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Synthesis and optimization of permselective polymer (polyindoline) film

Received: 10 November 1997 / Accepted: 27 January 1998

Abstract A polyindoline permselective polymer film was readily synthesized by an electrochemical polymerization of indoline in an aqueous solution of KCl at a potential of 0.4 V vs Ag/AgCl. The amperometric responses of the polyindoline film-coated platinum electrodes to electroactive (ascorbic acid, oxalic acid and hydrogen peroxide) and non-electroactive (lactose, sucrose and urea) substances were measured at a potential of 0.7 V. Effects of various variables such as film thickness, concentrations of monomer and electrolyte, and pH on the permselective behavior of the polymeric membrane were systematically investigated and the optimal values were determined. It was found that permselective polyindoline-coated electrodes prepared in this one-step procedure permitted hydrogen peroxide oxidation while it prevented interference due to oxidizable species such as ascorbic acid and oxalic acid. As a result, it is believed that this polymeric membrane, owing to its permselective character, can be used as the protective material in the construction of hydrogen peroxide-based biosensors.

Key words Polyindoline electrode · Permselective membrane · Permeation

Introduction

Polymer-modified and polymer-coated electrodes have been used for a variety of applications such as electroanalysis [1–4], electrochromic displays [5–6], biosensors [7–15] and recently for their permselective characteristics [16–24].

The most desired function of polymeric materials used in the construction of electrochemical biosensors is their selectivity to the relevant substrates.

For hydrogen peroxide-based biosensors, since interferents such as ascorbic acid and oxalic acid are electroactive at the potential used to measure hydrogen peroxide, the presence of these interferents in the amperometric measurement stage contributes to measured faradaic current. In addition to these potential interferents, electrode fouling is caused by the adsorption of some non-electroactive species, such as lactose, sucrose and urea.

To overcome these interference problems, it is necessary to synthesize permselective polymeric membranes that prevent direct oxidation of the mentioned electroactive interferents while allowing hydrogen peroxide oxidation.

In this paper, we have shown that a permselective polymeric membrane can easily be obtained by the electrochemical polymerization of indoline in aqueous solution. This permselective polymeric membrane can be optimized to circumvent the problem of interference by controlling electrochemical polymerization parameters, especially the film thickness, by monitoring the charge passed during electropolymerization.

Experimental

Reagents

Hydrogen peroxide was obtained as a 35% solution. The reagents indoline, ascorbic acid, oxalic acid, lactose, sucrose and urea were of analytical grade and purchased from Sigma (St. Louis, Mo., USA) or Merck (Darmstadt, Germany). Amperometric measurements were run in a PBS (phosphate buffer salts, pH = 7.0) solution. Ascorbic acid solution was prepared immediately before use. The nitrogen used for purging/blanketing was of high purity.

Apparatus

All the electrochemical techniques such as polymerization, cyclic voltammetry (CV), linear sweep voltammetry (LSV) and amperometric measurements were performed with a BAS 100 W (Bio-

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analytical Systems, West Lafayette, Ind., USA) electrochemical analyzer. A platinum disc (geometric area: 1.98 mm²) as a working and a Pt coil as an auxiliary electrode were used together with an Ag/AgCl reference electrode in a single electrolysis compartment. The pH measurements were made with a Jenway 3010 pH meter.

Polyindoline film synthesis

Platinum disc electrodes were cleaned according to standard procedure [25] and polished with successively finer grades of diamond polishing compounds and aqueous alumina slurry (Johnson Matthey, USA) down to 1.5 μm . The Pt electrode was immersed in a solution containing 20 mM indoline and 0.1 M KCl, which was deoxygenated for 10 min by nitrogen purging prior to electrochemical synthesis.

Then, electrochemical polymerization was performed under nitrogen atmosphere, at a potential of 0.4 V vs Ag/AgCl. The thickness of polyindoline films was controlled by monitoring the charge passed during the polymerization. After the electropolymerization, the polyindoline-coated electrodes were rinsed with deionized water. Visual examination showed the formation of a thin and homogenous film with a yellowish color on the electrode surface.

Amperometric measurements

LSV was used to determine the required potential for the determination of the electroactive hydrogen peroxide.

The amperometric responses to the electroactive substances on the polyindoline-coated electrodes were measured by chronoamperometry, using a three-electrode system consisting of the polyindoline-modified Pt working electrode, a Pt wire counter electrode and an Ag/AgCl reference electrode.

During the amperometric measurements, the solution was kept under gentle stirring at room temperature. Before the injection of electroactive substances into the PBS solution, the background current was allowed to decay to a steady state, which took 5 min at most. The anodic current obtained on the injection of electroactive substances was then measured as a function of time.

Results and discussion

The typical cyclic voltammograms obtained on the bare Pt electrode in the absence and presence of indoline in KCl solution are presented in Fig. 1. An anodic peak at ca. 0.65 V, which disappeared on subsequent cycles, is clearly seen on the first scan of the voltammogram. This behavior is typical of electrochemically grown non-electroactive films and can be explained by blockage of the access of monomer to the electrode surface on the subsequent cycles. The electrochemical polymerization potential for indoline was, however, chosen as 0.4 V to secure thin films at a slow electrolysis rate. Thus, for the passage of a typical charge of 1.10 mC, a period of ca. 17 ± 2 min was required.

Figure 2A, B represents the linear sweep voltammograms obtained with the polyindoline-coated electrode in the absence and presence of hydrogen peroxide in the PBS solution, respectively. A minimum potential of 0.7 V was chosen for hydrogen peroxide oxidation since

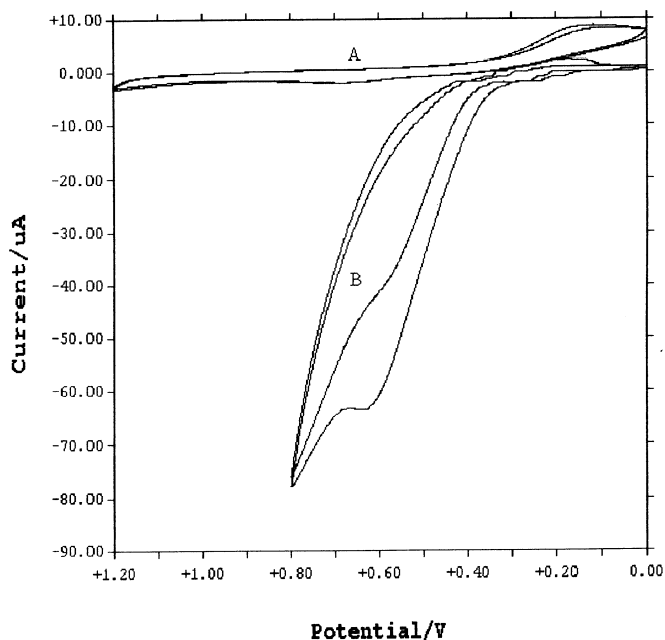


Fig. 1 Cyclic voltammograms of the bare Pt electrode in A 0.1 M KCl and B 0.1 M KCl + 0.10 M indoline. Scan rate: 50 mV/s

a reasonably measurable current was observed at this potential.

Polymer selectivity

Since both conducting and non-conducting polymers have been used as enzyme immobilization media in biosensor construction, it was wondered if a non-electro-

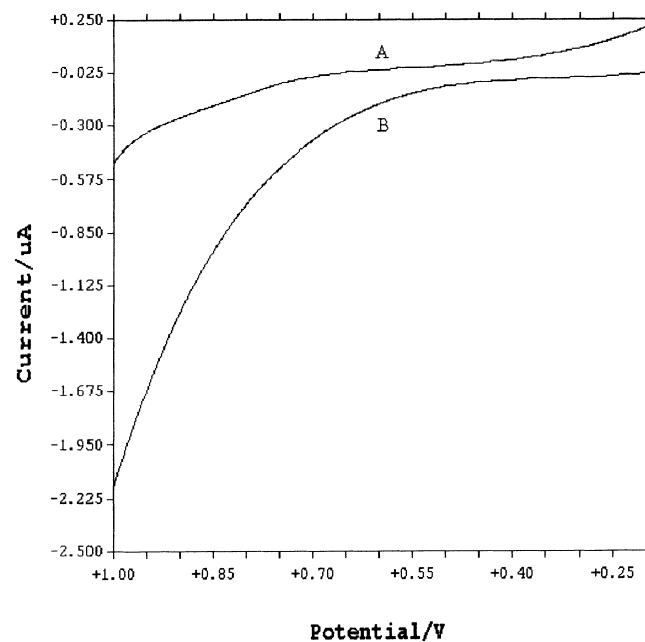


Fig. 2 Linear sweep voltammograms of the polyindoline Pt electrode in A PBS and B PBS + 25 mM H₂O₂. Scan rate: 50 mV/s

active polyindoline film could be used as the enzyme (glucose oxidase) immobilization matrix. For this reason, a polyindoline-glucose oxidase enzyme electrode (biosensor) was prepared in the presence of glucose oxidase in KCl solution.

Although it was found that this polymeric sensor responded to up to 30 mM glucose, its stability was not satisfactory, and its responses to successive glucose injections were irregular. Therefore, it was decided to test whether this polymeric film could be used as a protective membrane to prevent interference in the electrochemical biosensor applications.

The effect of film thickness

The most effective parameter that determines the permselective character of polymeric films is the thickness, which can be expressed as the charge consumed and adequately controlled during electropolymerization. Polyindoline film thickness on the Pt electrode surface was varied by changing the amount of charge consumed during electrochemical polymerization of indoline. Figure 3 reveals the effect of polyindoline film thickness on the responses of hydrogen peroxide, ascorbic acid and oxalic acid. With the hydrogen peroxide response, current rises to a maximum at a thickness of 1.1 mC, which can be attributed to the film morphology that somehow allows penetration of large amounts of hydrogen peroxide. On the other hand, responses of both ascorbic acid and oxalic acid diminish to zero for thickness larger than 1.00 mC.

The behaviors of ascorbic acid and oxalic acid at a polyindoline-coated electrode of optimal thickness, as depicted in Fig. 4, were again confirmed. While no responses were observed for either ascorbic acid or oxalic acid, both were electroactive at a bare Pt electrode at the potential applied (0.7 V).

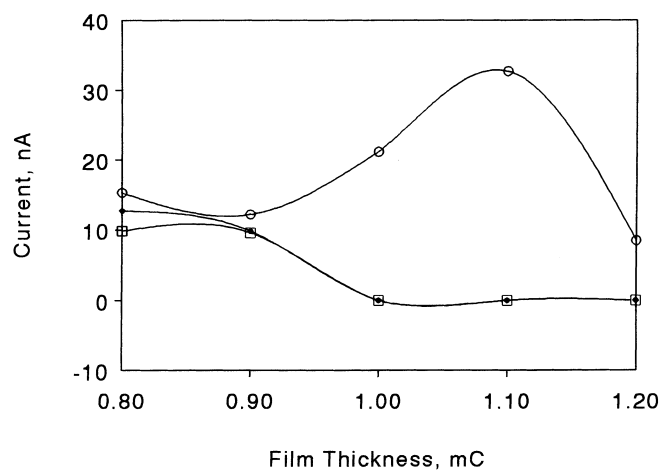


Fig. 3 The effect of film thickness of the polymer electrode on the response to 1 mM of H₂O₂ (○), oxalic acid (●) and ascorbic acid (□)

Effect of monomer concentration

The effect of the monomer (indoline) concentration used during the electrochemical polymerization on the amperometric response of hydrogen peroxide for polyindoline films of the same thickness was investigated in the range 10–40 mM. It can easily be seen in Fig. 5 that the maximum amperometric response for hydrogen peroxide was obtained with the electrode coated in a solution containing 30 mM monomer.

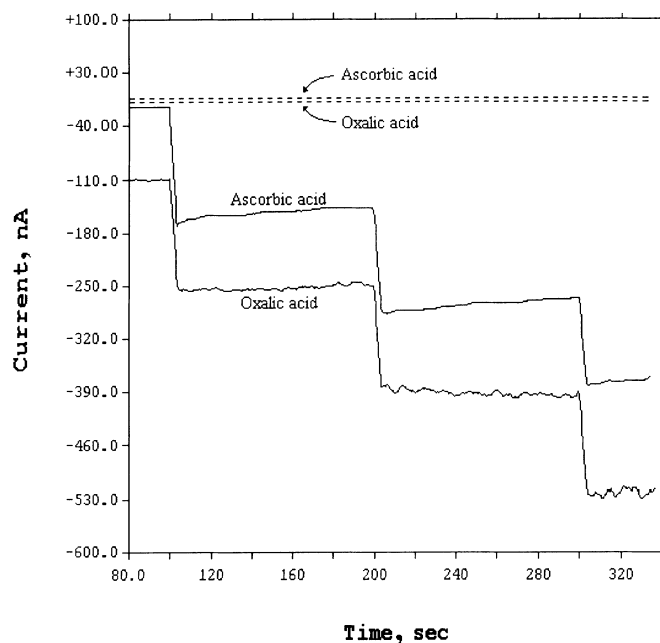


Fig. 4 The behavior of ascorbic acid and oxalic acid on the polyindoline (dashed lines) and the bare Pt electrode (solid lines). Three injections of each substance on both electrodes were made. Each step corresponds to 1 mM of interferents

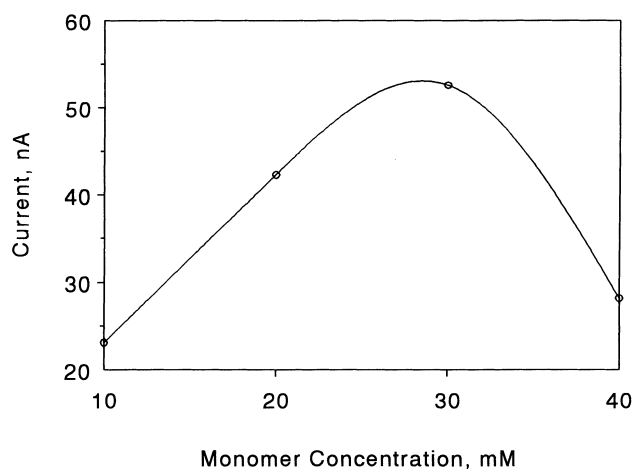


Fig. 5 The effect of monomer concentration on the response to hydrogen peroxide

Effect of electrolyte concentration

Figure 6 depicts the effect of the electrolyte (KCl) concentration used in the electropolymerization solution on the amperometric response of hydrogen peroxide at the polyindoline electrode. As the figure indicates, optimal concentration of the electrolyte corresponding to maximum hydrogen peroxide response was found to be 200 mM.

Effect of pH

The effect of pH of the PBS medium on the amperometric response of hydrogen peroxide on the polyindoline-coated electrode was examined in the range 5–9. As shown in Fig. 7, the highest amperometric response was observed at pH 7.

After the optimization of the mentioned parameters for hydrogen peroxide oxidation, amperometric responses to the electroactive substances, such as ascorbic

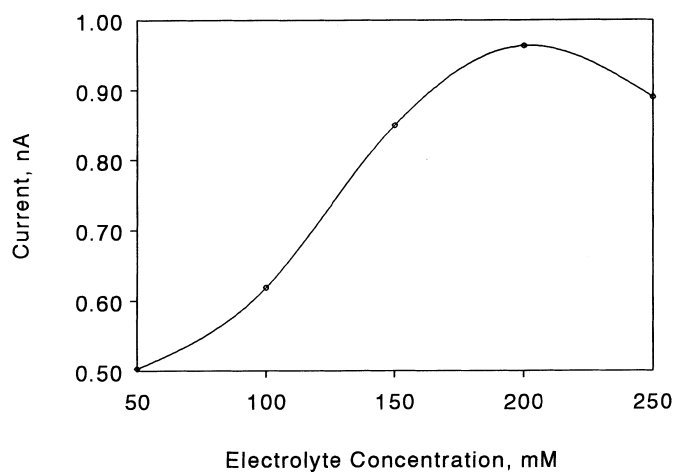


Fig. 6 The effect of electrolyte (KCl) concentration on the response to hydrogen peroxide

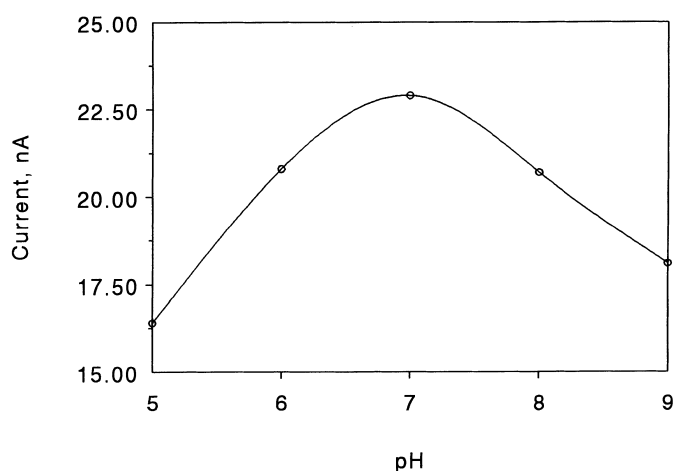


Fig. 7 Effect of pH on the response to hydrogen peroxide

acid, oxalic acid and hydrogen peroxide on the optimized polyindoline electrode were investigated, and the results are depicted in Fig. 8.

This figure confirms that a polyindoline film electrode responds only to hydrogen peroxide among the electroactive substances examined.

Moreover, Fig. 9 reveals that the polyindoline film-coated electrode responded to successive hydrogen peroxide

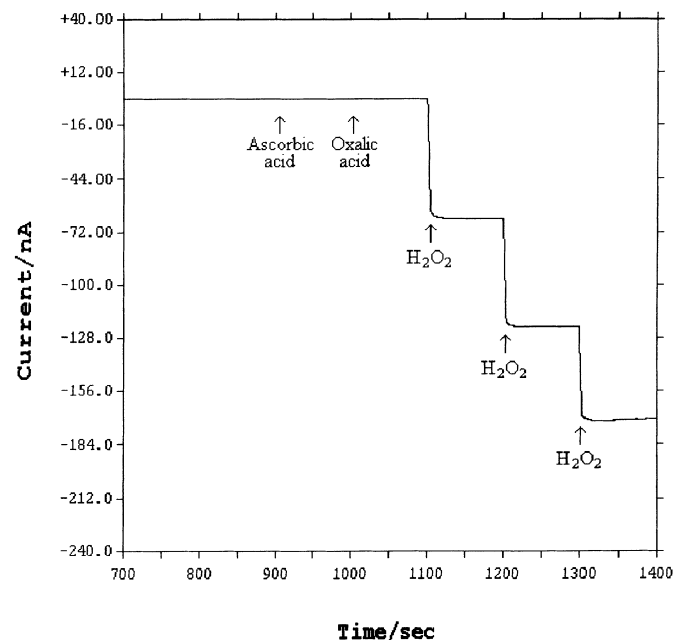


Fig. 8 The permselectivity of the optimized polyindoline electrode. Times of injections are indicated by arrows. (Each injection corresponds to 1 mM of the electroactive substances)

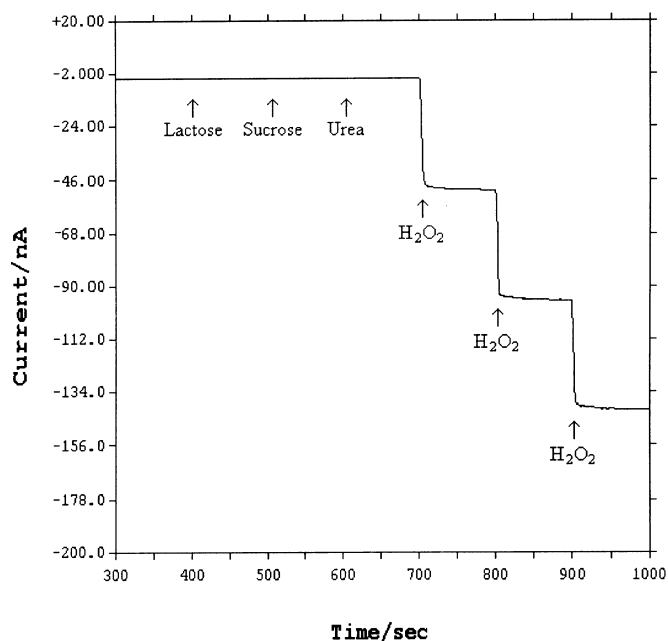


Fig. 9 The permselectivity of the optimized polyindoline electrode. Times of injections are indicated by arrows. (Each injection corresponds to 1 mM of the non-electroactive substances and H₂O₂)

oxide injections in the presence of lactose, sucrose and urea.

Conclusion

A permselective polymeric membrane (polyindoline), easily prepared by the electropolymerization of the relevant monomer, overcomes interference problems occurring in the use of hydrogen peroxide-based biosensors. The permeability of the polyindoline membrane, prepared in this one-step procedure, to the electroactive (ascorbic acid, oxalic acid and hydrogen peroxide) and non-electroactive (lactose, sucrose and urea) substances was controllable by varying the film thickness of the polymer.

As a result, it was found that this polyindoline electrode permitted hydrogen peroxide oxidation and prevented direct oxidation of the electroactive interferent species such as ascorbic acid and oxalic acid. Therefore, this polymeric membrane can be used as a protective membrane in a double-layer biosensor construction.

Acknowledgements This work has been supported by the Scientific and Technical Research Council of TURKEY (TÜBİTAK) through grant KTÇAG-DPT-6.

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