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Preconcentration and electroanalysis of silver species at polypyrrole film modified glassy carbon electrodes

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Dedicated to Fred C. Anson for his distinguished contributions to electrochemistry

Abstract

Silver species can be entrapped in electropolymerized polypyrrole films without deliberate incorporation of chemically active counterions. The effects of polypyrrole coverage and preparation condition, oxidation states, solution composition, pH and the presence of other metal ions on the preconcentration have been investigated. Experimental results showed that the peak current and the integrated charge for incorporated silver species showed good linear concentration dependence in the range of 2–150 μM. The detection limit was estimated to be about 2 μM (about 0.2 ppm Ag). Most of the metal ions studied, including cobalt, nickel, cadmium, lead, zinc and iron, did not show obvious interference on the determination. Copper and mercury species were also extracted onto polypyrrole film electrodes and caused significant interference in the determination of silver species. The mechanism involved in the preconcentration of silver species at polypyrrole electrodes was explored. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Polymer film deposition is possibly one of the most versatile approaches for preparing chemically modified electrodes. Electropolymerization of heteroaromatic compounds at electrode surfaces has become one of the many effective ways to produce chemically modified electrodes with high electrical conductivity [1]. Among the various conducting polymers, polypyrrole (PPy) is one of the most frequently investigated. PPy film modified electrodes can be easily prepared by electrochemical oxidization of the pyrrole monomers in aqueous or non-aqueous media [2,3] and PPy can be used as a conducting substrate to incorporate different functional groups for different purposes [2–6]. The potentiometric responses of PPy film electrodes to anions and cations have been studied extensively [7–12]. The attachments of hetero- and iso-polyanions in PPy films have been reported and have shown applications in electrocatalysis [13,14]. Glucose oxidase can be immobilized onto PPy films during electropolymerization and the modified electrode obtained can be applied to the detection of glucose [15,16].

Wallace and coworkers [17,18] have reported the application of PPy containing chemically active counterions for analytical purposes. They reported the preconcentration and determination of silver species on PPy electrodes incorporated with various counterions, including chloride, bromide, perchlorate, 2,6-pyridine dicarboxylic acid, and ethylenediamine tetraacetic acid [17]. The uptake of silver ions possibly resulted from the combination of the precipitation by chloride or bromide ions and the complexation interactions due to the presence of complexing ligands in the polymer. However, they reported that the silver species loaded on the PPy–Cl electrode surface was difficult to remove, resulting in poor reusability [17].

Recently, Wong and coworkers [19] have reported the extraction of silver species by PPy films that had undergone a base–acid treatment. The base–acid treatment was employed to dedope the PPy for 5 h in 0.5 M NaOH, followed by a 20 h preconcentration of silver in

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0.5 M HNO$_3$. Their results showed that the acid treatment of the deprotonated PPy resulted in reprotonation of the film and the recovery of PPy to the oxidized state. In the presence of silver ions (0.5–25 ppm) in 0.5 M HNO$_3$, electroless reduction took place and the silver metal was entrapped in the PPy structures. The amount of silver entrapped in pretreated PPy films was determined by voltammetric stripping analysis. The extraction of silver resulted from electroless reductive deposition on the PPy films. However, the overall process required extensive time for the base–acid pretreatment and preconcentration.

One of our research interests is to develop possible applications of conducting polymer modified electrodes in electroanalytical chemistry and to improve the selectivity and sensitivity of the analysis. Shiu and coworkers [20–22] have reported that some complexing ligands, such as alizarin red S, bathophenanthroline disulfonate and bathocuproine disulfonate, became incorporated into PPy films during electropolymerization and the modified electrodes obtained were found to show sensitivity to copper species (both Cu$^+$ and Cu^{2+} ions). However, there have been very few reports so far on the electroanalytical determination of metal ions at PPy film electrodes without deliberate incorporation of chemically active counterions. In this study, the incorporation of silver species and the interaction mechanism between the PPy films and metal ions have been examined. The results showed that silver species could be extracted onto electropolymerized PPy film electrodes without incorporated precipitants or complexing ligands.

2. Experimental

Pyrrole was obtained from Aldrich (Milwaukee, WI, USA) and was distilled under reduced pressure before use. All other chemicals used were of reagent grade. All solutions used were prepared using doubly distilled deionized water. Electrochemical experiments were performed using a BAS 100B/W electroanalytical analyzer (Bioanalytical Systems Inc., West Lafayette, IN, USA) in a conventional three-electrode arrangement, equipped with a glassy carbon working electrode, a platinum counter electrode and an Ag│AgCl reference electrode. The reference electrode was connected using a salt bridge with 0.2 M KNO$_3$ solution in order to avoid interference from chloride ions. Potentials are quoted versus the Ag│AgCl reference. Glassy carbon electrodes (3.0 mm diameter, obtained from Bioanalytical Systems Inc.) were polished using 1.0 and 0.3 μm alumina powder and cleaned in an ultrasonic bath before use. Electrolyte solutions were degassed before being subjected to voltammetric experiments. All electrochemical measurements were conducted at room temperature of about 20°C.

PPy–NO$_3$ films were prepared from 0.1 M pyrrole (Py) + 0.2 M KNO$_3$ solutions employing chronocoulometry at +0.9 V for different periods of time (0.2 to 10 s). The charge consumed during electropolymerization of pyrrole was used for the control and estimation of the film thickness. Freshly prepared PPy film electrodes were subjected to continuous potential scans (from +0.6 to −0.7 V) at 100 mV s^{-1} for ten cycles in acidified 0.2 M KNO$_3$ electrolyte (pH 2) to remove excess hydrogen ions, monomers and oligomers present in the PPy films. The PPy film electrode was generally held at an end potential E_e of −0.7 V for conditioning. Preconcentration of silver species in the PPy film under open-circuit potential was usually performed by simply immersing the PPy film electrode in the silver nitrate solution for 10 min. The PPy film incorporated with silver species was rinsed thoroughly with deionized water and then voltammetric determination of the silver content was carried out in fresh supporting electrolyte. Usually, voltammetric measurements were conducted with a scan rate of 100 mV s^{-1}.

X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) measurements of the surface structures of the PPy film electrodes were performed with a VG Clam4 spectrometer (Vacuum Generator Inc., UK) using an Al–K$_\alpha$ X-ray source with an energy of 1486.6 eV. The pressure in the analysis chamber was usually maintained at around 2×10^{-7} Pa during measurements. Glassy carbon disks of 5 mm diameter were obtained by wire-cutting a glassy carbon rod (Atomergic Chemetals Corp., Farmingdale, NY, USA) into pieces 2 mm thick. The glassy carbon disk was then mounted onto a Teflon sheath. The glassy carbon disk electrode was polished thoroughly and electropolymerization of pyrrole was conducted by continuous potential cycling between 0 and +1.0 V. The PPy film electrode was exposed to silver nitrate solution as usual. The electrode was then washed thoroughly with deionized water and the air-dried carbon disk was removed from the Teflon sheath and subjected to XPS and AES measurements.

3. Results and discussion

3.1. Preconcentration and voltammetric behavior of silver species at PPy film electrodes

The preconcentration of metal ions on the surface of electrodes can be carried out generally in two ways: electrochemical deposition and chemical incorporation via complexation, redox and precipitation reactions or by an ion exchange process. In this work, no potential was applied during preconcentration, so only chemical incorporation was possible during the preconcentration. Wallace and coworkers [17,18] reported that silver spe-

cies could be preconcentrated on PPy films previously incorporated with different precipitants and complexing ligands. The possible preconcentration of silver species at PPy film without previous incorporation of complexing ligands or precipitant was investigated.

A freshly prepared PPy–NO$_3$ film electrode was conditioned by potential cycling with a final potential of −0.7 V. It was expected that PPy films thus obtained would be in the reduced state. The charge for the preparation of PPy film was usually of about 2.2 mC, corresponding to a PPy coverage of about 1.4×10^{-7} mol cm^{-2}, assuming that the electrochemical polymerization process of pyrrole involved 2.3 electrons [23]. After being immersed in a 0.1 mM AgNO$_3$ solution for 10 min under open-circuit conditions, the PPy film electrode was subject to voltammetric measurements in a blank 0.2 M KNO$_3$ electrolyte solution at pH 2. Fig. 1(a) shows the cyclic voltammogram of a PPy film electrode incorporated with silver species. For simplicity, only the first cycle is shown. A large anodic peak was observed at +0.46 V when PPy was exposed to silver species. A small cathodic peak was observed at −0.30 V. The anodic peak current varied with the concentration of silver species in the test solution. The peak current also decreased gradually on continuous

cycling, which was probably due to the electrochemical degradation of the polymer, as reported elsewhere [20].

Fig. 1(b) shows the background voltammetric response of the PPy film electrode in pure supporting electrolyte. It should again be pointed out that no precipitants or complexing ligands were present in the PPy film electrode. This indicated that silver species had been preconcentrated on the PPy film electrode after exposure to silver species. The anodic peak at +0.46 V should correspond to the oxidation of silver metal and the corresponding peak current (or integrated charge) could be used as the signal for the quantitative analysis of silver species in solution. The cathodic peak at +0.30 V corresponded to the reduction of the oxidative silver species incorporated in the PPy film. The peak separation was about 150 mV. The peak width at half height was only 50 mV for the oxidation of silver species at the PPy film electrode. The cathodic process also produced a broad tail extending to zero potential and the reduction peak current was much smaller than the oxidation peak current.

Experimental results showed that silver species were also adsorbed on a bare glassy carbon electrode (GCE), as shown in Fig. 1(c). However, the peak current was about tenfold smaller than that obtained at a PPy film electrode. This indicated that the incorporation of the silver species resulted mainly from the bulk of the PPy film rather than the GCE substrate. The sensitivity for the determination of the silver species at the PPy film electrodes improved significantly. The incorporation of silver species at PPy film might result from the electroless reduction of silver species [19], or the formation of a complex between silver ions and the amine groups of PPy [10,24].

The effects of the composition of the supporting electrolyte on the measurement results were investigated. The two parameters explored included chloride ion concentration and pH. The acidity of the supporting electrolyte affected the voltammetric behavior of PPy film in the potential range from −0.6 to +0.1 V. However, there was no significant change in the peak shape of silver species incorporated in a PPy film electrode when the pH changed. Detailed voltammetric parameters obtained at different pH values for the silver species incorporated in PPy film electrodes are listed in Table 1. There was no significant difference in the anodic peak potential E_{pa} of silver species incorporated in PPy film electrodes between pH 2 and 6. Both the anodic peak current I_{pa} and the integrated charge Q_{pa} increased with decreasing pH. This might be related to the higher conductivity of the PPy film in strongly acidic solution. In addition, our experimental results showed that the reproducibility for the repeated usage of the same PPy film electrode was better at pH 2. The PPy film was found to degrade gradually with increasing use and repeated scans at pH 6. Therefore, an
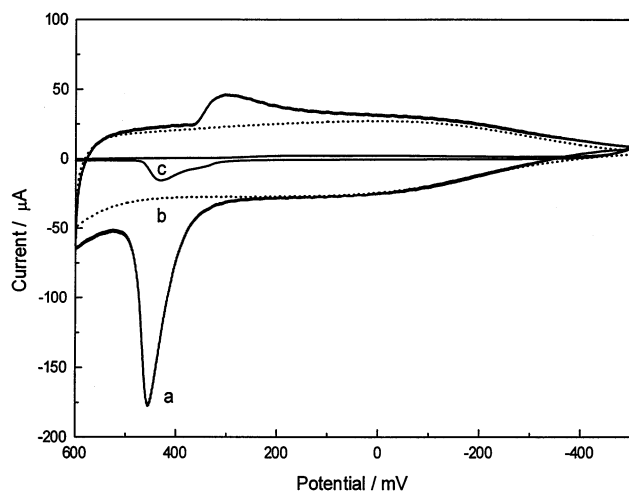

Fig. 1. Cyclic voltammograms of (a) a PPy film electrode incorporated with silver species; (b) the background response of the PPy electrode; (c) a bare GCE with adsorbed silver species. Supporting electrolyte: acidified KNO$_3$ solution at pH 2. Note: the cathodic current is taken as positive.

Table 1
Voltammetric parameters for PPy film electrodes incorporated with silver species

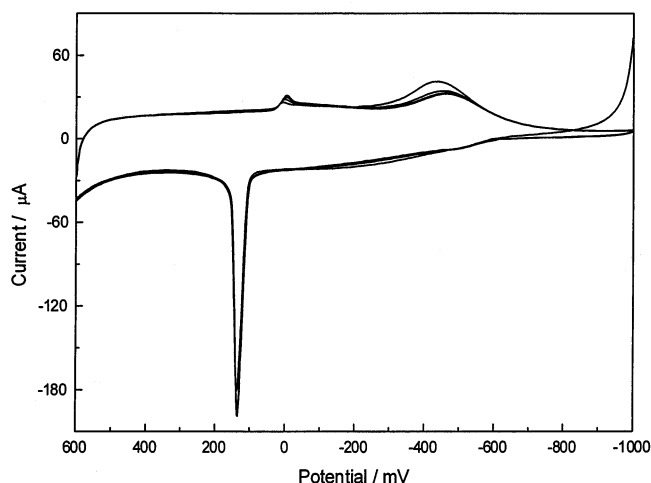| pH	E_{pa}/mV	I_{pa}/μA	Q_{pa}/μC
2	+457	145.9	53.8
4	+460	106.7	44.3
6	+458	85.5	39.5

Fig. 2. Cyclic voltammograms of silver species incorporated in a PPy electrode in 0.2 M NaCl solution. $[Ag^+] = 0.1$ mM; preconcentration time: 10 min; scan rate: 100 mV s^{-1}. Note: the cathodic current is taken as positive.
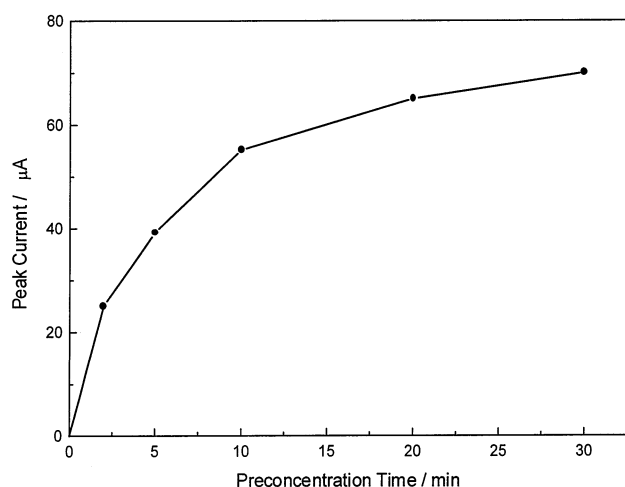

Fig. 3. Effects of preconcentration time on the anodic peak current resulting from silver species incorporated in PPy electrodes. $[Ag^+] = 50$ μM.

Table 2
Effect of solution composition during preconcentration on the silver incorporation at PPy electrodes

Solution composition	I_{pa}/μA	Q_{pa}/μC
Pure 0.1 mM AgNO$_3$	143	56.3
0.1 M KNO$_3$ + 0.1 mM AgNO$_3$	152	61.5
0.1 M HNO$_3$ + 0.1 mM AgNO$_3$	68.8	24.9

acidified KNO$_3$ solution (pH 2) was chosen as the medium for the determination of silver species incorporated in PPy film electrodes.

Experimental results showed that the presence of chloride ions in the supporting electrolyte significantly affected the electrochemical behavior of the silver spe-

cies incorporated in PPy films. Fig. 2 shows the cyclic voltammograms of silver species incorporated in the PPy electrode in 0.2 M NaCl solution. In the presence of chloride ions, the oxidation potential of incorporated silver species, at a value of +0.13 V, was about 300 mV more negative than that obtained in acidified KNO$_3$ solution. The peak width at half height was only about 25 mV, which was about half of that obtained in KNO$_3$ solution. This behavior was probably caused by the precipitation reactions between chloride and silver ions. It was also very difficult to remove the silver species completely from the polymer film. This caused a serious problem in the possible reusability of PPy film electrodes. The results agreed with those reported by Wallace and Lin [17]. It should be pointed out that a KNO$_3$ salt bridge was used to separate the reference electrode from the supporting electrolyte solution during voltammetric measurements, so as to avoid interference from chloride ions.

3.2. Effects of preconcentration conditions

3.2.1. Preconcentration time

The preconcentration time dependence of the peak current resulting from silver species incorporated in PPy film was examined and the results are shown in Fig. 3. The concentration of silver species in the exposure solution was 50 μM in this study. The polymerization charge for the preparation of PPy film was also 2.2 mC, corresponding to a PPy coverage of 1.4×10^{-7} mol cm^{-2}. The peak current increased sharply at short preconcentration time and then increased gradually, finally approaching a saturation value of 70 μA after 30 min. The results indicated that the preconcentration of the silver species at a PPy film electrode was a fast process and a 10 min preconcentration time was chosen in this study.

3.2.2. Test solution pH

The effects of the composition and pH of the test solution on the preconcentration efficiency of silver species at PPy films were explored. The PPy films were prepared as usual and conditioned by potential cycling with an end potential of −0.7 V. Following preconcentration in different test solutions containing the same concentration of silver species, electrochemical measurements were performed in KNO$_3$ electrolyte at pH 2; the results are given in Table 2. The charge for the PPy film electrode examined was 3.7 mC, corresponding to a coverage of about 2.3×10^{-7} mol cm^{-2}. The anodic peak charge for incorporated silver species was 56.3 μC, corresponding to a silver coverage of 8.3×10^{-9} mol cm^{-2}, when the electrode was exposed to a pure 0.1 mM silver nitrate solution. The corresponding peak charge obtained in neutral 0.1 M KNO$_3$ electrolyte was slightly greater than that obtained in pure

silver nitrate solution. In contrast, if the test solution contained 0.1 M HNO$_3$, both the peak current and integrated charge resulting from incorporated silver species were less than one half of the corresponding values obtained in pure silver nitrate solution. It is obvious that the 0.1 M KNO$_3$ solution would serve better as the medium for the extraction or preconcentration of silver species at PPy film electrodes.

Experimental results showed that the amounts of silver species incorporated at PPy film electrodes decreased significantly in the highly acidic solution. This also suggested that the formation of a complex between silver ions and the amine groups of PPy might occur, as proposed by Chen and coworkers [10,24]. Hydrogen ions competed well with silver ions for the nitrogen sites present in the PPy backbones and the presence of the high hydrogen ion concentration might enhance the dissociation of the silver–PPy complex. Literature data usually indicated that there were higher affinities between hydrogen ions and nitrogen-based ligands, such as pyridine, pyrrolidine and bipyridine, than the corresponding silver complexes [25]. The addition of nitrate ions to the test solution would also assist the neutralization of the positive charges caused by the incorporation of the silver ions on PPy films.

3.2.3. Oxidation states of PPy films

The effect of the oxidation states of the PPy film on the silver response was studied by controlling the end potential employed during the conditioning of PPy electrodes. Preconcentration of silver species at a thin PPy film electrode with a polymer coverage of 1.3×10^{-7} mol cm^{-2} (at different oxidation states) was conducted by exposing the electrode to a neutral solution containing 0.1 M KNO$_3$ + 0.1 mM AgNO$_3$, followed by voltammetric measurements as usual. The results are listed in Table 3. When the end potential was -0.7 V, at which the PPy was in the reduced state, the anodic peak current and the integrated charge obtained were three times as great as those for the oxidized PPy film conditioned with an end potential of $+0.6$ V. This showed that the amount of silver species preconcentrated on the PPy film was related to the redox state of the PPy film. Furthermore, when a thick PPy film at a coverage of 6×10^{-6} mol cm^{-2} in the reduced state was immersed in 1 mM AgNO$_3$ for 30 min, visible

smooth silvery white deposits were observed on the surfaces of the polymer electrode. The deposits could not be removed, even by repeated rinsing with deionized water. On the contrary, no apparent silvery white deposits were observed on the thick PPy film in the oxidized state when exposed to silver nitrate solution. The results suggested that the preconcentration of the silver species was partially (or primarily) due to the electroless (chemical) reduction of silver cations and deposition of metallic silver on the PPy film electrodes in the reduced state. Wong and coworkers [19,26] reported on the electroless reduction preconcentration of silver and mercury species in base–acid-treated PPy film. However, the effect of the end potential of the PPy film was not examined in their studies.

Interestingly, virtually no incorporation of silver species on the oxidized PPy film was observed when the preconcentration was performed in a strongly acidic medium (0.1 M HNO$_3$ + 0.1 mM AgNO$_3$). Under these preconcentration conditions, neither electroless reduction of silver nor complex formation took place. The presence of hydrogen ions at high concentration hindered the possible complex formation between PPy and silver ions. The oxidized state of PPy obviously did not favor the electroless reduction of silver ions either. In contrast, a peak current of 43 μA (or an integrated charge of 14.8 μC) was obtained for incorporated silver species when the same oxidized PPy electrode was immersed in neutral silver nitrate solution. This observation suggested that the complex formation between silver ions and the amine groups present in PPy film also contributed to the incorporation of silver species. In addition, it seemed that the electroless reduction of silver ions at the reduced PPy film electrodes provided the major contribution.

3.2.4. PPy films with different dopants

The incorporation of the silver species on PPy films doped with different ions was investigated further. PPy films doped with chloride ions (PPy–Cl) can be obtained either by electropolymerization from pyrrole solution containing chloride ions or by ion-exchanging the counter nitrate ions of the PPy–NO$_3$ films with chloride ions. Experimental results showed that there was no significant difference in the electrochemical responses for PPy–Cl film electrodes obtained by the different means mentioned above. Following the preconcentration of silver species at reduced PPy films under identical conditions, voltammetric measurements were carried out in 0.2 M NaCl supporting electrolyte. The voltammetric response of silver species incorporated in the PPy–Cl film electrode was almost identical to that for a PPy–NO$_3$ film electrode immersed in NaCl electrolyte (Fig. 2). The voltammetric parameters for both PPy–NO$_3$ and PPy–Cl obtained in NaCl supporting electrolyte are summarized in Table 4. It is obvious

Table 3
Effect of end potential for film conditioning of PPy–NO$_3$ electrodes on the silver incorporation

End potential	I_{pa}/μA	Q_{pa}/μC
-0.7	136	48.6
0.0	123	47.8
$+0.6$	43	14.8

Table 4
Effect of dopant counterions in PPy films on the silver incorporation

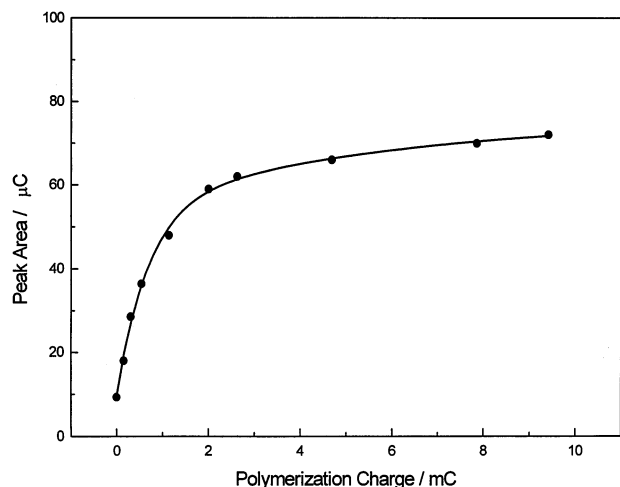| Film composition	E_{pa}/mV	I_{pa}/μA	Q_{pa}/μC
PPy–NO$_3$	+134	173	30.6
PPy–Cl	+136	174	31.5

Fig. 4. Effects of the polymerization charge on the anodic peak area of silver species incorporated in PPy electrodes. [Ag$^+$] = 0.1 mM; preconcentration time: 10 min.
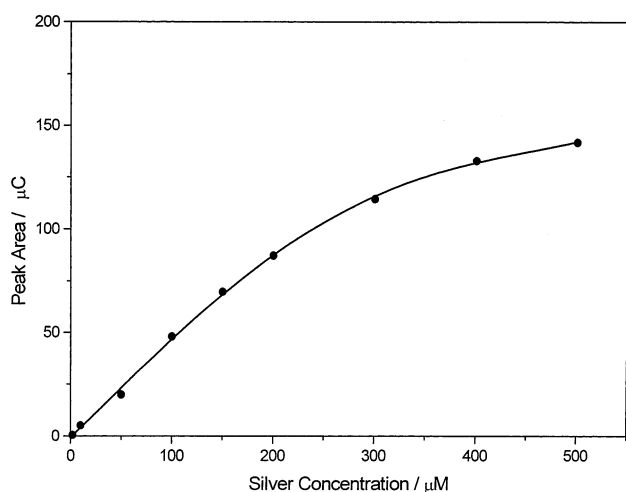

Fig. 5. Analytical calibration curve for the determination of silver species at PPy electrodes. Preconcentration time: 10 min.

that the anodic peak potential, peak current and peak charge were almost identical for both the PPy–NO$_3$ and PPy–Cl film electrodes. The results showed that there was no significant difference between the two PPy films.

However, when the end potential for film conditioning was +0.6 V, at which PPy was in the oxidized or doped state, the surface concentration of chloride counterions in the PPy–Cl film should be greater than that in the reduced or dedoped PPy film. After preconcentration of silver species, the peak current obtained at the oxidized PPy film would be greater than that obtained at the reduced PPy film if the preconcentration of silver species resulted mainly from the precipitation reaction of chloride ions. However, experimental results showed that the peak current obtained in NaCl supporting electrolyte was only about 70 μA at the oxidized PPy film after incorporation of silver species, which was significantly smaller than that obtained at a reduced PPy film. These results indicated that the incorporation of silver species on PPy films resulted mainly from the PPy film itself and not the chloride counterions incorporated into the PPy films. It was demonstrated further that the electroless reduction was the main cause of the preconcentration of silver species at PPy film electrodes. Wallace and coworkers [17,18] reported on the incorporation of silver ions on the PPy film containing chemically active counterions. However, they did not report whether the silver ions were preconcentrated on PPy films without chemically active counterions; neither did they report the effects of the end potential of the PPy film electrodes on the silver responses.

In addition, experimental results showed that the PPy films doped with trifluoroacetate and tetrafluoroborate ions (prepared from non-aqueous acetonitrile medium) also displayed similar silver responses. This indicated that the silver response of PPy film electrodes resulted mainly from the PPy films themselves and was independent of the composition of the PPy films or the dopant anions.

3.2.5. Polymerization charge dependence

Fig. 4 shows the dependence of the anodic peak area (integrated charge) of silver species incorporated in PPy film on the oxidation charge during electropolymerization. It was assumed that the polymer film thickness and the surface coverage of pyrrole were both proportional to the polymerization charge. The anodic peak charge increased with increasing polymerization charge (polymer coverage). There was no significant difference in peak area (integrated charge) when the polymerization charge was more than 3 mC, or of a PPy coverage of about 1.9×10^{-7} mol cm^{-2}. This again indicated that the incorporation of silver species was related to the thickness or the PPy coverage and resulted mainly from the PPy film itself rather than the glassy carbon substrates. Additionally, this seemed to suggest that silver species were entrapped in the PPy film and the interaction was actually occurring throughout the bulk of the polymer.

3.3. Concentration dependence of the characteristic peak charge

Fig. 5 shows a typical calibration curve for the determination of silver species at PPy film electrodes. The PPy coverage was estimated to be about 1.9×10^{-7} mol cm^{-2} for this study. The integrated charge for the incorporated silver species increased with the silver concentration in the exposure solution. The linear range was from 2 to 150 μM, with a slope of 0.47 C M^{-1} and a correlation coefficient of 0.999. The anodic peak charge reached a constant value of 142 μC, corresponding to a silver coverage of 2.1×10^{-8} mol cm^{-2}, when the silver concentration was about 0.5 mM. This indicated that the incorporation of silver species on the PPy film had reached saturation. The detection limit was estimated to be about 2 μM (0.2 ppm). If the preconcentration process was performed under stirring or the preconcentration time was increased to 30 min, the detection limit could be lowered to 0.2 μM (20 ppb). The reproducibility was found to be less than 10% R.S.D. for seven replicate preconcentration/measurement cycles. The mean value of the peak charge was about 48.0 μC at a silver concentration of 100 μM (without stirring).

The PPy film modified electrodes could easily be regenerated for repeated use. The silver species incorporated in the PPy film electrode was readily removed from the polymer film by simple immersion of the PPy–Ag film in 1 M HNO$_3$ solution for a few minutes. A cyclic voltammogram almost identical to Fig. 1(b) was observed after treatment with nitric acid, indicating that the incorporated silver species had been completely removed from the PPy electrode. Experimental results for the reusability study are shown in Fig. 6. The integrated charge for incorporated silver species decreased gradually with the number of repetitive uses. A decrease of about 18% in peak charge was observed after ten successive preconcentration/determination cycles. Meanwhile, the polymer background response decreased after each preconcentration and determination cycle. According to the measurement of the background current of PPy at $+0.4$ V, the polymer background response decreased by about 30% after ten replicate measurements. The decrease in the integrated charge resulting from the silver species incorporated in the polymer was possibly caused by the decrease of the polymer coverage or activity. If the gradual loss of the polymer activity was not recognized, the reproducibility was about 9.6% R.S.D. for ten replicate preconcentration/measurement cycles in a 0.03 mM AgNO$_3$ solution using the same PPy film with a polymerization charge of 2.3 mC. In the presence of chloride ions, AgCl precipitates formed at the PPy electrodes and were very difficult to remove completely from the PPy electrode. Although the silver species can be removed through a complicated chemical treatment, e.g. immersion in concentrated ammonia for 10 min and then in 1 M HNO$_3$ for 5 min, the reusability was found to be very poor, consistent with that reported by Wallace and Lin [17].
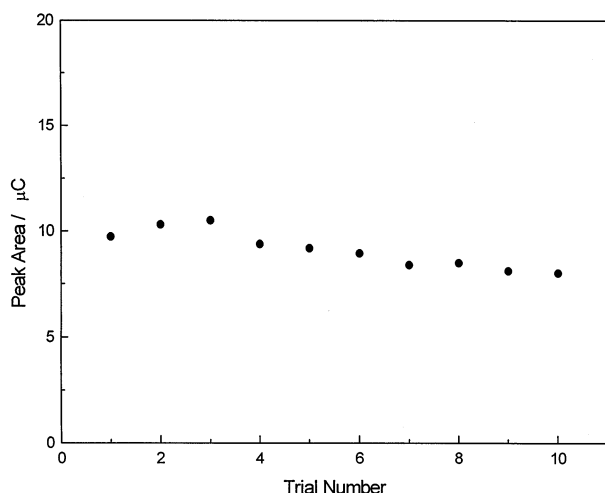

Fig. 6. Reusability data of PPy electrodes in the electroanalysis of silver species. [Ag$^+$] = 30 μM; preconcentration time: 10 min.

Table 5
Interference data for the voltammetric determination of silver species at PPy film electrodes

Interferent	Relative I_{pa}	Relative Q_{pa}
Ag$^+$	100.0	100.0
Ag$^+$/Cd^{2+}	105.2	104.0
Ag$^+$/Co^{2+}	107.1	106.0
Ag$^+$/Fe^{3+}	90.0	90.9
Ag$^+$/Ni^{2+}	91.0	92.0
Ag$^+$/Pb^{2+}	92.0	93.1
Ag$^+$/Zn^{2+}	91.9	93.1
Ag$^+$/Cu^{2+} (1:1)	98.0	98.0
Ag$^+$/Cu^{2+} (1:10)	40.0	42.0

3.4. Interferences

The interference of silver incorporation at PPy electrodes from heavy metal ions has been investigated. Interference studies were conducted by exposing the PPy film electrode in a solution containing 0.05 mM silver nitrate and the interfering ions for 10 min at open-circuit potential. Voltammetric measurements were performed as usual. Voltammetric responses resulting from the presence of interfering ions were then compared with that obtained for pure silver incorporation. For the pure silver nitrate test solution, the peak current (or peak charge) obtained was taken to be 100. Experimental results are shown in Table 5. In the presence of cobalt, nickel, zinc, lead, iron and cadmium at 0.1 mM, no significant interference was observed and the change in relative peak charge was usually less than
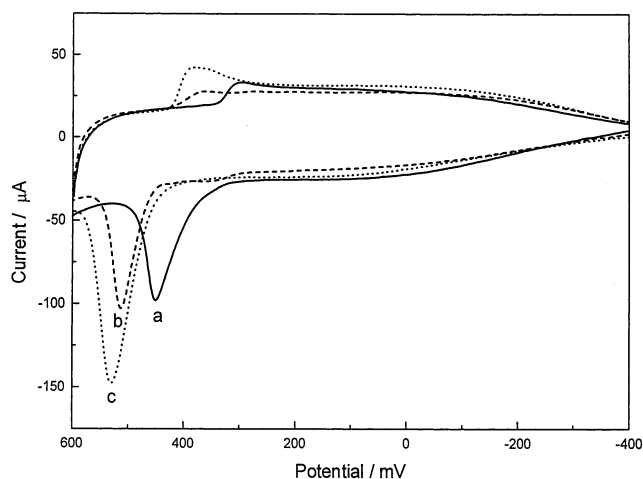
Fig. 7. Cyclic voltammograms of the PPy electrodes (a) after incorporation with silver species; (b) after exposure to mercury species; (c) after exposure to a solution containing both silver and mercury species. Note: the cathodic current is taken as positive.

10%. No additional voltammetric peak from these interferents was observed either. Copper ions at comparable concentration did not cause significant interference. However, the voltammetric peak charge resulting from the incorporated silver species decreased by 60% in the presence of 0.5 mM copper nitrate (at tenfold excess).

The presence of mercury ions caused serious interference in the determination of silver species. Fig. 7(a) shows the cyclic voltammogram of the PPy electrode incorporated with silver species. The anodic peak potential of incorporated silver species was about +0.45 V. Mercuric ions were found to be readily incorporated in PPy film electrodes. When a freshly prepared PPy electrode was exposed to mercuric nitrate solution, the resulting voltammogram gave an anodic peak at +0.53 V, as shown in Fig. 7(b). Interestingly, when the PPy electrode was exposed to a solution containing both silver and mercury species, only one anodic peak was observed at +0.53 V (Fig. 7(c)). This anodic wave was very similar to that observed for incorporated mercury species, except that there was a large increase in the peak current. 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. When electrodeposition of silver was conducted at PPy electrode previously incorporated with mercury species, the resulting voltammogram was almost identical to that shown in Fig. 7(c).

The above observations can be explained by the reduction of both the silver and mercury species in terms of their respective standard electrode potentials $E°$ [27]:

$$Hg^{2+} + 2e^- = Hg \quad E° = +0.854 \text{ V}$$

$$Ag^+ + e^- = Ag \quad E° = +0.799 \text{ V}$$
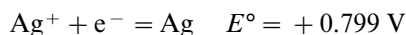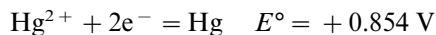
Both Hg^{2+} and Ag^+ ions are strong oxidizing agents, and could oxidize the reduced PPy and themselves become reduced to the metallic states at the PPy electrodes. Imisides and Wallace [28] have reported the deposition and electrochemical stripping of mercury ions on PPy-based modified electrodes, in which mercury ions were preconcentrated by electrodeposition at PPy film electrodes. Interestingly, our experimental results showed that mercury ions could be preconcentrated on PPy films under open-circuit conditions (i.e. no potential was applied) and then determined by electrochemical stripping in the blank supporting electrolyte solution. Preliminary results showed that the voltammetric peak current was also dependent on the mercury concentration in the test solution. Thus, this method could also be applied for the preconcentration and determination of mercury ions.

Additionally, interference studies suggested that the preconcentration of metal ions on PPy electrodes resulted mainly from the electroless reduction at the PPy films. The metal ions studied are all known to have moderate complexing abilities with amine groups. These ions are not strong oxidizing agents and no influence on the silver response was observed. This indicated that complex formation was not the major cause of the incorporation. If the preconcentration was mainly caused by complex formation, significant interference from these ions should be observed.

3.5. XPS and AES studies of silver deposition at PPy film electrodes

In order to obtain a better understanding of the preconcentration mechanism of silver species at PPy film electrodes, XPS was used to examine the chemical states of silver deposits and the structural differences of PPy films after silver incorporation. A representative thicker PPy film on a GCE was prepared by cyclic voltammetry in 0.1 M Py + 0.2 M KNO_3 solution with ten deposition cycles in the potential range from 0 to +1.0 V. The PPy coverage thus obtained was usually from 3×10^{-6} to 5×10^{-6} mol cm^{-2}, corresponding to a film thickness of about 2 to 4 µm. After pretreatment by continuous potential cycling in 0.2 M KNO_3 solution, PPy film electrodes in the oxidized and reduced states were prepared with end potentials of +0.6 and −1.0 V during film conditioning respectively. The wide-scan XPS spectrum of the oxidized PPy film before exposure to silver solution is shown in Fig. 8(a). Emissions of photoelectrons with different binding energies due to the presence of various elements (carbon, nitrogen and oxygen) were observed. Characteristic peaks corresponded to C 1s (285.2 eV), N 1s (400.2

eV), and O 1s (532.2 eV). These peaks were also observed for the oxidized PPy films after exposure to silver solution, as shown in Fig. 8(b). There were no observable changes in their respective binding energies upon silver incorporation. After exposure to silver nitrate solution, additional peaks were observed at 367.9 eV and 373.9 eV in Fig. 8(b). These two peaks were due to the Ag $3d_{5/2}$ and Ag $3d_{3/2}$ photoelectron emissions respectively. This indicated that silver species were present on the oxidized PPy film electrode after exposure to silver solution. Fig. 8(c) shows the XPS spectrum for the reduced PPy film electrode after exposure to silver solution. Likewise, the peaks corresponding to C 1s, Ag 3d, N 1s and O 1s photoelectron
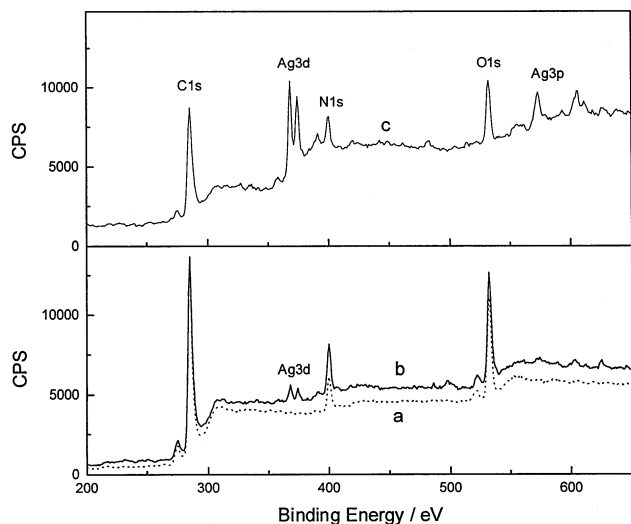
emissions were observed. There were no observable changes in their respective binding energies, even when a detailed XPS scan was conducted. The relative peak strengths for C 1s, N 1s and O 1s decreased, whereas Ag 3d peaks increased significantly compared with the oxidized PPy film shown in Fig. 8(b). Furthermore, the insensitive Ag 3p peaks at 573.2 and 605.2 eV became quite apparent on the reduced film (Fig. 8(c)). This indicated that a much larger amount of silver species was incorporated in the reduced PPy film. The results again demonstrated that the incorporation of silver ions at PPy film electrodes resulted mainly from the electroless reduction of silver ions on PPy films, consistent with the results of voltammetric measurements discussed above.

The appearance of silvery white deposits on the surface of the polymer electrodes after the exposure to silver solution confirmed the presence of metallic silver. This also suggested that redox reactions between silver ions and reduced PPy films were involved. Analysis using AES can provide additional information on the chemical states of the silver species deposited on PPy film electrodes. Fig. 9 shows the Ag MVV Auger electron spectra of silver species incorporated in the oxidized and reduced PPy films. Two Auger peaks, namely Ag M_4VV and Ag M_5VV, were observed for both the oxidized and reduced PPy films. The Auger peaks were at 1130.0 and 1136.1 eV for the oxidized PPy film, as shown in Fig. 9(a). There was a significant shift of 1.6 eV in the respective Auger peaks when the oxidation states of PPy film changed. For the Auger peak M_4VV, for silver species incorporated in the reduced PPy films shown in Fig. 9(b), the binding energy was found to be 1128.5 eV. The corresponding kinetic energy for the M_4VV Auger electron was then 358.1 eV. Based on the values of the $3d_{5/2}$ binding energy and the M_4VV kinetic energy, it could be deduced that the silver species present in the reduced PPy films were in the zero valence metallic state [29]. This demonstrated that the electroless (chemical) reduction of silver ions took place and resulted in the deposition of the metallic silver at the reduced PPy film electrodes. Similarly, the silver species present at the oxidized PPy films were found to be in the +1 valence state. This indicated that complex formation between silver ions and PPy contributed to the incorporation of silver species at oxidized PPy film electrodes.

Fig. 8. Wide-scan XPS of the PPy electrodes: (a) oxidized PPy–NO$_3$ film before exposure to silver solution; (b) oxidized PPy–NO$_3$ film after exposure to silver solution; (c) reduced PPy film after exposure to silver solution.
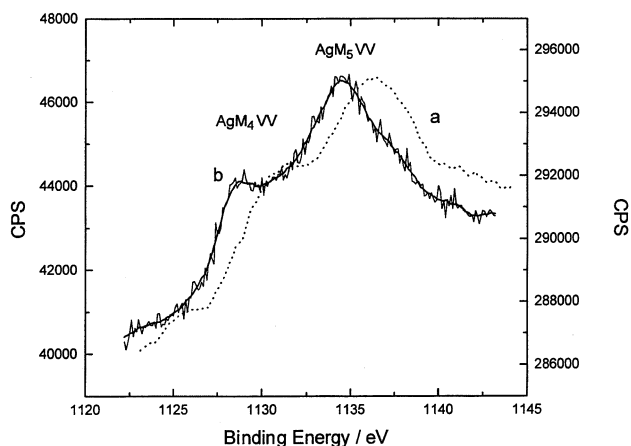

Fig. 9. Ag MVV Auger electron spectra of PPy film electrodes with incorporated silver species: (a) oxidized PPy–NO$_3$ film electrode; (b) reduced PPy electrode.

3.6. Incorporation mechanism of silver ions on PPy film electrodes

The results discussed above show that the preconcentration of silver ions at a PPy film modified GCE was directly related to the PPy itself rather than the GCE substrate. Under open-circuit preconcentration, chemi-

cal reactions were the primary means for the incorporation of silver species in PPy film. Experimental results showed that the incorporation of silver species was related to the thickness and oxidation state of the PPy films, and was independent of the dopant anions. PPy, especially reduced PPy, is well known to be oxidized easily by dissolved oxygen [6], so a redox reaction between silver cations and reduced PPy was possible. Studies on the effects of the oxidation state indicated that a redox reaction between silver ions and the amine groups in PPy also took place. XPS and AES results confirmed the presence of metallic silver and the redox reaction at the reduced PPy film electrodes. It is also possible that the nitrogen moieties present in the PPy backbone might react with silver ions to form complexes. Acidity effects, as well as XPS and AES results, indicated the formation of a few complexes between silver ions and amine groups. Actually, Bidan et al. [30] have reported the formation of a complex between pyrrole and phosphotungstic acid, as suggested by spectroscopic evidence. Chen and coworkers [10,24] have also proposed the possibility of complexation between PPy and various metals, such as Au(I), Au(III) or Ag(I). Holdcroft and Funt [31] reported that a PPy film containing Pt micro-particles could be prepared by chemical reduction of $PtCl_6^{2-}$ on the PPy film in a reduced state and resulted in the formation of complex between platinum and PPy. These literature results support our proposed mechanism. Therefore, the incorporation of silver species at PPy film electrodes results mainly from the electroless reduction and complex formation of silver ions with PPy films, when no chemically active dopants are present.

4. Conclusions

In summary, silver species were found to be readily preconcentrated onto PPy films without chemically active counterions. Prolonged base–acid pretreatment and preconcentration were not necessary. The preconcentration mechanism involved the combination of electroless reduction and complex formation of silver ions on the PPy films. XPS and AES results showed that silver ions were reduced by PPy in the reduced state to metallic silver and deposited onto the PPy film. Experimental results showed that the anodic peak current was proportional to the silver ion concentration in solution in the range of 2–150 μM. The detection limit was about 0.2 ppm.

References

[1] M.D. Imisides, R. John, P.J. Riley, G.G. Wallace, Electroanalysis 3 (1991) 879.
[2] A.F. Diaz, J.I. Castillo, J. Chem. Soc., Chem. Commun. (1980) 397.
[3] F. Beck, P. Hulser, R. Michaelis, Bull. Electrochem. 8 (1992) 34.
[4] B. Scrosati, Applications of Electroactive Polymers, Chapman and Hall, London, 1993.
[5] S. Dong, Z. Sun, Z. Lu, J. Chem. Soc., Chem. Commun. (1988) 993.
[6] J. Bobacka, Z. Cao, A. Ivaska, A. Lewenstam, J. Electroanal. Chem. 368 (1994) 33.
[7] A. Wojda, K. Maksmiuk, J. Electroanal. Chem. 411 (1998) 204.
[8] S. Dong, G. Che, Talanta 38 (1991) 111.
[9] V.M. Jovanovic, L. Markicevic, S. Stankovic, R. Stankovic, M.S. Jovanovic, Electroanalysis 7 (1995) 574.
[10] S.H. Chou, J.R. Rau, S.C. Chen, Electrochim. Acta 42 (1997) 2313.
[11] Z. Gao, J. Bobacka, A. Lewenstam, A. Ivaska, Electrochim. Acta 39 (1994) 754.
[12] J. Tamm, A. Alumaa, A. Hallik, V. Sammelselg, J. Electroanal. Chem. 448 (1998) 24.
[13] K.K. Shiu, F.C. Anson, J. Electroanal. Chem. 309 (1991) 114.
[14] F. Song, S. Dong, Chin. J. Anal. Chem. 20 (1992) 1140.
[15] D. Belanger, J. Nadreau, G. Fortier, J. Electroanal. Chem. 274 (1989) 143.
[16] Y. Kajiya, H. Sugai, C. Iwakura, H. Yoneyama, Anal. Chem. 63 (1991) 49.
[17] G.G. Wallace, Y.P. Lin, J. Electroanal. Chem. 247 (1988) 144.
[18] R. Jone, G.G. Wallace, J. Electroanal. Chem. 283 (1990) 87.
[19] N.L. Pickup, J.S. Shapiro, D.K.Y. Wong, Anal. Chim. Acta 364 (1998) 41.
[20] K.K. Shiu, O.Y. Chan, J. Electroanal. Chem. 388 (1995) 44.
[21] K.K. Shiu, S.K. Pang, H.K. Cheung, J. Electroanal. Chem. 367 (1994) 114.
[22] K.K. Shiu, O.Y. Chan, S.K. Pang, Anal. Chem. 67 (1995) 2828.
[23] A. Deronzier, J.C. Moutet, Acc. Chem. Res. 22 (1989) 249.
[24] J.R. Rau, J.C. Lee, S.C. Chen, Synth. Metals 79 (1996) 69.
[25] S. Kotrly, L. Sucha, Handbook of Chemical Equilibria in Analytical Chemistry, Ellis Horwood, Chichester, 1985 Chapter 7.
[26] N.L. Pickup, M. Lam, D. Milojevic, R.Y. Bi, J.S. Shapiro, D.K. Wong, Polymer 38 (1997) 2561.
[27] D.A. Skoog, D.M. West, F.J. Holler, Analytical Chemistry, 5th edn, Saunders College Publishing, Philadelphia, 1990, p. 594.
[28] M.D. Imisides, G.G. Wallace, J. Electroanal. Chem. 246 (1988) 181.
[29] G.E. Muilenberg, Handbook of X-Ray Photon Spectroscopy, Perkin–Elmer, Minnesota, 1987, p. 112.
[30] G. Bidan, E.M. Genies, M. Lapkowski, J. Electroanal. Chem. 251 (1988) 297.
[31] S. Holdcroft, B.L. Funt, J. Electroanal. Chem. 240 (1988) 89.