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Original research article

Elaboration and characterization of ITO electrode modified by transition metal dispersed into polyaniline thin films

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ABSTRACT

This work presents the characteristics of composite materials thin films of polyaniline (PAni) and nickel (Ni) particles deposited onto indium tin oxide (ITO) substrate. The electropolymerization of aniline was performed in acidic medium by potentiodynamic methods. The nickel particles were electrochemically deposited on the surface of PAni/ITO by reducing metal ions (Ni^{2+}) using a potentiostatic method from a separate solution. The effect of applied potential as well as immersing time of complexation on the amount of nickel dispersed was investigated. Different characterization techniques were employed to study the electrochemical behavior and surface characteristics of the Ni-PAni/ITO thin films such as Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry, Fourier Transform Infrared Spectroscopy (FTIR), UV–vis Spectroscopy, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM).

The morphology of the obtained composites shows a uniform dispersion of nickel particles onto the polyaniline matrix and reveals that the immersing times of complexation has a significant effect on the amount of incorporated particles. The impedance spectroscopy study reveals that the conductivity of the composite film increases with the amount of nickel incorporated. UV–vis and FTIR results confirm the presence of PAni and Ni particles on the electrode surface.

1. Introduction

Polyaniline is an intrinsic organic conjugated polymer [1] and is one of the major interesting materials studied due to facility of synthesis, low monomer cost, good environmental stability and redox properties. There is a range of technological important areas from anti-corrosion coatings to rechargeable batteries and solar cells where application of such materials is advantageous [2–9].

Composite materials based on π-conjugated polymers are also currently subject to a growing number of studies. The incorporation of noble metal [10–12], non-noble metal [13,14] and metal oxide [15] particles in conducting polymer films is the current focus of research regarding their tunable properties for potential applications [16,17].

Most recently, many reports have been published about the study of various properties of composites obtained after incorporation of metallic particles within the matrix of conducting polymers like polyaniline and polypyrrole [18–21]. This incorporation can be

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accomplished by method of reduction of metal salts at the interface of conducting polymer. These new and promising materials exhibit many interesting properties for catalysis [22,23], electrocatalysis [24], memory devices [25], sensors [26], corrosion protection [27] and active layers of energy storing devices [28].

Expensive materials limit its practical applications. For this reason, a transition metal such as nickel was chosen, due to its cost-effectiveness compared to noble metals, it can reduce the cost of products in practical applications.

In the present study, Polyaniline films were electro synthesized in acidic medium by potentiodynamic electropolymerization on ITO surfaces. To improve the electronic conductivity of the polyaniline, nickel particles were deposited electrochemically by steeping the film in a nickel solution for 30 min to put Ni^{2+} ions on the surface of PAni. Then the reduction of $Ni2^{+}$ ions can be carried out using a supporting salt (electrolyte is free of nickel ions) under different applied potentials. The effect of the immersion time was also studied. The amount of deposited metal thus can be estimated from the amount of filler used in the electroplating process.

2. Experimental procedures

2.1. Chemicals and solutions

Analytical reagent grade aniline ($C_6H_5NH_2$), sulfuric acid (H_2SO_4), nickel sulfate ($NiSO_4$), sodium sulfate (Na_2SO_4) and lithium perchlorate ($LiClO_4$, Fluka) were purchased from Sigma-Aldrich. All aqueous solutions were prepared by using distillate water.

ITO with surface area of 1×1 cm^2 was used as substrates for the elaboration of our modified electrodes. Before the electrodeposition, the ITO working electrode was sonicated in acetone, ethanol then in water for 15 min, successively. After the cleaning procedure, the working electrode is immediately transferred to the electrochemical cell containing a solution of 0.1 M aniline dissolved in 0.5 M sulfuric acid and lithium perchlorate ($LiClO_4$) as the supporting salt. Finally, the obtained PAni films was cleaned in distilled water and dried in air. The electrodeposition of nickel onto PAni/ITO films was conducted in an aqueous solution containing 0.1 M $NiSO_4$ and 0.1 M Na_2SO_4.

2.2. Preparation and characterization of the films

Voltalab PGZ 301 Potentiostat controlled by a computer was used for electrochemical measurements at room temperature without stirring. Saturated calomel electrode and platinum wire were used as reference and counter electrode, respectively. ITO, PAni/ITO and Ni–PAni/ITO were the working electrodes in current study with exposure area of 1 cm^2. After the deposition of polymer on ITO, the modified electrode was immersed in an aqueous solution of metal salt $NiSO_4/Na_2SO_4$ 10^{-1} M for 30 min. The electrode was subsequently thoroughly washed with distillate water several times to remove excess metal ion not associated with the polymer and then immersed in a 10^{-1} M aqueous Na_2SO_4 solution under different potentials to electro-precipitate the metal in the polymer film. The effect of immersing time was investigated to increase the amount of metal incorporated in the polymer. Then, the anodic nickel metal dissolution was studied by CV in clean Na_2SO_4 electrolyte.

The electrochemical impedance spectroscopy measurements were carried out under alternating voltage of 10 mV, in frequency range between 100 kHz and 10 mHz. The cell used during the impedance measurement was a traditional cell containing Na_2SO_4 10^{1-} M solution without the monomer. PAni and Ni-PAni composites were characterized by UV–vis absorption spectroscopy using Shimadzu UV–vis (NIR) spectrophotometers. Scanning Electron Micrographs were obtained by Neoscope Microscope. Fourier Transform Infra-Red (FTIR) analysis was performed by mixing the sample with KBr powder to realize a pellet by using a pellet hydraulic press.

3. Results and discussion

3.1. Electrochemical behavior of ITO

The preliminary step of this study was to identify the electrochemical behavior and the field stability with sulfuric acid as supporting electrolyte by cyclic voltammetry with a scan rate of 20 mV/s.

Before we proceed to PAni electropolymerization, it is necessary to study the electrochemical behavior of ITO substrate in the supporting electrolyte. Fig. 1 shows cyclic voltammogram recorded on ITO immersed in 0.5 M H_2SO_4 solution. The scan rate was 20 mV/s. As can be seen from Fig. 1, no obvious reduction or oxidation peak current was observed in the potential range from -1.2 to 1.2 V. Reduction peak observed at -1 V corresponds to the hydrogen evolution reaction. This result validates that the ITO substrate is electrochemically stable in the experimental conditions.

3.2. Potentiodynamic deposition of PAni

In general, Electropolymerization of PAni is achieved in acid solutions [29]. Fig. 2 shows a successive record of voltammogram (Aniline 10^{-1} M dissolved in a H_2O/ (0.1 M $LiClO_4$ + 0.5 M H_2SO_4) solution, carried out over a potential range of between -0.2 and $+0.9$ V / SCE, at the potential sweep rate v = 10 mV/s. Cyclic voltammetry was chosen to obtain a PAni film with better electrochemical characteristics.

Fig. 2(a) shows the experimental voltammetry curve obtained during the first cycle. In the positive scan, the current density increases at 0.85 V due to the monomer oxidation [30]. The current loop in the negative scan is due to the initial stage of the