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Article

Incorporation and Voltammetric Determination of Silver (I) at an Electrode Electrochemically Modified with a Poly-Benzidine Film

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Eletrodos modificados com filmes de poli-bendizina são quimicamente estáveis no intervalo de pH entre 0 e 7 e podem ser ciclados de -0.200 a 0.850 V sem evidência de decomposição. Conseqüentemente, neste intervalo de potencial, eles podem ser usados como material eletródico para a oxidação ou redução de diferentes espécies. Uma propriedade interessante deste eletrodo modificado é sua capacidade de capturar e quantificar o íon Ag(I) presente na solução. Para obter resultados reproduzíveis a etapa de acumulação foi realizada numa solução de $AgNO_3$ com um tampão de acetato de pH = 7. Após redução para Ag(0) na mesma solução, a etapa de determinação foi executado por voltametria cíclica. A resposta analítica corresponde à oxidação para Ag(I) e a quantia de prata incorporada ao filme foi determinada a partir da carga do pico anódico. O uso potencial deste método para a determinação analítica da prata é discutido.

Electrodes modified with poly-benzidine films are chemically stable in the pH range between 0 and 7, and can be cycled from -0.200 to 0.850 V with no evidence of decomposition. Consequently, in this potential range, they can be used as electrode material for oxidation or reduction of different species. One interesting property of this modified electrode is its capacity to capture and quantify Ag(I) ion present in solution. To obtain reproducible results, the accumulation step was carried out in a $AgNO_3$ solution with acetate buffer at pH = 7. After reduction to Ag(0) in the same solution, the determination step was performed by cyclic voltammetry. The analytical response corresponds to silver oxidation to Ag(I), and the amount of silver incorporated into the film was determined from the charge of the anodic peak. The potential use of this method for analytical determination of silver is discussed.

Keywords: *modified electrodes, poly-benzidine, electroanalysis, silver(I)*

Introduction

In the context of metal ion analyses, chemically modified electrodes (CMEs) possessing properties have emerged as one of the most attractive areas for research[1-4]. Among their advantages are their inherent high selectivity and sensitivity. Methods that have been used for electrode modification include physical coating, covalent attachment and electropolymerization. Particularly, electropolymerization offers an effective and versatile way to deposit polymer film on a substrate electrode[5-8].

The electrooxidation of aromatic amines is well known, and different aspects of their mechanism have been elucidated[9,10]. Previous studies show that when aromatic amines such as naphtidine[5], 1-naphtylamine[6], and benzidine (Bz)[7] are electrooxidized, they follow a complex reaction to give a polymer that adheres to the electrode surface. These polymers which adhere to a base metal are conductors, and their doping grade can be controlled[9,11,12].

Recently, a number of investigators have demonstrated a new variation in electrochemical trace-metal analysis in which analyte preconcentration is carried out at CMEs. The preconcentration is achieved by a purely non-electrochemical deposition step, and the subsequant quantification of the accumulated analyte can be carried out by normal voltammetric measurements[4,13].

CMEs have been used as working electrodes in the determination of silver and mercury[14,15]. In both cases, the metal ions were chemically preconcentrated on CMEs.

In this article we report the incorporation of Ag(I) ion into poly-benzidine (poly-Bz) films. The distribution of the Ag(I) ion between the solution and the film is established, and a probable analytical application is given.

Experimental

Chemicals and solutions

Benzidine (Bz) from Fluka was used as received. All of the other reagents were analytical grade unless otherwise stated. Water was obtained from LABCONCO equipment model 90901-01. The Bz solutions used to obtain the film were prepared by weighing Bz and dissolving it in the solvent-supporting electrolyte solution (0.3 M $NaClO_4$- 0.1 M $HClO_4$). The concentration of Bz was determined by spectrophotometric methods ($\lambda_{máx}$ = 250 nm, log ε = 4.2) as previously described[7,8].

Metal stock solutions were prepared by dissolving the appropriate salts in a solvent-supporting electrolyte solution or in an acetate buffer solution. The concentration of metal was determined by potentiometric titration using a standard KCl solution. Working solutions were freshly prepared by diluting from the stock solution. Acetate buffer solutions were obtained by adjusting 0.2 M sodium acetate solutions to pH = 7 with glacial acetic acid. All solutions were deaerated by bubbling pure nitrogen.

Apparatus

Cyclic voltammetric and electropolymerization experiments were carried out with an EG&G PAR 273 potentiostat/galvanostat. The output signal was recorded on a Hewlett-Packard Model 7015B X-Y plotting system. The values of the charges at the voltammetric peaks were determined by the integration of the current-time curves. A compensating polar planimeter (International Trade Associates, Japan) was used for this purpose. In each case, the appropriate background current values were subtracted[6]. Similar results are obtained if the signal is processed digitally, using the corresponding EG&G PAR software, however in this case the signal is much noiser than in the analogical one.

The UV-visible spectra were obtained with a Hewlett-Packard 8452A spectrophotometer. The working temperature was controlled using a LAUDA K4R thermostat-cryostat. A conventional three-electrode electrochemical cell was used[16]. A Pt wire with a surface area of 0.361 cm^2 was used as the working electrode, and a Pt wire with a surface area of 2 cm^2 in spiral form was used as the counter electrode. The reference electrode was an aqueous saturated calomel electrode (SCE).

Generation of the films

The poly-Bz films were obtained from a 5 x 10^{-4} M Bz solution in a supporting electrolyte at pH = 2.5, by cycling the potential between 0 and 0.800 V at a scan rate of v = 0.100 V s^{-1}. The temperature of the cell was maintained at 35 ± 0.1 °C. These experimental conditions led to the formation of an adherent film, which was mechanically stable and had a very reproducible electrochemical response[8]. In addition, the film thickness could be increased by increasing the number of potential cycles.

Once the polymer film was generated, the working electrode was rinsed with supporting electrolyte solution. Then, it was transferred to another cell containing the same electrolyte solution in the absence of the monomer, but at pH = 1 and 20 °C. The potential was cycled between -0.100 and 0.500 V for about 10 min. The film thus obtained is very stable for at least 24 h.

Results and Discussion

Electrochemical behavior of poly-Bz

A typical voltammogram of the poly-Bz electrode, prepared as described above, is shown in Fig. 1. Its redox response shows only one peak system, the anodic and cathodic peaks appearing at 0.185 and 0.160 V respectively. Although the voltammetric response was discussed in detail in a previous paper[8], some characteristics should be noted. The film can be repeatedly cycled from -0.200 V to 0.850 V with no evidence of decomposition. It can be used in this potential range as electrode material for selective oxidation or reduction of different electroactive species whose redox potentials also occur in the same range. The peak current depends linearly on the scan rate in the

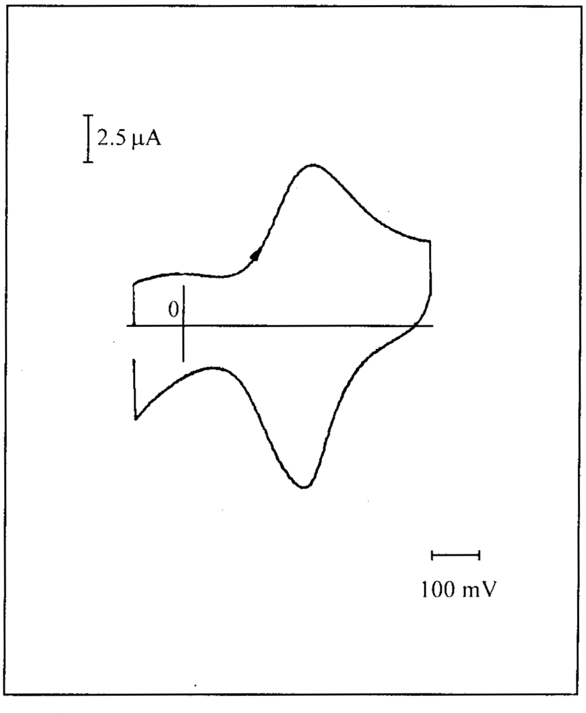

Figure 1. Voltammetric response of the poly-Bz modified electrode in supporting electrolyte solution at pH 1 and 20 °C. v = 0.025 V s^{-1}.

range of 0.005-0.100 V s^{-1}, and the peak potential is independent of v between 0.005 and 0.150 V s^{-1}.

The value of the anodic charge at the voltammetric peak (Q_{film}) was determined by integrating the current-time curve. As shown in Fig. 1, the base line was taken as a straight line joining points **a** and **b**.

As previously reported[8], the redox behavior of the film is strongly dependent on the pH of the electrolyte solution. It has reproducible behavior in the pH interval of 1-3.5, but at pH > 4 the electrochemical response is practically lost. Figure 2 shows a typical voltammogram of the film when it is transferred to the acetate buffer solution at pH = 7. The oxidation cycle shows only an increasing current with no defined peak, while in the reduction a peak at 0.100 V is observed.

Although the film response is not observed at pH > 4, the film is not destroyed and recovers its original response when the pH is restored to 1.

Incorporation of Ag(I) ion into poly-Bz film

This analyte was chosen because its redox potential is within the range in which the poly-Bz electrode is electrochemically stable. The general procedure included the following steps:

i) Stabilization and characterization of the poly-Bz electrode, as described above: the anodic charge was determined after the electrode potential was kept at -0.100 V for 10 min to allow the complete reduction of the film and to obtain material with reproducible behavior.

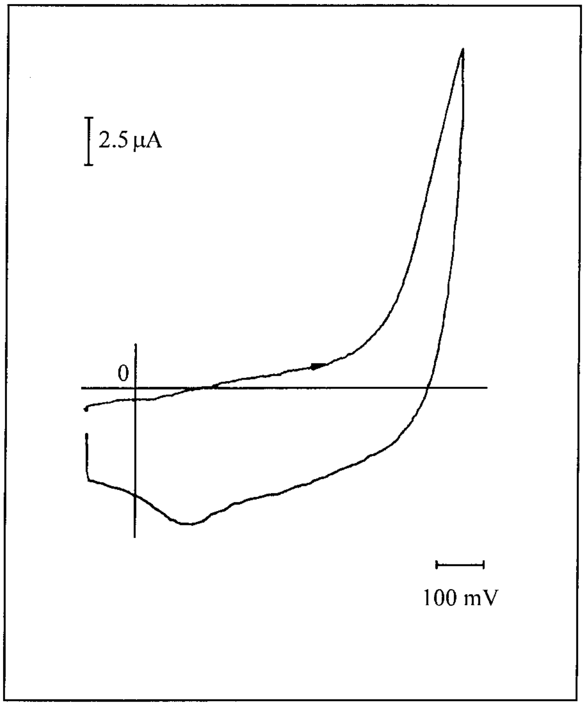

Figure 2. Cyclic voltammogram of the poly-Bz modified electrode in acetate buffer solution at pH 7 and 20 °C. v = 0.025 V s^{-1}.

ii) Preconcentration step: the poly-Bz electrode was placed in an open circuit in a well-stirred solution of $AgNO_3$ in a supporting electrolyte solution. Accumulation was carried out for a known amount of time, after which it was removed and rinsed with the electrolyte solution.

iii) Reduction to Ag(0): the electrode was transferred to the analysis cell containing the supporting electrolyte solution. The accumulated Ag(I) was reduced at a -0.100 V for 5 min.

There is a possibility of the spontaneous reduction of Ag(I) by the reduced film during the pre-concentration step. To test this possibility, step iii was omitted. It was observed that the charge (Q_{Ag}) does not give reproducible values, and is always smaller than the charge obtained after step iv.

iv) Determination step: performed by cyclic voltammetry. The analytical response corresponds to silver oxidation to Ag(I) and the quantity of silver incorporated into the film was determined from the charge involved in the anodic peak (Q_{Ag}).

Experiments were performed with a modified electrode stabilized at pH = 1, as described in the Experimental section. Typical results after the incorporation of silver into the poly-Bz electrode are shown in Fig. 3. The peak at +0.325 V is associated with the oxidation of the deposited silver, and shows a corresponding cathodic peak at +0.110 V.

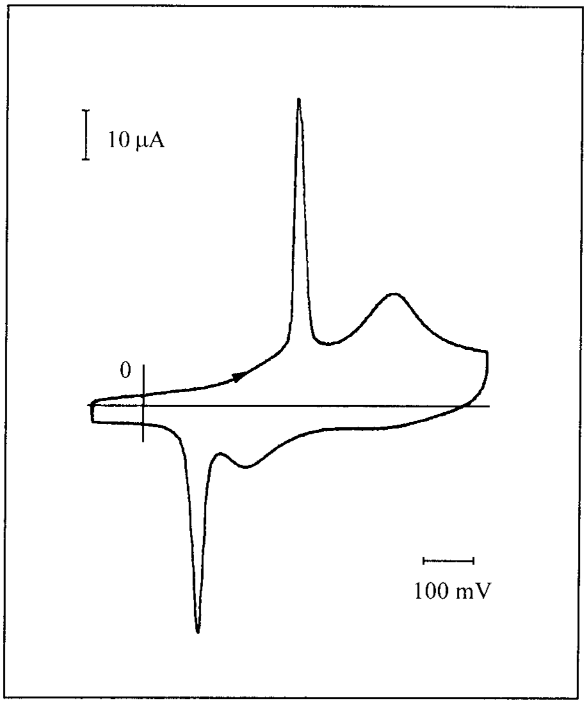

Figure 3. Cyclic voltammogram of the poly-Bz modified electrode at 0.025 V s^{-1} in supporting electrolyte solution at pH 1 and 20 °C, after being in contact with a solution containing silver at a concentration of 1 x 10^{-3} M for 5 min.

The anodic peak at +0.510 V corresponds to the oxidation of poly-Bz film. The shift of the potential peak with respect to the one in Fig. 1 may be due to the fact that the redox sites of the film complexed by Ag(I) make the redox process of the ligand more difficult.

However, experiments performed at several Ag(I) concentrations show lack of reproducibility, particularly at low ion concentrations. This problem may be due to variations in the H^+ concentration in the film, since these ions seem to compete with Ag(I) ions for the same "site" in the film.

In light of these results the studies were performed at pH = 7 introducing some variations in the stabilization and accumulation steps. The, the modified electrode stabilized at pH = 1 was transferred to an acetate buffer solution at pH = 7 for about 15 min to allow the protonic equilibrium in the polymer matrix. Then accumulation step was carried out in a $AgNO_3$ solution in the same acetate buffer. Accordingly, steps iii and iv were performed in the acetate buffer solution.

The cyclic voltammetric response obtained under these new conditions is shown in Fig. 4. The sharp peak at +0.530 V is due to the reoxidation of Ag(0). The sharpness of the wave and the relatively flat background current in this potential region makes it easily quantifiable. However, as can be observed in Fig. 4, the reduction process is ill-defined and seems to occur in a potential zone near the film reduction. In principle, it can be inferred that the reduction of the silver ion to metallic silver is a very slow process. The observed kinetic limitation may be due to (1) the high resistivity of poly-Bz at -0.100 V in pH = 7 solution or (2) the slow Ag(0) phase formation process under these conditions. Nevertheless, if the potential is maintained at -0.100 V for some time, a second positive sweep yields a voltammetric response virtually identical to the first.

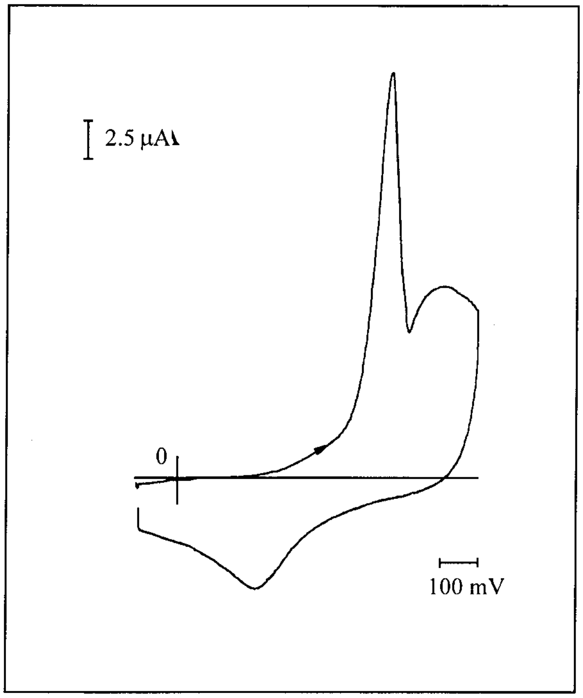

Figure 4. Cyclic voltammogram of the poly-Bz modified electrode at 0.025 V s^{-1} in acetate buffer solution at pH = 7 and 20 °C, after being in contact with a solution containing silver at a concentration of 1 x 10^{-3} M for 5 min.

From these results, we can deduce that the poly-Bz film enabled the accumulation and hence the preconcentration of Ag(I), being reproducible at pH = 7.

Incorporation of Ag(I) ion into poly-Bz film at different concentrations

General analytical procedure

The analytical application of this procedure is based on a working curve which correlates the amount of Ag(I) accumulated in the modified electrode and its concentration in solution, maintaining certain parameters constant, such as the accumulation time and the charge of the film (Q_{film}). Regarding the Q_{film}, it should be noted that it is quite difficult to obtain identical films. Thus, the working curves are constructed by normalizing Q_{Ag} using the ratio Q_{Ag}/Q_{film}. The experiments were performed at pH 7 as described, for different concentrations of $AgNO_3$ solution in acetate buffer during the accumulation step. The results are shown in Fig. 5. As can be observed, the Q_{Ag}/Q_{film} ratio increases with the Ag(I) concentration until it reaches a constant value of 25. Thus, the saturation charge of Ag(I) is much higher than the polymer itself. This may indicate that a redox site has several groups involved in the coordination of Ag(I).

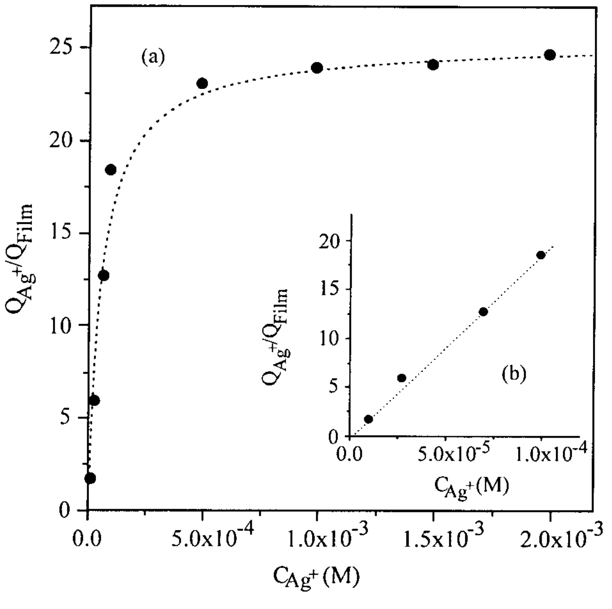

Figure 5. a) Dependence of Q_{Ag}/Q_{film} on the concentration of Ag(I). b) Inset: the linear region of the same plot.

The saturation value is the same for films of different thicknesses and is independent of the $AgNO_3$ concentration higher than 1×10^{-3} M. This indicates that the incorporation of Ag(I) ions follows a definite stoichiometry and there is a specific interaction between these ions and the polymer matrix. Hence, the plot in Fig. 5 resembles a distribution or partition of an ion between a solution and an ion exchange resin[17]. This can be regarded as an "exchange isotherm" and thermodynamically interpreted assuming an equilibrium between the Ag(I) ion inside and outside the film.

Regarding the possibility of using this method for the analytical determination of Ag(I), the inset of Fig. 5 shows that Q_{Ag}/Q_{film} is linear with C_{Ag} in the interval $0 < C_{Ag} < 1.5 \times 10^{-4}$ M. The minimum charge that can be detected by cyclic voltammetry under the conditions used in these experiments for the reduction peak of Ag(I) is 2.5 μC. Thus, considering a film with a charge of 10 μC, the minimum concentration of Ag(I) that can be detected is about 2×10^{-6} M. It should be noted that this is an approximate calculation, but one which shows the potential utility of this method, and which deserves detailed studies using more sensitive detection techniques, such as differential pulse voltammetry.

Conclusions

Electrodes modified with poly-Bz films show the ability to capture Ag(I) in solution. The process is based on the preconcentration of Ag(I) ions in the polymer matrix. The existence of a constant relation for the saturation quantities Q_{Ag}/Q_{film} and its high value (*i.e.*, 25) indicates the strong specific interactions involved between Ag(I) and the polymer.

The analytical signal is the stripping response due to silver oxidation obtained after the reduction of the preconcentrated Ag(I) ions. The analytical detection method seems to be quite promising, especially if techniques more sensitive than cyclic voltammetry are used for detection.

Acknowledgments

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