₆H₅NH₂ were prepared with deionized and triply distilled water.

The electrochemical equipment consisted of a Model 362 PAR scanning potentiostat and a model 8272 Philips x-2y recorder. The Raman spectra were recorded by a Spex 1877 spectrograph with a silicon photodiode array detector (IRY 512). The measured spectral range was from 580 to 1800 cm⁻¹ with a spectral resolution of 3 cm⁻¹. The spectra were excited by the 514.5-nm line of an Ar⁺ laser with a power of 100 mW measured on the spectroelectrolytic cell. The measurements were performed in a dark room at an ambient temperature of 20 ± 1 °C.

Results

In Fig. 1 are presented typical voltammograms recorded on a Pt electrode over the potential range from −0.65 to +0.25 V.

The increasing current indicates the growth of film thickness, and a pair of well-defined redox peaks A/a gradually form. The position of redox peaks does not shift with increasing cycle number, even after 50 cycles, which confirms that these are reversible redox reactions independent of the thickness of the film. A number of authors [16–18] agree that during cyclization transitions between a fully reduced and a fully oxidized film occur (Eq. 1).

\[
\text{H}_2\text{N}:\text{H}_2\text{N} \xrightarrow{2\text{H}^-+2\text{e}^-} \text{N}=\text{N} \xrightarrow{\text{H}^+} \text{H}_2\text{N}:\text{H}_2\text{N} \quad (1)
\]

On continued polarization toward higher anodic potential, up to +0.55 V, on the voltammograms, four pairs of redox peaks are observed (Fig. 2).

The multiple redox peaks indicate the complexity of the redox processes, involving coupled electron transfer...