

SEM study of the growth of electrochemically obtained polyselenophene thin films. Effect of electrolyte and monomer concentration in acetonitrile

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Received : 1 April 2003/Revised version : 4 August 2003/Accepted : 4 August 2003

Summary

The influence of electrolyte and monomer concentration on properties and morphology of electrochemically obtained polyselenophene films doped and undoped with hexafluorophosphate and tetrafluoroborate anions was analyzed. The films were deposited on SnO₂-coated glass in a classical three-electrode cell from the monomer and the electrolyte in anhydrous acetonitrile.

The electrochemical growth of polyselenophene thin films was studied by X-ray photoelectron spectroscopy (XPS), electron probe microanalysis (EPMA), and scanning electron microscopy (SEM). The morphology study revealed different three-dimensional (3D) and bidimensional (2D) growth, depending on monomer and electrolyte concentration.

Introduction

Conducting polymers obtained from the electropolymerization of heterocyclic monomers, such as pyrrole or thiophene, have been extensively studied over the past decade. It has been demonstrated that properties of deposited films are strongly dependent on the electropolymerization conditions. Although electron conduction occurs through the extended π -bonded system of the carbon backbone, the nature of the heteroatom has an important effect on the stability and electrical, redox, optical, and mechanical properties of these polymeric materials.

Glenis *et al.* [1] have investigated relatively new conducting polymers with five-member heterocyclic monomer, such as polyselenophene [2] and poly (3-methyl selenophene) [3]. It has been reported a study of electrochemically prepared polyselenophene (Pse) films. The polymer was characterized in both the oxidized

electrolyte-doped, and the neutral undoped states by UV-visible and infrared spectroscopy, x-ray photoelectron spectroscopy (XPS), electron-spin-resonance (ESR) spectroscopy, dc conductivity, and scanning electron microscopy (SEM). Polyselenophene films have been grown on the surface of electrodes by electropolymerization of selenophene. The basic selenophene ring is retained within the polymeric structure. The surface morphology depends on film thickness, and no correlation was found between ESR spectrum of the polymer and the electrical conduction mechanism.

Here we report the results obtained in the electropolymerization of selenophene on SnO_2 ("conducting glass") electrode by using acetonitrile media with electrolytes such as Bu_4NPF_6 , Bu_4NBF_4 and Et_4NClO_4 . The electropolymerization technique used was cyclic voltammetry, and the growth of polyselenophene was analyzed by scanning electron microscopy (SEM). Results obtained by x-ray electron spectroscopy (XPS) and electron microprobe analysis (EPMA) are also discussed.

Experimental

The setup for cyclic voltammetry was described previously [4]. A SnO_2 (geometrical area, 2 cm^2) and an Ag/AgCl in tetramethylammonium chloride (Me_4NCl) were used as working and reference electrodes, respectively. The potentials with respect to the latter were corrected to that of the saturated calomel electrode (SCE) [5]. A Pt gauze, separated from the working electrode compartment by a fine frit glass, was used as counter electrode.

Before each experiment, the working electrode was cleaned in a heated mixture of acetone, ammonia, and H_2O_2 with temperature. Prior to all the experiments, solutions were purged with high-purity argon and an argon atmosphere was maintained over the solution during measurements.

Anhydrous acetonitrile (Aldrich, HPLC grade) was stored in an atmosphere of dry argon and over a generous amount of molecular sieve (4 \AA). To ensure a minimum water content, the solvents were manipulated by syringes. The same procedure was applied to selenophene (Aldrich) and all the solutions employed. The background electrolytes were tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) and tetrabutyl ammonium perchlorate (Bu_4NClO_4), supplied by Aldrich.

Electrochemical polymerization and deposition of PSe was carried out from solutions containing 0.05-0.1M monomer and 0.05-0.1M supporting electrolyte. Polymerization was achieved by cyclic voltammetry (potentials between -0.20 and 2.00 V at $10 \text{ mV}\cdot\text{s}^{-1}$) and by single potential step experiments; the electrode was first switched from 0.0 to 0.8 V, for a period of either 2 or 7 s. Polymerization was achieved by a further step to potentials between 1.700 and 2.100 V.

Electron microprobe analysis (PGT-IMIX PTS model) was used to determine the composition of the films [6]. For the observation of their surface and cross-section morphology, a JEOL-type JSM 6400F SEM was employed.

XPS measurements were carried out with a Leybold LHS-12 spectrometer (XPS analysis was carried out at the University of Nantes, CNRS). XPS data were obtained with a magnesium source radiation (1253.6 eV) operating at 10 kV and 10 mA and the pass energy was set to 50 eV. High-resolution scans with a good signal-to-noise ratio were obtained in the C1s, Se3d, O1s, N1s, P2p, F1s, B1s and Cl2p regions of the

spectrum. Quantitative analysis was based on the determination of C1s, Se3d, O1s, N1s, P2p, F1s, B1s and Cl2p peak areas with 0.2, 0.57, 0.6, 0.36, 0.31, 1, 0.1 and 0.58 as sensitivity factors. The vacuum in the analysis chamber was about 10^{-6} Pa. All the spectra were recorded under identical conditions. The decomposition of XPS peaks into different components and the quantitative interpretation were performed after subtraction of the background by using the Shirley method [7]. The developed curve-fitting programs allow the variation of parameters, such as the Guassian-Lorentzian ratio, the full width at half-maximum (FWHM), the position, and the intensity of the contribution. The curve-fitting program optimized these parameters.

To check the surface contamination, some etching was done. Sputtering was accomplished at pressures of $<5 \times 10^4$ Pa, a 10-mA emission current, and a 3-kV beam energy using an ion gun. With these experimental conditions, all the surfaces of the sample were sputtered.

Results

Electrochemical polymerization

Figure 1 depicts the voltammetric profiles obtained at 10 mV s^{-1} , during electro-oxidation of selenophene in the presence of electrolytes with various anions. Different potential ranges were necessary to obtain reproducible curves and analogous deposits (0 to 1.8 V for PF_6^- , 0 to 2.0 V for BF_4^- , and 0 to 1.9 V for ClO_4^-), that show an effect of the anion on polymer growth.

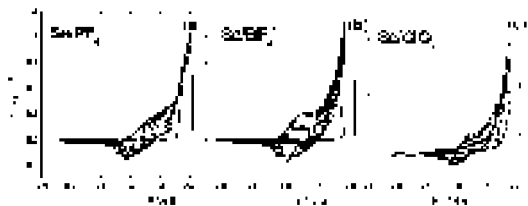


Fig. 1 Voltammetric profiles (cycles 1 to 10) of 0.1 M selenophene in CH_3CN with various 0.1 M electrolytes: (a) Bu_4NPF_6 ; (b) Bu_4NBF_4 ; (c) Bu_4NClO_4

EPMA study

The results shown correspond to homogeneous portions of the samples, and the details will be described along with the SEM experiment report. The average values obtained for different electrodeposit conditions are summarized in Table 1. The Se/C ratio is about 0.21 ± 0.01 when PF_6^- is used as dopant anion, and 0.15 ± 0.01 for BF_4^- , which means that a selenium deficiency is systemically present, because the theoretical ratio is 0.25.

Table I also shows that there is a surface contamination because the atomic concentration of Se increases systematically after etching while its etching rate is faster than that of carbon.

Table 1 Averaged EPMA analysis of polyselenophene obtained after 10 successive voltammetric cycles on SnO₂ electrode, in acetonitrile

selenophene concentration / M	electrolyte anion and concentration / M	atomic ratio Se/C
0.05	PF_6^- - 0.05	0.20
0.10	PF_6^- - 0.10	0.22
0.05	BF_4^- - 0.05	0.14
0.10	BF_4^- - 0.10	0.15

XPS analysis

The samples studied in this section correspond to polymers deposited after 10 voltammetric cycles. No tin was detected by the surface XPS study, which means that after ten cycles the SnO₂ coated glass substrates were wholly covered by the synthesized polymers.

The surface of electrochemically synthesized films depends strongly on the electrolytic solutions used.

Figure 2 shows that carbon peak is formed by four contributions. Table 3 shows different contribution present in polyselenophene. The first one, and most intense, situated at 284.5 eV is attributed to C-C bond since it corresponds to the C-C reference bond measured with the spectrometer apparatus used in the present study. As the bonding energy of C-Se is only 0.3-0.5 eV greater than that of C-C, the resolution of the decomposition software is not able to allow to discriminate between C-C and C-Se bonds. The second contribution at 286.3 eV can be assigned to C-OH contamination but also to C-F bonds related to the dopant used which F can react with during synthesis (doping-undoping process).

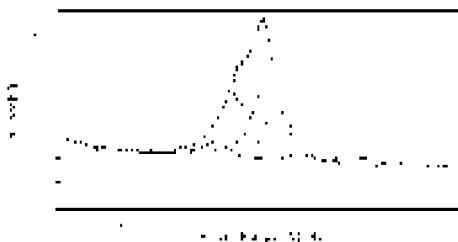


Fig. 2 C1s core level spectra of PF_6^- doped polyselenophene films: The features through the data correspond to the fitting with Gaussian functions.

Some C^+ can be formed during polymer doping but the relative dopant concentration cannot justify a large C^+ contribution, as shown by quantitative analysis.

The two contributions are relative to superficial contamination since they disappear after 1 min of etching. They can be assigned to C=O (around 288 eV) and C-OOH (around 290 eV). Quantitatively it can be seen that these two last contributions increase when monomer and electrolyte concentrations increase.

The Se3d peak can be attributed to selenium in the ring situated at 55.5 eV.

A little percentage of nitrogen has been detected on the surface situated at 400.1 eV, could be attributed to some solvent or electrolyte salt contamination of the film.

The O1s peak can be decomposed in two contributions corresponding to surface contamination, the first situated at 531.5 eV corresponds to C=O, while the other at 533.8 eV can be assigned to C-OH bonds.

Furthermore some fluorine and phosphorus were also detected. They are present in atomic ratios $[F]/[P] \cong 5$ and $[F]/[B] \cong 4$, but when doping is done with ClO_4^- the atomic ratio $[O]/[Cl]$ is greater than 4, indicating that polyselenophene has been doped.

Selenium deficiency is obtained when using BF_4^- and the surface contamination with oxygen is more important using either PF_6^- or ClO_4^- , indicating that the film surface is contaminated not only by air but also by the solvent and the electrolyte.

Table 2 XPS analysis after peaks decomposition

	C1s				Se3d		O1s	
	C-C C-Se	COH CF C ⁺	C=O	COOH	Se	Se ⁺	C=O	COH
PF_6^-								
E(eV)	284.5	285.3	286.7	288.4	55.8	56.6	531.5	533.8
Area%	42	25	28	5	60	40	63	37
FWHM	2.0	2.0	2.0	2.0	1.8	1.8	3.0	3.0
BF_4^-								
E(eV)	284.5	285.8	288.4		55.5	56.3	532	
Area%	74	22	4		60	40	100	
FWHM	1.4	1.4	1.4		1.6	1.6	3.3	
ClO_4^-								
E(eV)	284.5	286.1	287.9	289.9	55.7	56.5	532.0	534.6
Area%	61	27	9	3	60	40	72	28
FWHM	1.7	1.7	1.7	1.7	1.5	1.5	2.4	2.4

SEM Study

Using TBAPF₆ as electrolyte, and taking as reference the electrodeposit of Pse in PF₆⁻ in a concentration of 0.05 M for the monomer and for the support electrolyte, and with 1 cycle of electrodeposit (fig. 3), it was compared with the obtained morphology by increasing the concentration to 0.1 M (fig.4). Of such comparison, it can be deduced that an increase of the concentration creates a more compacted Pse film with an

evidence of progressive nucleation, which is manifested in the different sizes of the growing nucleus present in the microphotography.



Fig. 3 Microphotograph of doped ($E = 1.95$ V) polyselenophene obtained after 1 voltammetric cycle from 0.05 M selenophene + 0.05 M Bu_4NPF_6 in CH_3CN .



Fig. 4 Microphotograph of doped ($E = 1.80$ V) polyselenophene obtained after 1 voltammetric cycle from 0.1 M selenophene + 0.1 M Bu_4NPF_6 in CH_3CN .

In the case of electropolymerization of selenophene in BF_4^- , it is observed that for a concentration of 0.05M for Se/BF_4 (fig.5), the covering is not complete and the morphology is more heterogeneous. Therefore, is giving account of the existence of more than one involved process in the growing of the polymer. By increasing the concentration to 0.1M, as much of electrolyte as of monomer (fig 6.), is observed a much more homogenous growing with nucleus of similar sizes, which allows to say that the nucleation is instantaneous.



Fig. 5 Microphotograph of doped ($E = 1.95$ V) polyselenophene obtained after 1 voltammetric cycle from 0.05 M selenophene + 0.05 M Bu_4NBF_4 in CH_3CN .



Fig. 6 Microphotograph of doped ($E = 1.80$ V) polyselenophene obtained after 1 voltammetric cycle from 0.1 M selenophene + 0.1 M Bu_4NBF_4 in CH_3CN .

The figures 7 and 8 show the SEM for Se/PF_6 and Se/BF_4 , both to 0.1M, as much to the monomer as to the support electrolyte, by increasing to 10 the number cycles of electrodeposit. By comparing both microphotographs, can be deduced that the formed film in presence of PF_6^- anion shows much holes, that means, it is obtained a more porous deposit than the one with BF_4^- anion, which generates a more compact deposit. In both SEM it can be observed “cauliflower” nodules, typical of a three-dimensional growing. So, with 10 cycles the covering is total in both cases, but by using PF_6^- ,

apparently the solubility is lower, meaning that in to a greater number of nucleus originated from a shorter chain oligomer. This explains the generation of film with a rougher and less compact surface.



Fig. 7 Microphotograph of doped ($E = 1.95$ V) polyselenophene obtained after 10 voltammetric cycles from 0.1 M selenophene + 0.1 M Bu_4NPF_6 in CH_3CN .



Fig. 8 Microphotograph of doped ($E = 1.95$ V) polyselenophene obtained after 10 voltammetric cycles from 0.1 M selenophene + 0.1 M Bu_4NBF_4 in CH_3CN .

Discussion

EPMA analyses were corroborated by XPS, because it shows Se/C ratio for PF_6^- close to the theoretical value of 0.25. On the other hand, using BF_4^- the corresponding values were smaller than with PF_6^- .

By comparison with a similar study on polythiophene in identical experimental conditions [8] it looks like the covering of the whole substrate is faster in the case of polythiophene, since ten cycles are enough to obtain the tin XPS signal while it is still clearly visible in the former case. This means that probably a bidimensional (2D) nucleation process in polyselenophene is more active. Furthermore, a higher concentration causes the three-dimensional (3D) nucleation contribution to increase. When concentration increase the 3D contribution process also increases.

The voltammetric study illustrated in figure 1 clearly indicates the important effect of the electrolyte anion used during electropolymerization process. Although the working potential range to obtain a good deposit of PSe is similar (around 2 V), the oxidation profile observed after successive scans is different: the shape of the oxidation peak and the current raise is more uniform using BF_4^- whereas the use of ClO_4^- causes remarkable differences between one cycle and another.

This effect may be due to the lack of anhydrous perchlorate and, like other polyheterocycles including polythiophene [8], the presence of minimum amounts of water is deleterious. In the case of PF_6^- the deposit width is much larger as indicated by the current increase. However, once a maximum deposit thickness has been reached no significant current increase is observed because of the high film resistance. That is to say, the film does not grow any further.

Considering that the use of PF_6^- requires a fewer number of voltammetric cycles in order to cover completely the electrode the study of the influence of both the monomer and electrolyte concentrations will be done only using this anion.

Figures 3 and 4 as well as figures 5 and 6 clearly show that increasing monomer concentration the 3D film growth is favored. This effect can be explained considering that under these conditions the oligomeric chains before reach the length to which

they become insoluble, therefore, in less time takes place the saturation necessary to favor the formation of multiple nuclei at the electrode surface and, consequently, the 3D development of the deposit as the result of the more disordered growth.

On the other hand, the fact that film with thickness below (10^2 nm) appear homogeneous, whereas thick films (>0.5 μm) exhibit irregularities have already been shown by Spyridon [1]. They attributed this fact to an increases of cross-linking at the α - β carbon positions of ring with increasing film thickness.

Such cross-linking corresponds to same disorder in the film growth. If it is logical that disorder increases with time, i.e. with film growth, it is also expected that disorder increases with the growth rate of the films i.e. with the concentration of the solutions used, which is in good agreement with the present study.

Conclusions

It can be concluded that the cross linking at the α - β carbon positions of ring is present similarly with the 3D growth process and the effect increases with initial concentration used in the electrolyte during electropolymerization process.

To favor the growth of thin and uniform polyselenophene films diluted solutions of the monomer must be used because higher concentrations are favorable to a three dimensional development. With respect to the electrolyte the optimum concentration must be determined after a compromise of the required uniformity and the resistance of the electrolytic medium. Very low concentrations of supporting electrolyte are required and the limit will be determined by the solution resistance.

Finally, related with the electrolyte anion, it can be concluded that to obtain a porous film PF_6^- let is used, whereas for a more compact surface is advisable to use BF_4^- .

Acknowledgements. The authors thank FONDECYT-Chile for financial support through Grants 2000053, 1020520, and ECOS-CONICYT C99-E05.

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