



Elaboration and characterization of polyaniline films electrodeposited on tin oxides

C.C. Buron, B. Lakard*, A.F. Monnin, V. Moutarlier, S. Lakard

Institut UTINAM, UMR CNRS 6123, University of Franche-Comté, 16 route de Gray, 25030 Besançon Cedex, France

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ABSTRACT

This paper presents the electrochemical synthesis of polyaniline films on fluorine tin oxide (FTO) and indium tin oxide (ITO) in acidic medium by both potentiodynamic and potentiostatic methods. The use of potentiodynamic deposition showed that conductive polyaniline films were synthesized by the same process than on noble metals and allowed the determination of the electrodeposition potential used for further potentiostatic electrodepositions. The electropolymerization was then performed by chronoamperometry and appeared easier on ITO than on FTO. The electrodeposited polyaniline films were extensively characterized in terms of chemical nature, electrochemical growth, thickness, roughness and morphology. The chemical nature of the films was identified through infrared spectroscopy and X-ray diffraction analyses. The roughness and the morphology of the polymer coatings, determined by profilometry, scanning electron microscopy and atomic force microscopy, were correlated to the calculated thickness of each polyaniline film and to the nature of the substrate.

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1. Introduction

Conducting polymers have been studied extensively during the last two decades because of their possible applications as sensors [1–3], corrosion inhibitors [4,5], electrochromic devices [6,7], organic light emitting diodes [8], organic solar cells [9] and so forth. Among the conducting polymers, polyaniline (PANI) has been widely studied in the last decades due to its simple synthesis, stability in ambient environment, unique electrochemical properties and possibility of deposition on various substrates like platinum or carbon [10]. In particular, the emeraldine form of polyaniline, has gained interest among the scientific community for its easy synthesis, high stability, and interesting combination of redox [11] and proton doping [12,13] properties. PANI films can be synthesized by chemical oxidative reaction of aniline [14,15], by electropolymerization of aniline [12,13,15] or by electroless autocatalytic oxidation of aniline [15–18].

However, if the electrochemical synthesis of polyaniline on platinum substrates has been widely studied, this is not the case of the electrodeposition on metal oxides such as fluorine tin oxide (FTO) or indium tin oxide (ITO) despite the fact that these latter materials could be interesting substrates. Indeed, indium tin oxide is a conductive material that can be used as substrate for the deposition of PANI films. However, very few works are reported in the liter-

ature that used PANI-coated ITO. In these works, PANI films were deposited using three different ways. A first way used was the electrochemical deposition of PANI on ITO, mainly for electrochromic applications [19]. A second method to modify ITO substrates by PANI films consisted in the chemical oxidation of PANI films for incorporation in sensors dedicated to mercury detection [20]. A third method used to modify ITO substrates by PANI films was the electrophoretic deposition of PANI films used as sensitive layers for cholesterol biosensing [21]. Fluorine tin oxide (FTO) is another interesting substrate since the FTO is more stable than the ITO in acidic conditions and since the FTO is of excellent transparency. At the moment, electrodeposited PANI-coated FTO has only been used to elaborate a hydrogen peroxide sensor [22], to study the fluorescence emission of PANI films [23] and to develop counter electrode for dye-sensitized solar cell [24].

Since we would like to develop applications in biology, such as enzymatic biosensors or biological cell culture substrates, using both the properties of polyaniline (conductivity, amino groups useful for sensing or adhesion of enzymes and biological cells) and the properties of tin oxides (electrical conductivity, optical transparency allowing to follow easily the immobilization of enzymes or the adhesion and growth of biological cells on the substrates), it was necessary to perform the electropolymerization of PANI on tin oxides to determine the surface properties of the electrodeposited PANI films.

Consequently, the first aim of this work was to perform the electrodeposition of polyaniline on FTO and ITO in acidic medium by both potentiodynamic and potentiostatic methods. Then, after

* Corresponding author. Tel.: +33 3 81 66 20 46.

E-mail address: boris.lakard@univ-fcomte.fr (B. Lakard).

examination of the nature of the polymer films using InfraRed Reflection Absorption Spectroscopy (IRRAS) and X-ray diffraction (XRD), the polyaniline films were characterized using electrochemistry, profilometry, scanning electron microscopy (SEM) and atomic force microscopy (AFM). These techniques allowed us to access the surface features (thickness and roughness) and morphologies of the films, but also to evaluate the influence of the substrate on these parameters. PANI films of different thickness were also studied to determine the influence of the thickness on the film features and to follow the nucleation and growth mechanism of PANI on the tin oxides.

2. Experimental

2.1. Electrochemistry

Analytical grade aniline was freshly distilled under reduced pressure and stored in dark at low temperature (4 °C). Double deionized water (Milli-Q, resistivity 18 M Ω cm) and analytical grade hydrochloric acid were used to prepare the electrolyte solutions. Aniline was used at the concentration of 0.4 mol L⁻¹ in an aqueous solution of 1.2 mol L⁻¹ HCl. The substrates used for polymer deposition were either FTO substrates (from Balzers, $R = 120 \Omega$, thickness = 2 mm) or ITO substrates (from Solems, $R = 40 \Omega$, thickness = 110 nm) deposited on Si (100) wafers. The substrate's area coated by PANI films was 1.2 cm \times 1.5 cm for FTO substrates, and 1.0 cm \times 0.7 cm for ITO substrates.

The electrochemical experiments were carried out with a Voltalab potentiostat/galvanostat PGZ301 (Radiometer, France) coupled to a computer running the VoltaMaster software. All electrochemical measurements were performed using a single-compartment cell with three electrodes, at room temperature. The electrodes used were either a FTO or a ITO substrate as the working electrode, a Saturated Calomel Electrode (SCE) as the reference electrode (Metrohm), and a platinum wire (Metrohm) as the auxiliary electrode. The electropolymerization of polyaniline was performed either by cyclic voltammetry, with a sweep rate of 100 mV s⁻¹ between -0.2 and +1.2 V/SCE, or by chronoamperometry by applying an electrodeposition potential of +900 mV/SCE.

2.2. Surface characterization

Polyaniline samples were characterized by InfraRed Reflection Absorption Spectroscopy (IRRAS) and X-ray diffraction (XRD). Polymer samples were first investigated in reflection geometry under a grazing-incidence angle of 71° using a Vertex 70 FT-IR spectrometer equipped with a DTGS detector. Then, the structure of the polyaniline films was investigated by X-ray diffraction (XRD). XRD analyses were performed using a D8 Advance Bruker system with Cu K α radiation ($\lambda = 0.154$ nm) at 40 kV and 40 mA. The angular 2θ range was 15–30° in steps of 0.01° and the scan speed was 0.1 s/degree. The d-spacings were deduced from the Bragg equation: $\lambda = 2$ (d-spacing) $\sin \theta$, where λ is the wavelength of the X-ray, 2θ is the X-ray scattering angle and d-spacing is the inter-planar spacing.

The roughness of the polymer films was determined by stylus-based mechanical probe profiler (Alpha-Step IQ, KLA Tencor). Both average roughness (R_a) and peak to peak roughness (R_q) were estimated on a scan length of 1000 μ m at a scan speed of 20 μ m s⁻¹.

Polymer surface morphology examinations were performed using a high-resolution scanning electron microscope. Once synthesized and dried, polymer samples were examined in a LEO microscope (Scanning Electron Microscopy LEO stereoscan 440, manufactured by Zeiss–Leica, Köln, Germany) with an electron beam energy of 15 keV.

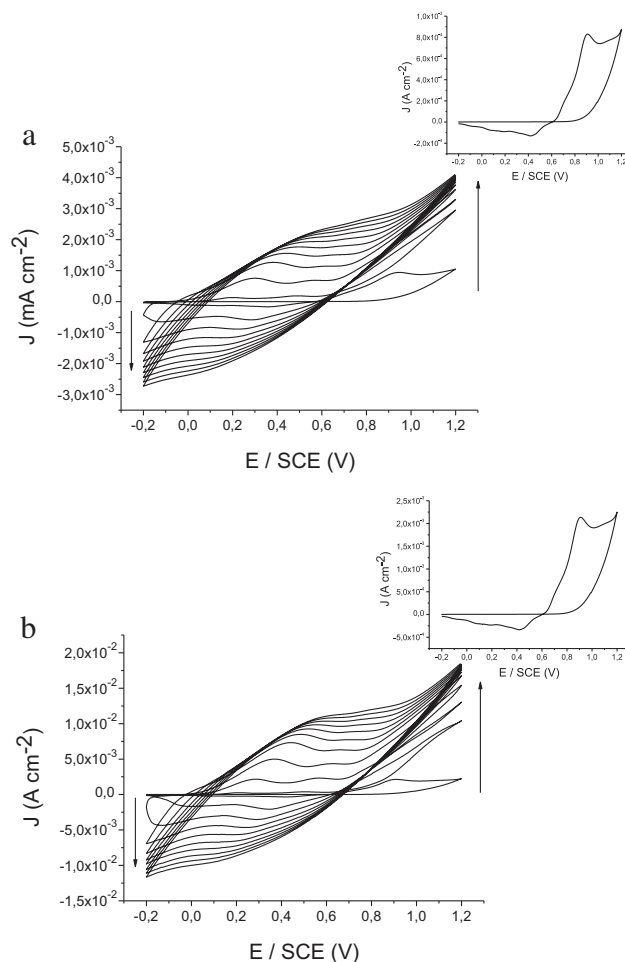


Fig. 1. Cyclic voltammogram at 100 mV s⁻¹ on a FTO (a) or ITO (b) electrode in 1.2 mol L⁻¹ HCl solution containing 0.4 mol L⁻¹ aniline.

The imaging of the surface topographies was performed, with a commercial atomic force microscope (AFM PicoSPM from Molecular Imaging, USA), in contact mode with aluminium coated silicon tip. The Si rectangular AFM cantilever was 450 μ m-long and its stiffness was about 0.27 N m⁻¹. The experiments were done at the air and at room temperature.

3. Results and discussion

3.1. Electrochemical polymerization of polyaniline on tin oxides

3.1.1. Potentiodynamic deposition

PANI films were grown on a FTO surface by sweeping the potential between -0.2 and +1.2 V/SCE at a scan rate of 100 mV s⁻¹ in a solution containing 0.4 mol L⁻¹ aniline and 1.2 mol L⁻¹ HCl. Fig. 1a shows the cyclic voltammogram (CV) obtained during the potentiodynamic electropolymerization of PANI. The first scan (inset of Fig. 1a) exhibited an anodic peak corresponding to the oxidation of the aniline monomers at +0.9 V/SCE that initiated the electropolymerization of PANI. The following scans showed the peaks corresponding to the oxidation and reduction of the polyaniline films (Fig. 1a). A very similar cyclic voltammogram was obtained on an ITO substrate (Fig. 1b). Indeed, the same anodic and cathodic peaks were observed at similar potentials. Only, the value of the current density, J , was really different since the measured current density was four times more important during the electropolymerization of PANI on ITO than during the deposition on FTO

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