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Polyaniline Formed in Alkaline Solution —A New Luminous Material

Nian Bing LI*
College of Chemistry and Chemical Engineering, Southwest China Normal University, Chongqing 400715
Sheng Tao ZHANG, Pei Dao DING
College of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044

Abstract: Electropolymerization of aniline in KOH solution and properties of the polymer are studied by using *in situ* reflex ellipsometry, cyclic voltammetry and fluorescence spectroscopic method. The change patterns of ellipsometric parameters and the thickness of film in the process of electropolymerization are investigated. The complex refractive indices and the fluorescence spectra of PAN indicate that the PAN is a new kind of luminous material.

Keywords: Polyaniline, electropolymerization, alkaline solution, luminous material.

Introduction

Polyaniline (PAN) prepared in acidic aqueous media has received a great deal of interest as one of the conductive polymers due to its straightforward methods of preparation and the stability of its conductive form in air[1,2]. Its applications as energy storage media[3] and as electrochromic device[4] have been discussed. But there are few reports about the electropolymerization of aniline in alkaline solution[5].

In this paper, we report the results of an ellipsometric study of the electropolymerization of aniline in alkaline solution. The patterns of ellipsometric parameters and the thickness of film in the process of electropolymerization are investigated. Both the complex refractive indices of the PAN film obtained from ellipsometrical parameter and the fluorescence spectra of the PAN indicate that the PAN formed in alkaline solution is a sort of luminous material.

Experimental

A three-electrode system is used in electrochemical experiment. Reference electrode is saturation calomel electrode (SCE), all the potential values mentioned in this paper are referred to the SCE, counter electrode is a piece of platinum, working electrode is round plate of platinum (∅=1.0cm). Electrolytes are prepared with analytically pure reagents of aniline and KOH solution.

Cyclic voltammetrical experiment is carried on with HDV-7 potentiostat with a DCD-1 function generator, and cyclic voltammograms are recorded by X~Y recorder. A rotating analyzer ellipsometer which model is Rodulph 2000FT with wavelength

546.1nm and the angle of incidence of 70° is used to monitor *in situ* the electropolymerization of aniline. The fluorescence spectrum measurements are carried out using a F-4500 Fluorescence Spectrophotometer (Hitachi,Ltd. Japan). All measurements are conducted at room temperature (about 28 °C).

Results and Discussion

A tangerine color film is formed on Pt electrode surface after the first cyclic from solution containing 0.1mol/L aniline in 0.25mol/L KOH by sweeping the potential continuously between 0.0V and 1.3V with a scan rate of 5 mV/s. The cyclic voltammogram (**Figure 1)** shows that two oxide current peaks appear at 0.6 V and 1.15V, respectively, but the reduce current peak does not appear during the sweeping potential from 1.3V to 0.0V. The origin of two oxidation peaks observed in **Figure 1** has been stated preliminarily[5]. In the process of electropolymerization of aniline, the *in situ* reflex ellipsometrical parameters are obtained. The relationships between ellipsometrical parameters and potential during the first potential cycle are shown in **Figure 2.** There are great changes of ellipsometrical parameters in the anode process, however in the cathode process the changes of ellipsometrical parameters are small.

Figure 1. Growth CV for polyaniline during the first cycle in 0.1 mol/L aniline and 0.25 mol/L KOH with scan rate of $5 mV·s^{-1}$

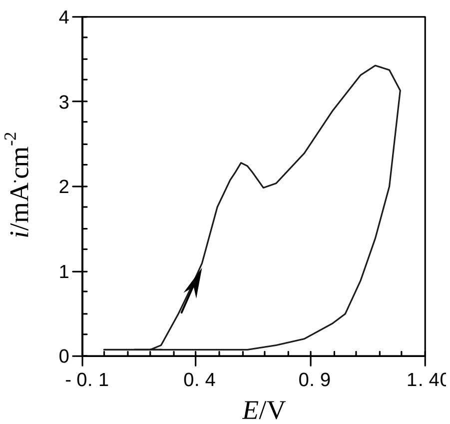
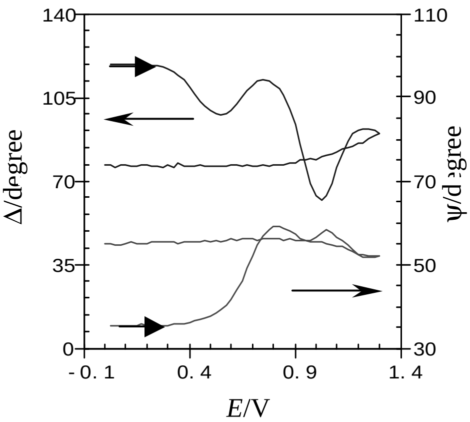


Figure 2. The relationships between ellipsometrical parameters and potential during the first potential cycle

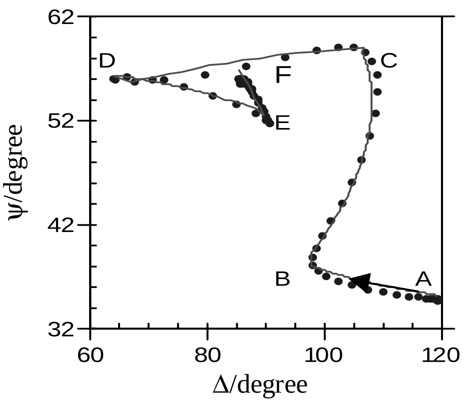


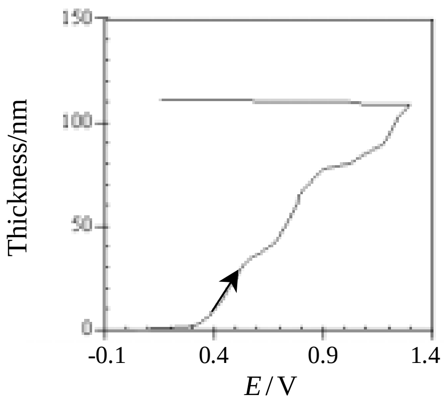
Using the *in situ* ellipsometrical parameters obtained from experiment, a comparison between experimental data (dot) and their numerical simulation (line) for PAN film with even film model is shown in **Figure 3** and then the thickness of the PAN film deposited on Pt electrode can be calculated. The relationships between the thickness of the PAN film and potential during the first potential cycle are shown in **Figure 4.** Although the growth rate of PAN film does not keep constant in different scope of potential, the polymer on the electrode is formed primarily and the thickness of film increased from 0 nm to 110 nm gradually in the anodic process of the first potential cycle.

For the cathode process of the first potential cycle, the thickness of the PAN film keeps constant on the whole.

Figure 3. Comparisons of experimental ellipsometric data (dot) and their numerical simulation (line) for PAN film

Figure 4. The relationship between the thickness of the PAN film and potential during the first potential cycle





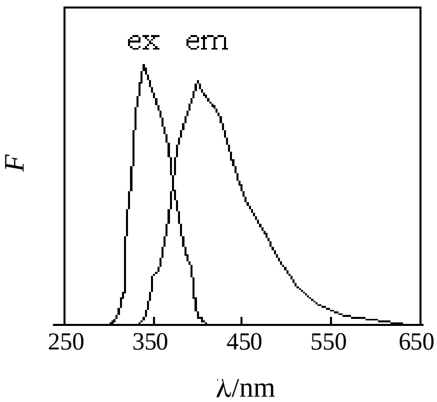
The refractive indices of the PAN film in different potential range (see **Figure 3**) are listed in **Table 1**.

Table 1 The refractive indices of the PAN film

Region	Potential range (V)	Refractive indices	
		n	*k*
A~B	0.0 ~ 0.6	1.55	-0.010i
B~C	0.6 ~ 0.9	1.18	+0.226i
C~D	0.9 ~ 1.15	0.70	-0.110i
D~E	1.15 ~1.3	1.75	+0.750i
E~F	1.3 ~ 0.0	0.75	-0.520i

The complex refractive indices of the PAN film in the potential ranges between 0.6-0.9V and 1.15-1.3V are positive at the comparison between experimental data and numerical simulation for the film with even film mode. In general, if the imaginary part of the complex refractive index is positive, the film is a sort of luminous material. A result that the polymer is a sort of luminous material can be obtained. In order to prove this conclusion, the fluorescence spectra of PAN are carried out. The PAN film deposited on Pt electrode was took out from the solution, and was washed with 0.25mol/L KOH and distilled water successively in order to remove aniline which may be absorbed on PAN film. As has been shown by many reports the PAN formed in acidic media can not be dissolved in acetone, but we found that the PAN prepared in alkaline solution could be dissolved easily. So the clean PAN film was dissolved with acetone. Using acetone as the blank, the fluorescence spectra measurements were conducted against the blank. The optimum excitation wavelength λex is 340 nm and the optimum emission spectra λem of PAN appears at 385 nm (see **Figure 5**). While the wavelength of polarized light

Figure 5. The fluorescence spectra of PAN



(546.1nm) uses as excitation wavelength, the emission spectrum of PAN appears at 570.0 nm. Usually, the fluorescence quantum coefficient of analine in solvent is low. The intensity of fluorescence of the polymer that electropolymerized in alkaline solution increase obviously, which indicate the rigidity of PAN increases evidently. Therefore the conclusion that PAN formed in containing aniline in KOH solution is a new kind of luminous material can be achieved. The detailed construction of the PAN is being studied.

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