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Stripping voltammetry of silver ions at polythiophene-modified platinum electrodes

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Abstract

The present work describes the development of a modified platinum electrode for stripping voltammetric determination of silver. The deposition of films based on electropolymerisation of the monomer thiophene was carried out by cycling the potential towards positive values between 0 and 1.6 V.

The preconcentration process of silver ions was initiated on the surface of the modified electrode by complexing silver with polythiophene (PTH) when a negative potential (−0.5 V) was applied; then the reduced products was oxidized by means of differential pulse stripping voltammetry and the peak was observed at 0.17 V. Parameters such as pH, supporting electrolyte and number of electropolymerisation cycles were studied. A linear relation between current peak and concentration of Ag(I) was obtained in the range 0.07–1.0 mg L^{-1}. The detection limit for Ag(I) was evaluated to be 0.06 mg L^{-1}. The reproducibility was tested carrying out 11 measurements at different electrodes and the relative standard deviation was 1.5%. The interference of several metals was investigated and showed negligible effect on the electrode response.

Keywords: Polylthiophene-modified electrode; Silver ion monitoring; Stripping voltammetry

1. Introduction

The polymer film deposition can be considered as one of the most versatile approaches for preparing chemically modified electrodes. The electropolymerisation of heteroaromatic compounds at electrodes surfaces has become one of the more effective ways to produce chemically modified electrodes with electrical conductivity. Among the various conducting polymers, polypyrrole (Ppy) is one of the most frequently investigated; it can be easily prepared by electrochemical oxidation of the pyrrole monomers [1] but the species loaded on a Ppy electrode surface containing chemically active counter-ions are difficult to remove resulting in poor reusability [2]. Wong at al. have reported the voltammetric extraction of silver species with Ppy film that had undergone a base–acid treatment but this was time consuming [3]. Song and Shiu found that silver species could be determined with Ppy film modified glassy carbon electrodes, but copper and mercury were also extracted onto Ppy film electrodes and caused significant interference in the determination of silver species. The Ppy electrode exposed to a binary mixture of silver and mercury showed only a large anodic peak at 0.53 V. According to the authors, this might be due to the reduction of both silver and mercuric ions at Ppy film to form the silver amalgam Ag(Hg) and simultaneous stripping of the two elements at the same potential during the anodic process [4]. Besides Ppy, the sulphur-containing polymers such as polythiocrown-ether, and poly-3-methylthiophene [5,6] are mostly used as modifiers for heavy metal due to their high affinity for different species. Some analytical technique have been employed in metal analysis, such as atomic absorption spectrometry (AAS) [7], X-ray fluorescence [8], UV-spectrophotometry [9], inductively coupled plasma atomic emission spectrometry (ICP–AES) [10] and inductively coupled plasma mass spectrometry (ICP–MS) [11]. These techniques, commonly used for trace measurement of heavy metal in the laboratory, are not suitable for the task of in situ testing and monitoring. Electrochemical methods are between the most favourable techniques for the determination of heavy metal ions because of its low cost, high sensitivity easy operation and the ability for carry out speciation analysis.

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In this paper, we present results of detecting Ag(I) at a polythiophene (PTH)-modified platinum electrode by an electrochemical controlled release of silver in 0.2 M KNO_3 solution. This method features fast experimentation time, good suitability for field trace silver analysis and an acceptable electrode lifetime. Analytical performances of the method and the PTH/Ag interaction were investigated using cyclic voltammetry (CV), differential pulse anodic stripping voltammetry (DPASV), scanning electron microscopy (SEM) coupled to energy-dispersive analysis of X-ray (EDAX) and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Reagents and materials

Thiophene (98%), dithizone, Nafion, 2,3-dibromthiophene, pyrrole, acetonitrile (HPLC grade) and tetrabutylammonium hexafluorophosphate (TBAHFP) were obtained from Aldrich (Steinheim, Germany). $AgNO_3$, $Cr(NO_3)_3$, $Cd(NO_3)_2$, $CuSO_4$, $ZnCl_2$, $FeCl_3$, $Ni(NO_3)_2$ and $K_2Cr_2O_7$ were all purchased from Riedel de Haen (Germany). Supporting electrolyte KNO_3 was from Panreac (Barcelona, Spain). All other chemicals used were of reagent grade. Solutions were prepared using deionised doubly distilled water with a measured resistance less than $15\,\mu S\,cm^{-1}$. Nitrogen (98%) used to purge electrochemical reaction media was obtained from Air Liquide (France).

2.2. Voltammetric techniques

All the electrochemical measurements were performed with an Autolab PGSTAT20 (Ecochemie, Utrecht, The Netherlands). The experiments were carried out in a three-electrode cell of 25 mL at room temperature (298 K) under nitrogen atmosphere; the counter electrode was a platinum wire (0.3 mm) and a Ag/AgCl, 3 M KCl electrode was used as the reference. A platinum electrode (0.35 mm i.d.) was used as the working electrode; its surface was polished with 0.5 μm alumina powder and then cleaned by ultrasonication prior to polymer electropolymerisation. Differential pulse anodic stripping voltammetry and cyclic voltammetry were the electrochemical techniques applied to study the behaviour of the modified platinum electrode. Instrumental parameters for DPASV were as follow: pulse amplitude ±60 mV, pulse repetition time 0.4 s, modulation time 0.06 s; a preconcentration potential of −0.5 V was applied for 2 min under stirring and a rest period of 5 s, followed by a potential scan from 0 to 0.7 V. Cyclic scan for CV were carried out between −0.25 and 1.25 V at a scan rate of $100\,mV\,s^{-1}$. After each measurement, the cleaning of the modified electrode was carried out by application five cycles of a potential scan from −1 to 1 V.

2.3. Preparation of the polythiophene-modified platinum electrode

The electropolymerisation of PTH was carried out as described previously [12], with the following modifications: the polymer synthesis was realized at 273 K in a cell containing deaerated acetonitrile, 0.01 M TBAHFP and 0.1 M thiophene. The synthesis was initiated by CV, scanning toward positive potentials from 0 to 1.6 V at a scan rate of $100\,mV\,s^{-1}$. After electrosynthesis, the PTH films were kept for a few minutes at a reducing potential, in contact with the original electrolyte anion, for undoping.

2.4. Scanning electron microscopy (SEM) measurements

To carry out these measurements, the microscope, a JSM 5400 type (JEOL, Japan), was coupled to the analyser, a link type with a Si/Li detector and an ultra thin window. The PTH film electrode were washed then dried; the films were then introduced into a high vacuum system before application of electron beam.

2.5. Electrochemical impedance spectroscopy measurements

The electrochemical impedance spectroscopy (EIS) measurements were performed with a Voltalab 100 type PGZ 10 from Radiometer. The impedance spectra were set up as described previously [13]. The initial frequency used was 100 KHz and the final one was 4 mHz with an ac amplitude of 10 mV. In order to insure the inert effect of PTH electrode during the experiment, a potential of 0.8 V was chosen.

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammograms of a modified electrode in absence of Ag(I), as well as those of a bare platinum electrode and a modified electrode, both in presence of Ag(I), were carried out. Neither the bare platinum electrode in presence of Ag(I) nor the modified electrode in absence of the ion, exhibited detectable peaks. On the other hand, when a modified electrode is dipped into a solution containing silver ion, a sharp anodic peak at around 0.15 V are observed. These results indicate the accumulation of Ag on the surface of the modified electrode, as consequence of a complexing interaction between silver ions and the polymer, that has been well described in literature [4,5], following by reduction of entrapped silver(I). The inductive effect of the C–S dipole, that makes the sulphur very reactive toward positively charged species, is one of the factors that explains the different behaviour of the polythiophene-modified electrode and the bare platinum electrode.

3.2. DPASV measurements

In order to explore the analytical performances of our system, the PTH electrode was immersed in a cell containing 0.2 M KNO_3 at pH 5. Ten microliters of a solution of $100\,mg\,l^{-1}$ Ag(I) was injected and a scan from 0 to 0.7 V was carried out. The modulation time was 0.06 s, the interval time was 0.4 s; a preconcentration potential of −0.5 V was immediately applied during 2 min under stirring followed by a rest period of 5 s. The

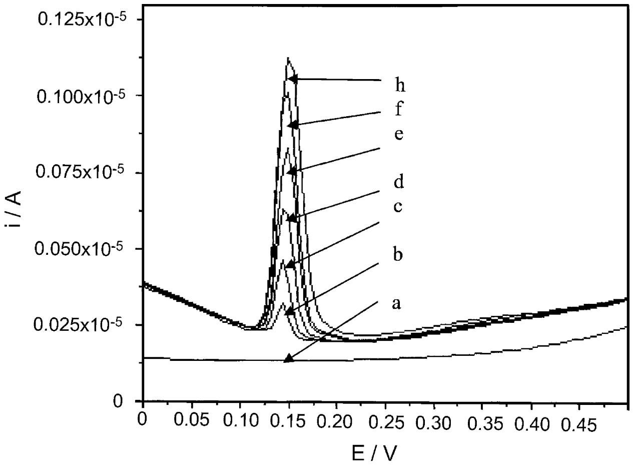

Fig. 1. DPASV response of the PTH-modified electrode in a solution of Ag(I); the concentration of the silver solution varies as follows: (a) supporting electrolyte; (b) 0.07; (c) 0.14; (d) 0.21; (e) 0.28; (f) 0.35; (h) 0.49 mg L^{-1}. Supporting electrolyte 0.2 M KNO_3 at pH 5.

stripping of silver(I) by a reoxidation process can be observed at 0.17 V thanks to the characteristic of the heavy metal anodic peaks. Fig. 1 shows the DPASV voltammograms obtained when increasing Ag(I) concentrations from 0.07 to 0.49 mg l^{-1}.

3.3. Influence of modifier and pH

The effect on the signal of Ag(I) of several polymers such as polypyrrole, polythiophene, Nafion, polydibromothiophene and dithizone, used as modifiers in the same conditions, were explored. PTH showed the higher peak current, consequently it was chosen to continue the studies.

The pH effect of the supporting electrolyte on the voltammetric behaviour of the PTH films versus Ag(I) species, was also investigated. Table 1 summarizes the results.

It clearly appears from these results that pH of supporting electrolyte plays an important role in the voltammetric response of the silver. Between pH 2 and 4 the peak of oxidation increased and reached a maximum value around pH 5; above pH 6 the peak height rapidly decreased, probably due to hydrolysis of the cation. Consequently, pH 5 was selected to carry out the determination. Finally it should be taken into consideration that hydrogen bonding between silver(I) and the sulphur atoms might also play a role in the electrochemical reduction of the cation.

Table 1
Effect of pH on the voltammetric response of the PTH-modified electrode

pH	I (A)
2	5.60×10^{-7}
3	7.00×10^{-7}
4	9.08×10^{-7}
5	1.04×10^{-6}
6	9.05×10^{-7}
7	7.05×10^{-7}
8	7.02×10^{-7}
9	6.59×10^{-7}
10	4.95×10^{-7}

Supporting electrolyte 0.2 M KNO_3; Ag(I) concentration 0.63 mg L^{-1}.

3.4. Calibration, reproducibility, detection limit and electrode stability

The reduction peak of the entrapped Ag(I) showed in the cyclic voltammogram of Fig. 1 was the signal used to determine the ion in solution. A calibration plot was carried out under the optimised conditions already described. A linear correlation between the concentration of Ag(I) and peak current for the range 0.07–1 mg L^{-1} was found, with a regression equation of $I_P = 3 \times 10^{-6} C - 2 \times 10^{-7}$ and a correlation coefficient, R^2, of 0.995. The test of reproducibility for 11 measurements of solutions containing a 0.63 mg L^{-1} concentration of Ag(I), carried out with electrodes polymerised each time, gave a relative standard deviation of 1.5%. Furthermore, there was no obvious deterioration of the electrodes during at least 2 weeks of successive operations. The detection limit, statistically calculated of the calibration plot as the concentration whose intensity is the intensity of the blank plus three times the standard deviation of the blank [14], was 0.06 mg L^{-1}. Such performance indicates that the modified electrode is very stable and reproducible and with a high response in addition with an easy and low cost preparation.

3.5. Study of interferences

The effect of several common metal ions on the Ag(I) signal was investigated. All the cations were submitted to the same preconcentration procedure described above; the scan in this occasion was realized from −1 to 0.75 V. The PTH-modified platinum electrode was immersed in a cell containing the support electrolyte and the procedure was run; then a standard addition of a solution containing Cr(III), Cd(II), Cu(II), Zn(II), Fe(III), Ag(I), Pb(II), Ni(II) (0.63 mg L^{-1} each) was done and the procedure again run. Fig. 2A shows the voltammogram of the

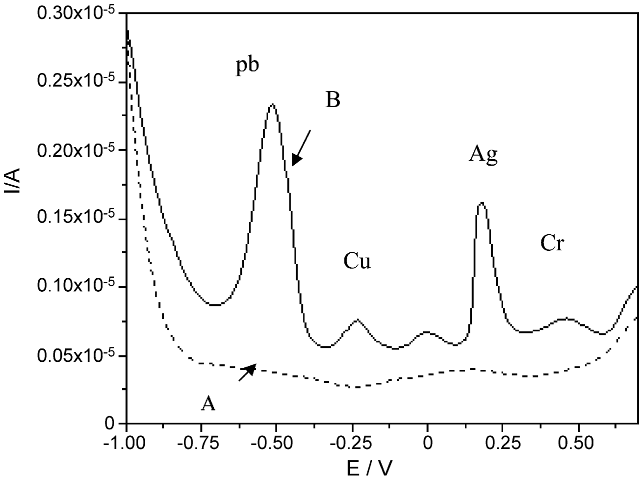

Fig. 2. DPASV on a PTH-modified electrode (A) solution of KNO_3 (0.2 M) supporting electrolyte; (B) solution containing a mixture of Cd(II), Cr(III), Cr(VI), Zn(II), Ni (II), Fe(III), Cu(II), and Ag(I) (0.63 mg L^{-1} each).

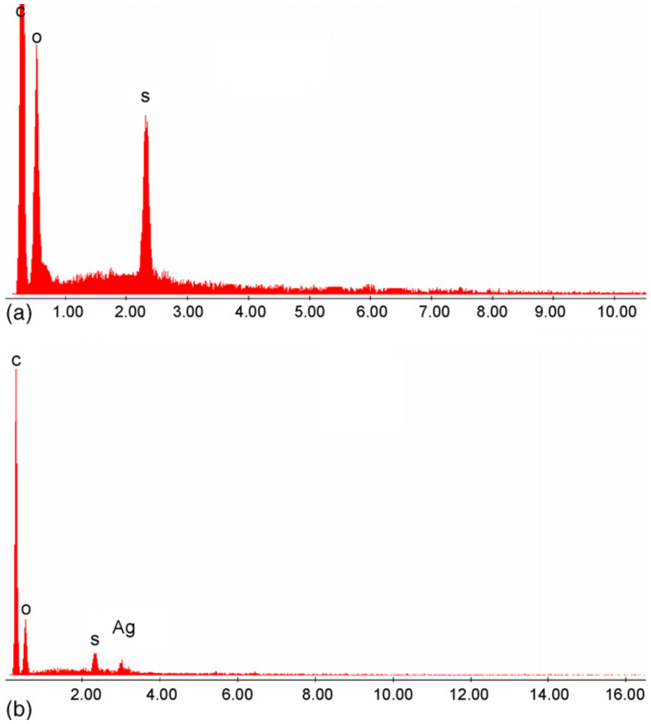

Fig. 3. EDAX spectra of (a) PTH film; (b) PTH film after being in contact with silver.

support electrolyte. Several well defined and separated peaks are observed in Fig. 2B; one of them can be attributed to silver (as compared to pure Ag(I) experiment) and another peaks attributed to other metals, but the values of their E_P are far from the position of Ag(I). This results clearly show the great selectivity of the modified electrode, which could be used to determine Ag(I) in waters without any harmful interference from other common metal ions.

3.6. SEM–EDAX measurements

To verify and confirm the silver presence in our polymer films, EDAX measurements were performed on both the silver-free and -containing PTH films. Fig. 3a shows the EDAX spectrum of the PTH film. As can be seen, no silver is detected in the film under the equipment sensitivity range. As expected, we can notice in the EDAX spectra a significant amount of sulphur coming from the thiophene structure of the PTH. On the other hand, Fig. 3b clearly shows silver content in the spectra of the films previously put in contact with Ag(I). It seems probably due to the strong silver–sulphur atom interaction. Fig. 4 is a scanning electron micrograph picture of the PTH film after exposure to a solution of Ag(I) 0.63 mg L^{-1}. It can be seen that the polymer maintains its regular and granular (porous) structure

3.7. EIS measurements

In order to confirm the mechanism suggested in the voltammetric part of this work regarding to the PTH/Ag(I) interaction, we have performed some EIS measurements. The impedance spectra (Fig. 5) were collected at 800 mV (versus SCE) in a frequency range from 100 to 4 mHz with an ac amplitude of 5 mV. The potential of 0.8 V was chosen in order to ensure the stability of the PTH/Ag(I) films during the measurements. Fig. 5a shows the Nyquist plot for the silver-free PTH-modified electrode. The high frequency arc observed may be associated to charge transfer at the PTH/solution interface. If we admit the Randel equivalent circuit model, the calculated (Voltamaster® 4.0 software) charge transfer resistance R_{ct} and the double layer capacitance C_d are, respectively: 38.92 kΩ cm^2 and 1 μF cm^{-2}. These data are typical of metal electrodes covered with polymeric films. On the other hand, Fig. 5b also exhibits an arc like Nyquist plot for the PTH/Ag(I) system. The electrical parameters calculated were: $R_{ct} = 30.3$ kΩ cm^2 and $C_d = 1.3$ μF cm^{-2}. It appears clearly from these data that the capacitance at the interface increases when the PTH film is exposed to Ag(I). The observed decrease of the charge transfer resistance means also that the modified electrode becomes more conductive which can be explained by the presence of silver on the electrode surface.

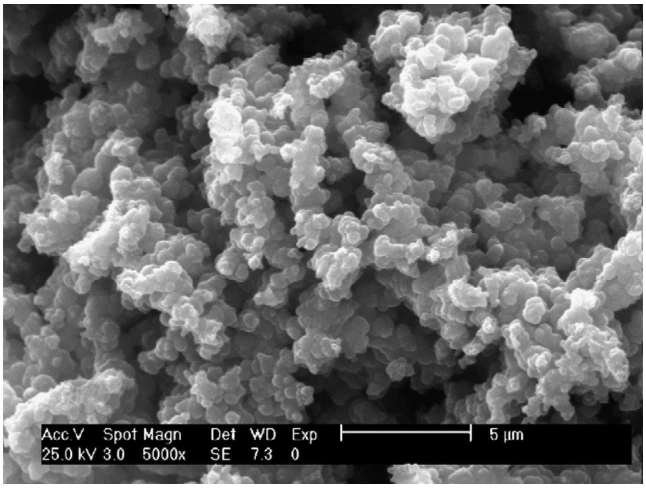

Fig. 4. Scanning electron microscopy (SEM) obtained at 25.00 KV with a 10,000× zoom of (a) PTH-modified electrode; (b) PTH-modified electrode after exposure to a Ag(I) solution.

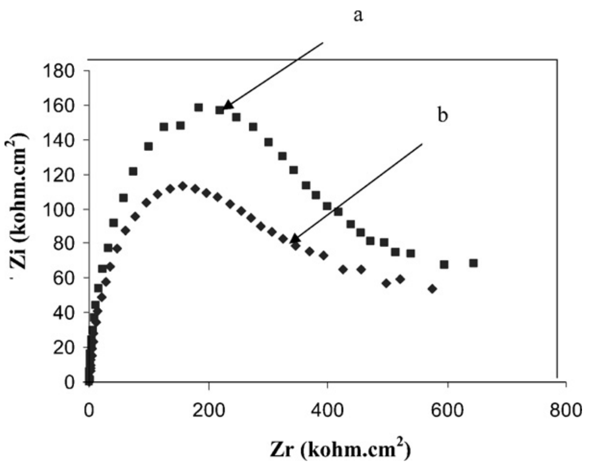

Fig. 5. Impedance spectra at 1000 V (vs. SCE): (a) PTH-modified electrode; (b) PTH/Ag(I).

3.8. Analysis of real samples

The analytical performance of the method was assessed by determination of silver in wastewaters, where possible interference due to complexity of the matrix can occurs. The samples were collected from four sites of the zone of Tangier, near to the places where the wastes were dumped: Oued El Kabire (S_1), Bay of Tangier (S_2), an industrial plant (S_3) and Malabata (S_4). The results were compared with those obtained by AAS; no silver was detected for samples S_1, S_2, S_4, as in electrochemical analysis; the concentration values obtained for sample S_3 by AAS ($0.11\,\mathrm{mg\,L^{-1}}$) were similar than those obtained by electroanalysis ($0.12\,\mathrm{mg\,L^{-1}}$), with a R.S.D. for the last technique of 1.9%.

4. Conclusion

The modified polythiophene platinum electrode proposed in this paper for the determination of ion silver shows good sensitivity and reproducibility and a great selectivity for Ag(I). Furthermore, it is of easy preparation, operation and regeneration, and can be used for more of 2 weeks of consecutive measurements. Its possibilities for field and on-site applications are being investigated.

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