



# Glow discharge optical emission spectroscopy: a complementary technique to analyze thin electrodeposited polyaniline films

V. Moutarlier <sup>a</sup>, S. Lakard <sup>a,\*</sup>, T. Patois <sup>b</sup>, B. Lakard <sup>a</sup>

<sup>a</sup> Institut UTINAM, CNRS-UMR 6213, Université de Franche-Comté, 16 route de Gray, 25030 Besançon, France

<sup>b</sup> Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Croix du Sud, 1/4, 1348 Louvain-la-Neuve, Belgium

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## ABSTRACT

Glow Discharge Optical Emission Spectroscopy (GDOES) has been developed to perform depth profiles of thick metallic films, in tens of microns range. GDOES spectroscopy can also be used to analyze thin organic polymer films since this technique has a great potential thanks to its high depth resolution, multi-element capability, sensitivity, and adaptability to solids or films and to conducting or non-conducting samples. In particular thin electrodeposited conducting polymer films remain an unexplored field of investigation for GDOES technique. However GDOES was used in this work to analyze electrodeposited polyaniline films, in addition to other techniques such as profilometry, electron microscopy and X-ray diffraction (XRD). More precisely polyaniline thin films were electrodeposited from HCl solutions and the presence of an anilinium chloride excess at the top surface of the polymer film was demonstrated using GDOES and XRD. Rinsing of these films with water led to the removal of this excess and to the partial dedoping of the polymer film due to the porous structure of polymer films. Polyaniline thin films were also electrodeposited from H<sub>2</sub>SO<sub>4</sub> solutions and an anilinium hydrogen sulfate was similarly observed at the top surface of the polymer. This excess was removed by rinsing, contrary to hydrogen sulfate anions incorporated into the polymer film during the electrochemical polymerization that were not completely expelled from the polyaniline films as proved using GDOES.

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## 1. Introduction

Since the first works of Walter Grimm at the end of the 1960s [1], glow discharge coupled to optical emission spectrometry (GDOES) has become a well-established technique for direct analysis of solid samples [2,3] thanks to its unique combination of high erosion rates and erosion depths, sensitivity, analysis of both conducting and non-conducting layers, possible quantification even for light elements such as C, N or O, and rapid depth profile analysis of coatings with high depth resolution [4,5]. Due to these main advantages, in particular its high depth resolution, rapidity of analysis and less expensive cost, GDOES is now become a very good complement to more traditional “near-surface” analytical techniques such as Secondary Ion Mass Spectrometry, Auger Electron Spectroscopy and X-ray Photo-electron Spectroscopy. Glow Discharges can also be coupled with Mass Spectrometry (GD-MS) to serve as sources for direct elemental analysis thus allowing to determine most of the elements of the periodic table and to reach low limit of detection [6]. The coupling of Glow Discharges to Time-of-Flight Mass Spectrometry also offers great potential in the field of ultrathin films, in particular because all ions of the pulse are extracted into a Glow Discharge Time-of-Flight Mass Spectrometry at the same instant leading to enhanced measurement precision.

Beginning with applications in the steel [7] and automotive [8] industry like surface contamination [9], galvanic coatings [10], passivation and oxidation treatments [11], or films deposited by physical vapor deposition [12], GDOES technique is now applied to other applications like analysis of photovoltaic layers [13,14], antibacterial coatings [15] or determination of trace elements [16]. Improvements in source and instrument design over the last years have led to the demonstration of the analytical potential of GDOES for the characterization of (ultra) thin films [17–21] including polymer thin films [22].

Despite the improvements of GDOES technique and despite the numerous application fields in which electrochemically deposited polymers (such as polyaniline, polypyrrole or polythiophene) are frequently used, there is currently no example of exhaustive study of electrodeposited polymers using GDOES. In fact, the rare works already published and combining GDOES and electrodeposited polymers concern: i) a study of the repartition of molybdate ions in a polypyrrole film electrodeposited under ultrasound irradiation [23], ii) the study of the corrosion protection properties of anodic alumina films, containing polyaniline and inorganic nanoparticles, electrochemically synthesized on an AA2024T3 aluminium alloy [24,25]. However there is a real interest in using GDOES for depth profiling of electrodeposited polymer films in particular to obtain information about the repartition of counter-anions in the polymer films since the presence and repartition of anions in the polymer matrix strongly impact on the morphology [26,27] and conductivity [28–30] of the polymer films. The information

\* Corresponding author. Tel.: +33 3 81 66 62 95; fax: +33 3 81 66 62 88.  
E-mail address: [sophie.lakard@univ-fcomte.fr](mailto:sophie.lakard@univ-fcomte.fr) (S. Lakard).

concerning the incorporation of counter-ions in polymer films is generally obtained using X-ray Photoelectron Spectroscopy (XPS) [31–33]. Unfortunately no depth profiling of electrodeposited polymer films was obtained over more than several tens of nanometers using XPS due to the limits of this technique.

That is why the present study aims at determining depth profiles of electrodeposited polyaniline films using GDOES. The electrolytic acidic solutions were composed of aniline and HCl or aniline and H<sub>2</sub>SO<sub>4</sub> in order to establish the influence of the counter-anion nature on the depth profile. For each electrolytic solution, polyaniline films of different thickness were prepared to determine if the incorporation of chlorine and sulfur elements depends on the thickness. The influence of the rinsing of the polymer film was also studied. In addition to GDOES experiments, profilometry was used to measure the thickness and roughness of each polyaniline film, SEM pictures allowed to observe their morphological features and X-ray diffraction analyses were performed to determine if the polymer samples are crystalline or not. All these experiments were used to discuss and interpret GDOES depth profiles so as to improve our understanding of anions incorporation into electrodeposited polymer films.

## 2. Experimental details

Analytical grade aniline, from Sigma-Aldrich, was freshly distilled under reduced pressure and stored in dark at low temperature (4 °C). Analytical grade hydrochloric acid and sulfuric acid, as well as double deionized water (Milli-QT, Millipore, resistivity 18 MΩ cm), were used to prepare the electrolyte solutions. Aniline was used at the concentration of 0.4 mol L<sup>-1</sup> in an aqueous solution containing either 1.2 mol L<sup>-1</sup> HCl or 1.0 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>.

Potentiodynamic and potentiostatic electrodeposition of polyaniline (PANI) films were performed using a PGZ 301 potentiostat (Tacussel-Radiometer Analytical SA, France) controlled by a computer via VoltMaster 4 Software interface. A three-electrode electrochemical cell was used in all cases. The working electrode was either a platinum electrode (0.785 mm<sup>2</sup>) or a Fluorine doped Tin Oxide (FTO) electrode (from Solems, R = 80 Ω/square). The FTO area coated by PANI films was 1.5 cm × 1.7 cm. The reference electrode was a Saturated Calomel Electrode (SCE), XR100 model from Radiometer analytical, and the counter-electrode was a platinum sheet. All electrochemical experiments were carried out at room temperature (293 K).

Thickness and roughness of each electrodeposited polymer film were estimated by profilometric measurements using a stylus-based mechanical probe profiler (Alpha-Step IQ, KLA Tencor). Both average roughness ( $R_a$ ) and quadratic average roughness ( $R_q$ ) were estimated on a scan length of 2000 μm at a scan speed of 50 μm s<sup>-1</sup>. For each polyaniline film, 9 measurements were done at different positions of the polymer coating. The average thickness value was calculated using these 9 measurements. The uncertainty was calculated using the following expression: uncertainty = (highest value – lowest value) / 2.

The morphology of each polyaniline film was studied by using a high resolution SEM (Quanta 450 W, FEI) with electron beam energy of 10 keV. Polyaniline films were also characterized by X-Ray Diffraction (XRD) on a D8 Advance Bruker, with Cu K<sub>α</sub> radiation. The diffraction data were collected with a 0.01° step-width over a 2 theta range from 10° to 40°.

Finally the most original characterization technique used in this work to study electrodeposited polymer films was Glow Discharge Optical Emission Spectroscopy (Model JobinYvon HORIBA GD Profiler). Characterizations were realized on polymer films before and after rinsing in distilled water. GDOES technique combines sputtering and atomic emission and was used to provide qualitative depth profiles. During operation, plasma is generated in analysis chamber by the applied voltage between the anode and the cathode (the sample) in presence of argon under low pressure. Ionized Ar atoms cause sputtering of sample area. Sputtered atoms excited in plasma rapidly

de-excite by emitting photons with characteristic wavelengths. GDOES measurements were carried out using a 4 mm diameter anode. Operating parameters were optimized: flush time (time to obtain pure argon atmosphere inside analysis chamber), pressure and power. For extreme surface analysis, the flush time should be longer than for bulk analysis to minimize pollution in the analysis chamber. Here a flush time of 60 s was applied. A moderate power (10 W) and a low pressure (400 Pa) were applied to improve depth resolution. The wavelengths of the spectral lines used were 156.144 nm (carbon), 288.158 nm (silicon), 134.724 nm (chlorine) and 180.734 nm (sulfur). As spectrometer was working with wavelengths below 180 nm, the purging of the polychromator with nitrogen was employed. Carbon element was used to follow the polymer film and silicon element the substrate since FTO is composed of fluor, silicon oxide and tin oxide. Chlorine and sulfur elements were used to follow their incorporation in the polyaniline films electrodeposited from HCl and H<sub>2</sub>SO<sub>4</sub> electrolytic solutions, respectively. The decrease of carbon signal in the depth profiles was used to estimate the location of the PANI/FTO interface. Three depth profiles have been done for each kind of polyaniline film and a very good reproducibility was observed when comparing these different depth profiles.

## 3. Results and discussion

### 3.1. Electrochemical deposition of polyaniline films

The voltammetric behavior of aniline was examined in HCl and H<sub>2</sub>SO<sub>4</sub> acidic solutions. Fig. 1a shows the cyclic voltammogram (CV) corresponding to the potentiodynamic electropolymerization of aniline in HCl solution recorded in the potential range going from +0.0 to

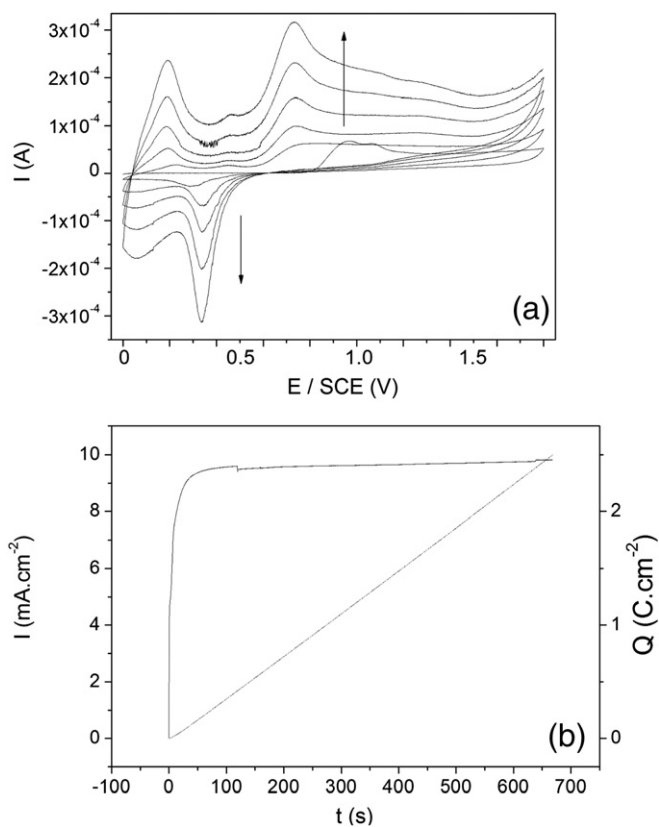


Fig. 1. Electrodeposition of polyaniline from an aqueous solution containing 0.4 mol L<sup>-1</sup> aniline and 1.2 mol L<sup>-1</sup> HCl: (a) by cyclic voltammetry on a Pt electrode (5.5 scans between 0 and +1.8 V/SCE, scan speed: 50 mV/s), (b) by chronocoulometry on a FTO electrode at +1.8 V/SCE ( $Q_{\text{total}} = 2.5 \text{ C cm}^{-2}$ ).

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