Synthetic Metals 239 (2018) 66–70

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Effect of aniline monomer concentration on PANI electropolymerization process and its influence for applications in chemical sensors

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ARTICLE INFO

Keywords:
Conducting polymers
Thin films
Polyaniline
Aniline monomer concentration
Structure-property relationships
Sensors

ABSTRACT

Galvanostatic electrodeposited polyaniline thin films were studied and analysed, focusing on the influence of aniline concentration in the polymerization process and hence the answer of Extended-Gate Field-Effect-Transistor pH chemical sensor. A competition between the deposition efficiency and deposition rate was observed in the polymerization process according to aniline monomer concentration. This competition influences the structure-property relationship of polyaniline thin films. The polymerization occurred over fluorine doped tin oxide substrates and the polymerization solution contained aniline monomer in four concentrations from 0.10 to 0.25 M. The current density was 1.0 mA/cm^2, the deposition time was 300 s, resulting in a deposited charge of 300 mC/cm^2. The thickness of the PANI thin films presented a dual behaviour, increasing up to 121 ± 5 nm for 0.20 M (sample PANI20), and then, decreasing down to 68 ± 3 nm for 0.25 M (sample PANI25). The optical properties presented an inverse behaviour compared to the thickness, as expected, with small brightness and optical reflectance for sample PANI20, once that it is the thicker sample and absorbs more light. PANI20 presented the optimized relation between deposition rate and deposition efficiency. The sensitivity depends on chemically-sensitive film's surface quality, which is determined by the deposition efficiency.

1. Introduction

Conducting polymers are largely used in chemical sensor applications [1]. One of the most used polymers is polyaniline (PANI). PANI is an oxidized conducting polymer that is presented in various distinct oxidation states, which are defined by the ratio of amine to imine nitrogen atoms in its backbone. Upon protonic acid or electrochemical doping, PANI can be protonated, undergoing an internal redox reaction, changing its properties, such as colour and conductivity [2]. Those changes are used as the basis of chemical sensors because they occur when the material is in contact to chemical species and they are converted into electrical or optical signal.

Chemical sensors are structured with a sensing stage that is usually a thin film connected to the transducer stage that can be a potentiometric, optical or conductometric device. The potentiometric chemical sensor measures the change in the electric potential caused by chemical reactions involving the chemical species in the medium [3]. The Extended-Gate Field-Effect-Transistor (EGFET) arose from a modification in the ion-sensitive field effect transistor (ISFET) structure where the sensing membrane was separately fabricated and connected to the transistor's gate. The EGFET is an example of such kind of device, often tested for pH measurements. It consists of a chemically-sensitive film connected to a high input impedance device [4]. When operational amplifiers are used, it leads to the Instrumental Amplifier EGFET (IA-EGFET) system. Several works had been done about EGFET sensor using metal oxides and polymers as chemically-sensitive material [5–9].

The electrodeposition technique is largely used to produce PANI thin films because the resultant film has good homogeneity, strong adhesion to the substrate, and chemical stability [10]. The electrochemical deposition can be divided into three categories: i) galvanostatic method, based on a constant current; ii) potentiostatic method, based on a constant potential; and iii) using a cyclic or variable potential [11]. PANI thin films were already galvanostatic electrodeposited and characterized as published by other authors before [12,13]. However, one concept related to galvanostatic electrodeposition is important. The deposition efficiency for galvanostatic electrodeposited polymers can be estimated by comparing the measured film thickness with the calculated theoretical film thickness, related to the total deposited charge [14,15]. The calculated theoretical film thickness is given by the expression:

$$\delta = \frac{j \cdot t \cdot M_W}{F \cdot z \cdot \rho} \quad (1)$$

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https://doi.org/10.1016/j.synthmet.2018.02.008
Received 9 January 2018; Received in revised form 9 February 2018; Accepted 26 February 2018
Available online 05 March 2018
0379-6779/

where j is the current density (mA/cm^2), t is the deposition time (s), M_W is the molecular weight of the polymer (g/mol^1), F is the Faraday constant (C/mol^1), z is the number of electrons transferred in the reaction and ρ is the polymer density (g/cm^3). The ratio between calculated and measured thickness estimates the deposition efficiency.

Several works can be found in the literature where the effects of processing and fabrication conditions on the final properties of PANI have been studied. Zeng and Ko showed that PANI synthesized by oxidative polymerization of aniline in a hydrochloric acid aqueous solution using potassium dichromate as an oxidant presented increased electrical conductivity. That was attributed to the iodine molar ratio dopant because the iodine-doping reactions formed charge transfer complexes [16]. Wang et al showed that PANI fibres in the emeraldine base oxidation state had their mechanical and electrical properties varied when doped with varied amounts of secondary amine additives, because the doping changed the gelation time [17].

Other works evaluated the relation between parameters of samples preparation of widely used chemical sensors materials, such as titanium dioxide (TiO_2), and EGFET sensors, showing that it is possible to establish a structure-property relationship between films structure and EGFET response [18]. The characteristics and structures of PANI films that influence their response as chemically-sensitive structures in EGFET chemical sensor can also be studied, when they are produced by the galvanostatic electrosynthesis, by changing and controlling the deposition parameters related to the electrolyte solution polymerization, more specifically, the concentration of aniline monomer in solution. We present here how the concentration of aniline monomer in the polymerization solution influences the polymerization process and hence the answer of EGFET pH chemical sensor.

2. Material and methods

2.1. Materials

Fluorine-doped tin oxide (FTO) thin films deposited on glass substrates were obtained from Sigma-Aldrich and they were used as substrate for PANI thin films. FTO was chosen due to its well-known properties, which include time stability, sensitivity and performance as pH sensors [19]. The substrates were cleaned with de-ionized water followed by acetone using the ultra-sonication method in order to remove contaminants from the surface. Aniline ($C_6H_5NH_2$) was supplied by Vetec Brazil and hydrochloric acid (HCl) by Sigma Aldrich.

2.2. Synthesis of PANI thin films

The samples were synthesized via the galvanostatic method. The polymerization was carried out in a two electrode system in a cell at 25 °C. The electric potential as function of time was recorded with a Data Acquisition model 34970A (HP). A platinum inert electrode was used as counter electrode and FTO was used as working electrode. The polymerization solution contained aniline monomer in four distinct concentrations 0.10, 0.15, 0.20 and 0.25 M (PANI films are thus identified by PANI10, PANI15, PANI20 and PANI25, respectively), HCl (1.0 M) and de-ionized water. The current density was 1.0 mA/cm^2 and deposition time was 300 s, for a deposited charge 300 mC/cm^2.

2.3. Characterization

PANI thin films were analysed by three characteristics. The first one is the thickness. It was done using a precision profilometer (Taylor Hobson) with spatial resolution of 0.1 nm. The morphology was studied using scanning electron microscopy (SEM). A JOEL microscope JSM-6610 model operating at 20 kV was used. A thin gold coating (≈20 Å) was applied to the samples. The third characteristic is the visible reflectance spectra. It was obtained non-destructively in the 400 nm to 700 nm range using a spectrophotometer model Colour-Guide, BYK-Gardner (Columbia, USA). The data were recorded in 20 nm step with a 20 mm diameter circular aperture and a 65/10° optical geometry. The device displayed the respective International Commission on Illumination (CIE) colour values: luminance (L*), position between red and green (a*), and position between yellow and blue (b*) [20]. For a polyelectrochromic and solid material as PANI thin films, reflectance analysis is of great value.

2.4. Sensors measurements

The potentiometric IA-EGFET sensor was described somewhere else [8,9]. It is based on potentiometric chemical sensors with high input impedance due to field effect transistors (FET) devices [4]. The electric potential data were recorded during 60 s for each pH. The films were carefully washed in de-ionized water in between each measurement. The sensitivity (S) and linearity (L) were measured in the pH buffer range from 2 to 8. The sensitivity was obtained from the sensor's calibration curve (for the IA-EGFET sensor, sensitivity´s unity is mV/pH). The sensor's linearity was obtained from the coefficient of determination (R^2) of fitted calibration curves. The linearity parameter L is calculated by R^2 times 100.

3. Results and discussion

The chronopotentiometric curves of PANI thin films deposited with different aniline concentrations are shown in Fig. 1. The curves show an induction period followed by a plateau that set the deposition potential, which is almost equal for all samples. The induction period refers to the main period of the polymerization process, when the polymer starts to be formed over the substrate. There is a relation between the induction time and monomer concentration. The inset shows the variation of the induction time of the galvanostatic deposited PANI films according to the aniline concentration. The induction time was obtained from the chronopotentiometric derivative curves as the time to the derivative to be null once the induction period is the time that the voltage takes to increase and reach a near-constant value. The induction time was about 150 s for sample PANI10 and decreased down to 70 s for sample PANI25. This behaviour is in agreement with Conroy and Breslin [21]. Polymer formation time depends on the monomer concentration, and this period of time is small for low monomers concentrations. This occurs because the concentration of radical cations is low at this condition and, consequently, generates a slow rate of

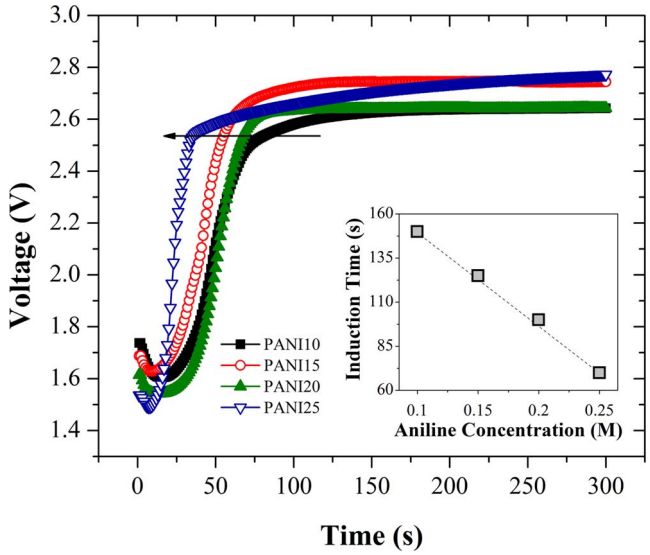

Fig. 1. Chronopotentiometric curves for galvanostatic deposited PANI thin films on FTO substrate at various aniline concentrations. The inset shows the variation of the induction time of the PANI films according to the aniline concentration.