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

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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 H2SO4 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-ions 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

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0040-6090/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.10.037
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 H₂SO₄ 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 chloride 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 distilled water (Milli-Q, Millipore, resistivity 18 MΩ cm), were used to prepare the electrolyte solutions. Aniline was used at the concentration of 0.4 mol L⁻¹ in an aqueous solution containing either 1.2 mol L⁻¹ HCl or 1.0 mol L⁻¹ H₂SO₄.

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 VoltaMaster 4 Software interface. A three-electrode electrochemical cell was used in all cases. The working electrode was either a platinum electrode (0.785 mm²) or a Fluorine doped Tin Oxide (FTO) electrode (from Solens, 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 profilometer (Alpha-Step IQ, KLA Tencor). Both average roughness (Rq) and quadratic average roughness (Rq) were estimated on a scan length of 2000 μm at a scan speed of 50 μm s⁻¹. 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 Kα 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 (10W) and a low pressure (400Pa) 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 H₂SO₄ 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 H₂SO₄ acidic solutions. Fig. 1a shows the cyclic voltammogram (CV) corresponding to the potentiodynamic electropolymization of aniline in HCl solution recorded in the potential range going from +0.0 to
+ 1.8 V/SCE. The first scan exhibited an anodic peak corresponding to the oxidation of the aniline monomers at + 0.95 V/SCE that initiated the electropolymerization of polyaniline. The following scans showed well-defined redox peaks corresponding to the oxidation and reduction of the polyaniline films. The redox peak currents gradually increased with the number of potential scans, indicating that the growing polymer film is conducting. This increase of the redox peak currents with potential cycling also confirms the works from Mu et al. demonstrating that the electropolymerization of aniline is an autocatalytic process [34].

More precisely two main pairs of the typically reversible redox peaks of PANI can be observed in these CVs. The first redox couple at lower positive potentials (≈ + 0.2 V/SCE) corresponds to the redox inter-conversion between leucoemeraldine and emeraldine. The redox couple at the higher potential (≈ + 0.75 V/SCE) corresponds to the redox reaction between emeraldine and pernigraniline [35]. For most of the scans shown in Fig. 1a, there is a middle redox couple observed between the two pairs mentioned above (≈ + 0.45 V/SCE). The middle peak frequently appears in the CV curves of PANI when the anodic limit is a little high, belonging most probably to quinone intermediates [36] or to the formation of cross-linked PANI chains [37]. The reduction peak, observed at ≈ + 0.35 V/SCE, corresponds to the redox reaction between pernigraniline and leucoemeraldine [38].

The cyclic voltammogram of aniline in H2SO4 solutions was performed in the same conditions (Fig. 2a). The voltammetric behavior of aniline in H2SO4 and HCl solutions was very similar. Only a few differences appeared: i) the anodic peak corresponding to the oxidation of aniline monomers during the first scan was far less pronounced in H2SO4 than in HCl solutions and it appeared at a more positive potential (+ 1.2 V/SCE), ii) the two oxidation peaks and the reduction peak corresponding to the transitions between leucoemeraldine, emeraldine and pernigraniline appeared at the same potential for both acids but the middle redox peak, present at + 0.45 V/SCE, was more pronounced in H2SO4 than in HCl solutions. Taking into account the works from Genies et al. [37], this could be due to the formation of cross-linked PANI chains, thus resulting in a more compact structure. SEM experiments (presented in Section 3.3.) confirm this hypothesis.

To perform these electrochemical measurements, we used a platinum wire with a diameter of 1 mm inserted in a glass cylinder connected to a potentiostat. Unfortunately, it was not possible to use such electrodes to perform SEM and GDOS experiments. That is why polyaniline films were electrodeposited on FTO surfaces since such substrates can be easily used for SEM and GDOS analyses. Taking into account the voltammetric behavior of aniline, polyaniline films were electrodeposited on FTO surfaces by applying a potential of + 1.8 V/SCE until reaching the desired total electrical charge density. The chronocoulometries obtained in HCl and H2SO4 are given in Figs. 1b and 2b, respectively. They correspond to the thickest polyaniline films electrosynthesized in these electrolyte solutions. The shape of these curves was very usual since an increase of the current density was firstly observed, corresponding to the oxidation of aniline monomers at the FTO surface, followed by a steady state corresponding to the growth of the polyaniline backbone. It can be remarked that the value of the current density was similar (10–11 mA cm−2) whatever the acid used. The voltammetric behavior was studied with platinum electrodes rather than with FTO electrodes since the redox peaks are less easily visible on FTO surfaces than on platinum substrates as shown in our previous works [39].

### 3.2. Thickness of polyaniline films

The electrical charge density was varied to electrodeposit polyaniline films of different thickness on FTO substrates. The thickness of each PANI film was calculated using Faraday’s law (Eq. (1)) and assuming a current efficiency of 100% for the electropolymerization reaction:

\[
t = \frac{QM}{\rho A z F}
\]

where \( t \) is the film thickness (cm), \( Q \) is the electrical charge associated with polyaniline formation (C), \( M \) is the molar mass of the aniline monomer (93.13 g mol−1), \( \rho \) is the density of the polymer (1.4 g cm−3), \( A \) is the area of the working surface (cm²), \( z \) is the number of electrons involved which is in this case of 2.5 [40,41], and \( F \) is the Faraday constant (96500 C mol−1). Using these data and (Eq. (1)), it comes that the required charge density to grow a PANI film with an average thickness of 0.1 μm is 36.3 mC cm−2.

Since the chronocoulometries obtained during the polymer electropolymerization gave access to the total electrical charge associated with polymer growth, it is possible to calculate the average thickness of each polymer film using Faraday’s law. The calculated thicknesses of all PANI films are gathered in Table 1. These calculated thicknesses are comprised between 0.7 μm and 6.9 μm depending on the applied electrical charge density.

Profilometric measurements were also performed to measure polymer thickness. Before performing profilometric measurements a stripe was done with metallic point in the middle of the polymer film in order to generate a step between the FTO substrate and the polymer film. The step was done in the middle of the polymer film because this latter is more homogeneous in the middle of the film than on its edges due to edge effects. Indeed, the thickness measured at the edges of the film (at the interface polymer/electrolyte) was approximately 3–4 times higher than the thickness measured in the middle of the polymer film. The measured thicknesses of all PANI films are gathered in Table 1, as well as the calculated thickness. However, it is difficult to compare the thickness obtained through Faraday’s law and profilometric measurements since Faraday’s law leads to an estimation of the average thickness of the polymer films, considering that these films are both compact and homogeneously
PANI/HCl2500 structure varies with the electropolymerization parameters. The and PANI/H2SO4 to describe a PANI in Section 3.5 that this increase of porosity is due to the removal by porous layer having a thickness of 13.6 μm than the calculated values. This is probably due to the very porous electropolymerization of aniline in HCl solution are strongly higher observed that the measured thicknesses of polymer measurement of the fi

Thickness of the electrodeposited polyaniline films determined by calculations using Faraday’s law and through profilometric measurements (6 measurements were performed on each polymer sample to determine their measured thickness).

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Electrical charge density (mC cm⁻²)</th>
<th>Calculated thickness (μm)</th>
<th>Measured thickness (μm)</th>
<th>Sample name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline + HCl</td>
<td>2500</td>
<td>6.9</td>
<td>13.6 ± 4.1</td>
<td>PANI/HCl2500</td>
</tr>
<tr>
<td>500</td>
<td>1.4</td>
<td>4.9 ± 1.9</td>
<td>PANI/HCl500</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>0.7</td>
<td>3.4 ± 0.8</td>
<td>PANI/HCl250</td>
<td></td>
</tr>
<tr>
<td>Aniline + H2SO4</td>
<td>2500</td>
<td>6.9</td>
<td>9.6 ± 4.3</td>
<td>PANI/H2SO4-2500</td>
</tr>
<tr>
<td>500</td>
<td>1.4</td>
<td>3.3 ± 1.1</td>
<td>PANI/H2SO4-500</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>0.7</td>
<td>1.5 ± 0.5</td>
<td>PANI/H2SO4-250</td>
<td></td>
</tr>
</tbody>
</table>

distributed on the surface, when profilometry leads to a local measurement of the film thickness.

Nevertheless, taking into account these remarks, it is possible to discuss the thickness values given in Table 1. Indeed it can be observed that the measured thicknesses of polymer films obtained by electropolymerization of aniline in HCl solution are strongly higher than the calculated values. This is probably due to the very porous structure of polyaniline films grown in HCl as it will be shown using SEM imaging in Section 3.3. Indeed it can be supposed that a very porous layer having a thickness of 13.6 μm contains approximately the same amount of polyaniline that a totally compact layer, as supposed by the Faraday’s law, having a thickness of 6.9 μm. It can also be observed that the thicknesses of PANI/HCl films are higher than the thickness of PANI/H2SO4 films for similar electroposition parameters. This indicates that the electropolymerization is easier in HCl solutions than in H2SO4 solutions and/or that the porosity of PANI/HCl films is higher than the porosity of PANI/H2SO4 films, thus leading to a higher thickness for the same applied electrical charge density.

As indicated in the last column of Table 1 we will use in the following sections the acronym PANI/HCl to describe a PANI film electro-synthesized in HCl using an electrical charge density q (in C cm⁻²) and PANI/H2SO4 to describe a PANI film electro-synthesized in H2SO4 using an electrical charge density q.

3.3. Morphological features of polyaniline films

Scanning electron micrographs of polyaniline films grown either in HCl or H2SO4 solutions were performed on FTO surfaces and gathered in Fig. 3. SEM pictures were performed before and after rinsing with water of the PANI samples.

Polyaniline films electrosynthesized from aniline and HCl solutions possess a porous structure. This is particularly true for the thickest PANI/HCl film which exhibits a sponge-like and branched structure (Fig. 3a), this structure being typical of an electrodeposited PANI film [35,42]. This sample also presents a very high porosity that is probably responsible from the strong difference between the calculated thickness and the measured one (Table 1). Other PANI/HCl films also possess a sponge-like and porous structure even if it seems that the porosity decreases when the thickness of the PANI/HCl films decreases too (Fig. 3c and e).

Rinsing PANI/HCl films with water leads to an increase of the polymer film’s porosity. This is particularly visible when comparing PANI/HCl2500 films before and after rinsing (Fig. 3a and b). We will see in Section 3.5 that this increase of porosity is due to the removal by rinsing of an excess of aniline partially filling the pores of PANI films. Looking more closely, it appears that the structure of the polymer films consists of nanowire networks in which the individual wire structure varies with the electropolymerization parameters. The diameter of these individual wires can be estimated to be around 100 nm when the length of the nanowire networks is up to several micrometers. It can also be observed that several successive layers of nanowires are formed on the FTO substrates. Consequently, if the surface of the film seems smooth at first sight, it is in fact inhomogeneous due to the high porosity caused by the intertwined nanowire network.

The structure of the PANI films grown in H2SO4 solutions is very similar and also consists in a porous structure made of intertwined nanowires even if it seems that PANI/H2SO4 films are more compact and slightly less porous than PANI/HCl films. This is particularly when comparing the thickest film obtained in HCl (Fig. 3a) and H2SO4 (Fig. 4a). This difference results in a better correlation between calculated and measured thickness (Table 1) since a dense and homogeneous structure is more easily modelized by Faraday’s law than a very porous and inhomogeneous one. It is also noticeable that all PANI/H2SO4 films present similar porosity whatever the thickness, contrary to PANI/HCl films whose porosity depends on the polymer film thickness.

The morphology of the PANI films can also be explained by the electropolymerization mechanism. Indeed, since HCl and H2SO4 are concentrated at more than 1 mol L⁻¹, aniline monomers present in the electrolyte are all present in a protonated form. These protonated monomers allow fast reaction kinetics to oxidize aniline monomers into aniline cation radicals by lose of an electron. Then, the aniline cation radicals quickly delocalize the lone electron to the para-position and react the ones with the others to form head to tail addition product. The fast kinetics of this reaction allow a rapid build-up of the PANI coating on the substrate without requiring preferential sites, thus leading to a random deposition of the long elongated PANI oligomers nanowires on the substrate.

3.4. Roughness of polyaniline films

A stylus-based mechanical probe profiler, enabling surface mechanical scanning without damaging it, was used to obtain additional information about the surface characteristics of polymer films. These profilometric measurements were performed to measure the roughness of the polyaniline films grown in HCl or H2SO4 solutions. For each polyaniline film, 9 measurements were done at different positions of the polymer coating. The average roughness (R_a) and the average quadratic roughness (R_q) were deduced from these measurements as well as the associated measurements uncertainty (Table 2). The influence of rinsing on the roughness of the PANI films was also studied. An increase of the average roughness of PANI/HCl and PANI/H2SO4 films was observed when the thickness of PANI films increased too. For example, R_a increased from 99 nm for the thinnest PANI/HCl film to 265 nm for the thickest one and from 89 nm for the thinnest PANI/H2SO4 film to 146 nm for the thickest one. The same trend was observed for average quadratic roughness. The roughness of each polyaniline film was also measured after rinsing with water. In the case of PANI/HCl films, this rinsing led to an increase of the roughness. This is particularly true for PANI/HCl2500 films whose roughness increased from 265 nm (without rinsing) to 468 nm (after rinsing). These results are consistent with SEM observations since the structure of rinsed PANI/HCl2500 appeared less compact and less homogeneous than the other ones. This difference of structure due to water rinsing could be due to desorption of an excess of aniline monomers or short oligomers present on the surface before rinsing. Similarly the roughness of PANI/H2SO4-2500 increased with rinsing. This behavior is comparable with the evolution observed for PANI/H2SO4 and PANI/HCl250 films and so it may be due the presence of an excess of aniline monomers or short oligomers present on the surface before rinsing. Similarly the roughness of PANI/H2SO4-2500 increased with rinsing. This behavior is comparable with the evolution observed for PANI/HCl2500 and PANI/HCl250 films and so it may be due the presence of an excess of aniline monomers or short oligomers present on the surface before rinsing. Similarly the roughness of PANI/H2SO4-2500 increased with rinsing. This behavior is comparable with the evolution observed for PANI/HCl2500 and PANI/HCl250 films and so it may be due the presence of an excess of aniline monomers or short oligomers present on the surface before rinsing. Similarly the roughness of PANI/H2SO4-2500 increased with rinsing. This behavior is comparable with the evolution observed for PANI/HCl2500 and PANI/HCl250 films and so it may be due the presence of an excess of aniline monomers or short oligomers present on the surface before rinsing. Similarly the roughness of PANI/H2SO4-2500 increased with rinsing. This behavior is comparable with the evolution observed for PANI/HCl2500 and PANI/HCl250 films and so it may be due the presence of an excess of aniline monomers or short oligomers present on the surface before rinsing.

3.5. GDOES analysis of polyaniline films

3.5.1. PANI/HCl polymer films

Fig. 5 shows the qualitative GDOES depth profiles of PANI/HCl films formed under 2500, 500 and 250 mC cm⁻². Polymer films were
followed by the carbon element and FTO substrate by silicon element. PANI/FTO interface could be located by the decrease of carbon signal. Thus, polymer/substrate interface was reached after an erosion time of 55 s for PANI formed at 250 mC cm$^{-2}$ and increased to about 100 s and 130 s for PANI formed at 500 mC cm$^{-2}$ and 2500 mC cm$^{-2}$, respectively. Of course, it is logical to observe an increase of the sputtering time when the polymer thickness increases too. It can be observed that sputtering time required to remove PANI-HCl film was not proportional to the measured thickness of the PANI-HCl films because these films do not have the same morphology and porosity as shown by the SEM pictures of Fig. 3. An increased Cl yield in the region of the FTO substrate can be observed. This latter is probably a background signal increased due to the change of sputtering rate. Furthermore, GDOES profiles indicate a non-uniform repartition of carbon and chlorine elements into the polymer film. The high C peaks observed at the beginning of the sputtering (during the first seconds) are probably due to surface contamination. Then, enrichments of C (intensity at 0.8 a.u.) and Cl (intensity at 0.6–0.7 a.u.) are observed at the surface of the polymer film during the first 20 s of analysis. This could be due to an inhomogeneous distribution of the Cl$^-$ anions in the PANI film (with a higher concentration of Cl$^-$ at the top surface than inside the PANI matrix) and/or to the presence of a compound containing Cl and C that would be incorporated at the top surface of the PANI film.

GDOES depth profiles of rinsed PANI films are also shown in Fig. 5. For rinsed polymer films, the amounts of Cl and C at the top surface of the films strongly decreased. This could be due to the expulsion of chlorides from the polymer surface (leading to a dedoping of the polymer film) and/or to the expulsion of the compound containing C and Cl previously observed at the polymer top surface. Except the signal obtained at the top surface, the signal of carbon (0.5 a.u.) was similar for rinsed and not rinsed PANI samples indicating that this signal corresponded to the carbon from the PANI matrix. Consequently, in this part of the film, the distribution of the carbon is homogenous.

To understand exactly what happens during the rinsing of the polymer films, XRD analyses were performed for all PANI/HCl samples.
Fig. 6 shows the XRD patterns obtained before and after rinsing of a PANI/HCl2500 film (the same patterns were obtained with PANI/HCl500 and PANI/HCl250). Before rinsing, a small peak was present at 26° that can be attributed to the FTO substrate. All other peaks (observed at 11°, 21°, 22°, 23° and 35°) were due to the presence of anilinium chloride (JCPDS 07-0508). Indeed, in parallel with the electropolymerization of polyaniline from protonated aniline, another reaction (see Eq. (2)) takes place in the electrolytic solution that consists in the formation of anilinium chloride salt from aniline and hydrochloric acid [43,44]:

\[ C_6H_5NH_2 + HCl \rightarrow C_6H_5NH_3^+ Cl^- \]  

Since it is not possible for this crystalline aromatic ammonium salt to get into the pores of the polymer film due to its important size, it remains at the top surface of the polymer film. Consequently, the important amount of C and Cl observed in the GDOES profiles at the top surface of the polymer film is probably due to the presence of an excess of anilinium chloride.

After rinsing, XRD peaks due to this compound disappeared, indicating that the excess of anilinium chloride was removed by rinsing with water. This is consistent with the GDOES profiles after rinsing that can be attributed to the FTO substrate. All other peaks (observed at 11°, 21°, 22°, 23° and 35°) were due to the presence of anilinium chloride (JCPDS 07-0508). Indeed, in parallel with the electropolymerization of polyaniline from protonated aniline, another reaction (see Eq. (2)) takes place in the electrolytic solution that consists in the formation of anilinium chloride salt from aniline and hydrochloric acid [43,44]:

<table>
<thead>
<tr>
<th>Sample name (aq)</th>
<th>Rinsing</th>
<th>Ra (nm)</th>
<th>Rq (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI/HCl2500</td>
<td>no</td>
<td>265 ± 38</td>
<td>324 ± 48</td>
</tr>
<tr>
<td></td>
<td>yes</td>
<td>468 ± 152</td>
<td>589 ± 203</td>
</tr>
<tr>
<td>PANI/HCl500</td>
<td>no</td>
<td>130 ± 20</td>
<td>159 ± 22</td>
</tr>
<tr>
<td></td>
<td>yes</td>
<td>152 ± 29</td>
<td>188 ± 37</td>
</tr>
<tr>
<td>PANI/HCl250</td>
<td>no</td>
<td>99 ± 8</td>
<td>132 ± 7</td>
</tr>
<tr>
<td></td>
<td>yes</td>
<td>114 ± 9</td>
<td>138 ± 11</td>
</tr>
<tr>
<td>PANI/H2SO4–2500</td>
<td>no</td>
<td>146 ± 44</td>
<td>171 ± 53</td>
</tr>
<tr>
<td></td>
<td>yes</td>
<td>121 ± 43</td>
<td>153 ± 47</td>
</tr>
<tr>
<td>PANI/H2SO4–500</td>
<td>no</td>
<td>104 ± 23</td>
<td>131 ± 28</td>
</tr>
<tr>
<td></td>
<td>yes</td>
<td>144 ± 44</td>
<td>178 ± 49</td>
</tr>
<tr>
<td>PANI/H2SO4–250</td>
<td>no</td>
<td>89 ± 5</td>
<td>109 ± 6</td>
</tr>
<tr>
<td></td>
<td>yes</td>
<td>83 ± 3</td>
<td>102 ± 11</td>
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Fig. 4. SEM images of PANI films grown in H2SO4 aqueous solutions (magnification: 3000× for all images). (a) PANI/H2SO4–2500, (b) PANI/H2SO4–500, (c) PANI/H2SO4–250, (d) rinsed PANI/H2SO4–2500, (e) rinsed PANI/H2SO4–500, (f) rinsed PANI/H2SO4–250.
demonstrated a decrease of the signal of C and Cl elements (only a residual anilinium chloride was observed at the top surface for rinsed HCl/PANI250). Furthermore, XRD and GDOES results seem consistent with profilometry measurements. Indeed it could be proposed that anilinium chloride excess was removed by rinsing from the top surface and from the pores of the polyaniline films. This removal from the pores leads to an increase of the film roughness since the roughness was decreased by the presence of anilinium chloride into the polymer's pores. It could also be supposed that some Cl\(^{-}\) anions are expelled from the pores of the PANI film during rinsing. The high porosity of the polymer film combined with the small size of the anions is certainly favorable to the anion rejection from the polymer film.

3.5.2. PANI/H\(_2\)SO\(_4\) polymer films

GDOES depth profiles of PANI/H\(_2\)SO\(_4\)–2500, PANI/H\(_2\)SO\(_4\)–500, and PANI/H\(_2\)SO\(_4\)–250 films electrodeposited on FTO substrates are shown in Fig. 7. Polyaniline/FTO interface is reached after 25 s of erosion for PANI/H\(_2\)SO\(_4\)–250, after 45 s of erosion for PANI/H\(_2\)SO\(_4\)–500, and after 70 s of erosion for PANI/H\(_2\)SO\(_4\)–2500. The sputtering time required to remove PANI-H\(_2\)SO\(_4\) films is not proportional to the measured thickness of the PANI-H\(_2\)SO\(_4\) films because these films do not have the same morphology and porosity as shown by the SEM pictures of Fig. 4. Furthermore, these erosion times are lower than the ones obtained for PANI/HCl films, thus confirming that PANI/H\(_2\)SO\(_4\) films are thinner than PANI/HCl films, as previously shown using profilometric measurements. The depth profiles of polyaniline films electrosynthesized in H\(_2\)SO\(_4\) acid are dependent on the polymer thickness. Indeed, for the lowest thickness (PANI-H\(_2\)SO\(_4\)–250), sulfur element is present everywhere in the polymer.

![Fig. 5. GDOES profiles of: (a) PANI/HCl2500, (b) PANI/HCl500, (c) PANI/HCl250, (d) rinsed PANI/HCl2500, (e) rinsed PANI/HCl500, and (f) rinsed PANI/HCl250.](image)

![Fig. 6. XRD pattern of PANI-HCl250: a) before rinsing and b) after rinsing.](image)
film (Fig. 7c). Consequently, it can be deduced that the compounds containing sulfur are homogeneously distributed in polyaniline films. For the highest thicknesses (PANI-H2SO4–2500 and PANI-H2SO4–500), sulfur element is also incorporated in the entire polymer matrix (Fig. 7a and b) and enrichments in C and S at the top surfaces are observed. In the polymer bulk, as the value of the S signal intensity is higher for PANI-H2SO4–250 (0.4–0.5 a.u.) than that for PANI-H2SO4–500 and PANI-H2SO4–2500 (both around 0.2 a.u.), it can be deduced that the amount of sulfur is higher in PANI-H2SO4–250 film than that in PANI-H2SO4–500 and PANI-H2SO4–2500 films. Similar to the phenomenon observed for PANI-HCl films, the presence of sulfur element could be due to either an inhomogeneous distribution of HSO4− or SO42− anions in the PANI film and/or to the presence of a compound, containing S and C elements, incorporated in the PANI film.

GDOES analysis of each PANI-H2SO4 film has also been performed after rinsing. Resulting GDOES profiles are also given in Fig. 7. The S and C peaks observed at the top surfaces in Fig. 7a and b disappear from the depth profile indicating that the compound containing sulfur and carbon excess has been removed from the film. The S signal has significantly decreased after rinsing but it remains a not negligible amount of sulfur element inside the film (around 0.1 a.u.).

To obtain more information about the compounds present at the surface or inside the polymer film, XRD analyses of PANI/H2SO4 coatings were performed before and after rinsing (Fig. 8). XRD pattern of non-rinsed PANI/H2SO4 films exhibited a small peak at 26° due to the FTO substrate and several other peaks (at 11°, 17.5°, 19.5°, 23°, 25.5° and 34.5°) due to the presence of anilinium hydrogen sulfate (JCPDS 30-1523). Similar XRD patterns were obtained for all other PANI/H2SO4 films. Indeed, the formation of crystalline anilinium hydrogen sulfate, C6H5NH3+HSO4−, takes place when aniline is put into sulfuric acid (see Eq. (3)). This reaction, very similar to the one observed in HCl solution, has been highlighted by Noutobba et al. who also demonstrated that cations and anions are linked to each other in this compound through N⋯H⋯O hydrogen bonds, formed by all H atoms covalently bonded to the N atoms [44,45]. In addition, strong O⋯H⋯O anion—anion hydrogen-bond interactions were observed. The size of this crystalline ammonium salt is bigger than the size of anilinium chloride. So a smaller amount of salt may fill the pores of polyaniline films in the case of ammonium salt than in the case of chloride salt.

\[
\text{C}_6\text{H}_5\text{NH}_2+\text{H}_2\text{SO}_4\rightarrow\text{C}_6\text{H}_5\text{NH}_3^+\text{HSO}_4^- \quad (3)
\]

After rinsing, the peaks attributed to anilinium hydrogen sulfate disappeared, thus indicating that this crystalline anilinium salt, that was present in excess on the top surface, was removed from the polymer film surface by rinsing with water. This is coherent with
polymer films and to be a good complement to other techniques such as X-ray Photoelectron Spectroscopy or Auger Electron Spectroscopy.

Acknowledgments

This work was partly supported by the French RENATECH Network and its FEMTO-ST Technological Facility. GDOES and XRD experiments were performed in Chemistry’s Plateform of UTINAM.

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