Electrochemical Preparation of Poly(*o*-toluidine) Film and Its Application as a Permselective Membrane

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Received 29 December 1997; accepted 25 May 1998

ABSTRACT: Poly(*o*-toluidine) films were electrochemically synthesized on Pt electrodes at a constant potential (0.75 V versus Ag/AgCl) from a deoxygenated aqueous solution of 0.1M toluidine dissolved in 0.1M KCl. To form permselective polymeric film electrodes, poly(o-toluidine) films at different thicknesses were prepared by varying the amount of charge consumed during electrochemical polymerization. Then, experimental parameters (e.g., concentrations of monomer and electrolyte and pH of the phosphate buffer salt solution) affecting the polymeric film thickness were optimized. Permeation of the various electroactive and nonelectroactive species such as ascorbic acid, oxalic acid, hydrogen peroxide, lactose, sucrose, and urea through the optimized poly(o-toluidine)-coated electrodes was investigated using a chronoamperometric technique. From experimental results, it was found that a poly(o-toluidine)-coated electrode permitted the oxidation of hydrogen peroxide and prevented the permeation of the mentioned electroactive and nonelectroactive species. In other words, it was seen that this polymeric electrode responded to only hydrogen peroxide selectively. Thus, it has been claimed that a poly(o-toluidine)-coated Pt electrode can be used as a permselective polymeric membrane to overcome interference problems occurring in the hydrogen peroxide-based biosensor applications. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2141-2146, 1999

Key words: poly(*o*-toluidine) film electrode; permselectivity; selective membrane

INTRODUCTION

Conducting or nonconducting polymeric materials prepared by electrochemical polymerization of a number of monomers have recently received considerable attention because of the large variety of their potential applications such as in energy storage,¹ batteries,^{2,3} electrocatalysis,^{4,5} gas sensors,⁶⁻¹⁰ and biosensors,¹¹⁻¹⁶ and for their permselective characteristics.¹⁷⁻²² Interferences

resulting from electroactive substances (e.g., ascorbic acid and oxalic acid) and electrode fouling are the most important problems occurring in the electrochemical biosensor applications based on hydrogen peroxide detection. To circumvent the mentioned problems, it is necessary to prepare permselective polymeric membranes which would allow hydrogen peroxide oxidation while preventing unwanted amperometric responses from the interfering species.

Film thickness is the most effective parameter in the determination of the permselective character of the polymer obtained. By using the electrochemical polymerization method in the polymer synthesis, it is possible to prepare polymeric films at the desired thickness by varying

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Contract grant sponsor: Scientific and Technical Research Council of Turkey (TÜBİTAK); contract grant number: KTÇAG-DPT-6.

Journal of Applied Polymer Science, Vol. 71, 2141-2146 (1999)

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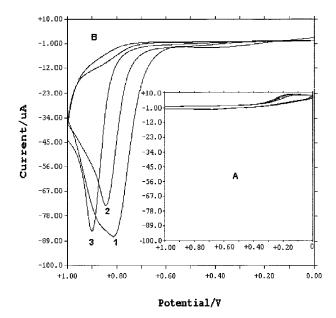


Figure 1 Cyclic voltammograms of the bare Pt electrode in (A) 0.1M KCl and (B) 0.1M KCl + 0.10M *o*-toluidine. Scan rate: 50 mV/s.

the amount of charge passed during electropolymerization.

In the present article, we report the electrochemical synthesis, optimization, and electrochemical behavior to the electroactive (e.g., ascorbic acid, oxalic acid, and hydrogen peroxide) and nonelectroactive (e.g., lactose, sucrose, and urea) substances of the poly(*o*-toluidine)-coated film electrodes obtained by the electropolymerization of the relevant monomer in an aqueous solution.

EXPERIMENTAL

Materials

Hydrogen peroxide was obtained as a 35% solution. All other chemicals used such as *o*-toluidine, ascorbic acid, oxalic acid, lactose, sucrose, and urea were of analytical grade and purchased either from Sigma Chemical Co. (St. Louis, MO) or from E. Merck (Darmstadt, Germany).

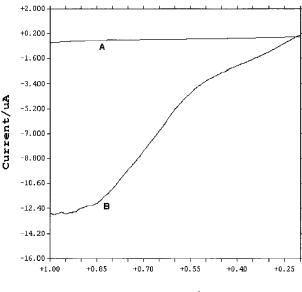
Electropolymerization solutions consisted of a monomer (*o*-toluidine) dissolved in an electrolyte (KCl) were purged with high-purity nitrogen for 15 min prior to electrochemical polymerization and a nitrogen atmosphere was maintained over the surface of the solution during polymerization. In chronoamperometric measurements, a phosphate buffer salt (PBS, pH 7.0) solution was used as the electrolyte. Ascorbic acid solutions were prepared immediately prior to the permselectivity measurements. All the aqueous solutions were prepared with deionized and doubly distilled water.

Apparatus

A BAS 100W (Bioanalytical Systems, Inc. West Lafeyette, IN) electrochemical analyzer was used for the electrochemical techniques such as polymerization, cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronoamperometric measurements. In all the mentioned electrochemical experiments, a single-compartment cell with threeelectrodes was employed. A platinum disc having a surface area of 1.98 mm² and a Pt wire coil were used as working and auxiliary electrodes, respectively. The reference electrode was a Ag/AgCl (BAS, MF-2063). pH measurements were carried out using a Jenway 3010 pH meter.

Preparation of Poly(*o*-toluidine) Coatings and Amperometric Measurements

A platinum disc electrode used as the working electrode was cleaned according to a standard procedure²³ and polished with successively finer grades of diamond polishing compounds and aqueous alumina slurry (Johnson Matthey Catalog Comp., USA) down to 1.5 μ m. First, an electropolymeriza-



Potential/V

Figure 2 Linear sweep voltammograms of the poly(*o*-toluidine) electrode in (A) PBS and (B) PBS + 25 mM H₂O₂. Scan rate: 50 mV/s.

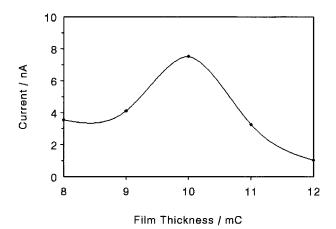


Figure 3 Effect of film thickness of the poly(o-tolu-idine) electrode on the response to 1-mM hydrogen peroxide.

tion potential of *o*-toluidine dissolved in an aqueous KCl solution was determined by cyclic voltammetry. Then, poly(*o*-toluidine)-coated film electrodes were prepared by applying a predetermined constant potential to the working electrode in an aqueous solution of KCl containing the *o*-toluidine. Electropolymerization was allowed to continue at a constant potential until the required amount of charge passed.

After completion of the electropolymerization, the poly(*o*-toluidine)-coated working electrodes were removed from the polymerization solution and then rinsed thoroughly with distilled water prior to the amperometric current measurements for hydrogen peroxide or interferents contained in the PBS solution.

RESULTS AND DISCUSSION

To determine the electropolymerization potential, cyclic voltammograms were taken with a bare platinum electrode in the absence and presence of 100 m*M* o-toluidine in 0.1M KCl solution. Three successive voltammograms shown in Figure 1(B) indicate an oxidation peak that shifted to higher potential values with each cycle. This behavior is typical for electrochemically grown electroactive polymers. There seemed, however, to be no film formation with cyclic voltammetry. Therefore,

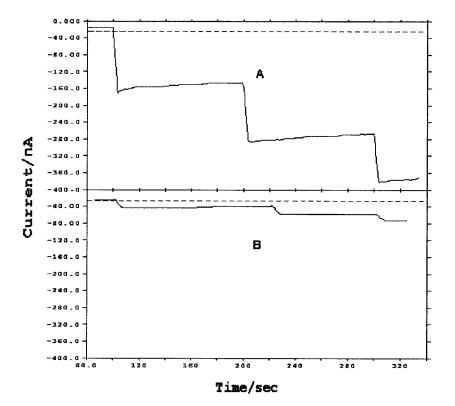


Figure 4 Behavior of (A) ascorbic acid and (B) oxalic acid on the (dashed line) poly(o-toluidine) and (solid line) bare electrode. Each step corresponds to 1 mM of interferents.

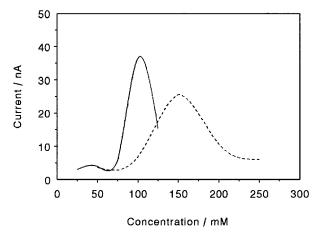


Figure 5 Effects of (solid line) monomer and (dashed line) electrolyte concentrations on the response to 1 mM of hydrogen peroxide.

electropolymerization was attempted at constant potential of 0.75 V, slightly lower than the oxidation potential of the first peak, to enable a controllable polymer film growth.

Under these conditions, approximately 20 min were required for a passage of a 10 mC charge, and visual inspection revealed the formation of a thin, insoluble, adherent, and homogeneous-looking film with a dark copper color. This polymer electrode was used to evaluate the hydrogen peroxide response, and as Figure 2 depicts, an appreciable current with respect to the background was obtained at 0.7 V for 25 mM hydrogen peroxide.

Effect of Poly(o-toluidine) Film Thickness

The electrochemical polymerization method allows the preparation of the polymeric films at a desired thickness on the electrode surface. In previous works,^{24,25} we reported that film thickness was one of the most important parameters to be considered in improving of the permselectivity property of the polymer films obtained.

The effect of the film thickness of the poly(*o*-toluidine)-coated electrodes on the amperometric response of hydrogen peroxide was studied in the range of thickness corresponding to 8–12 mC of charge passage. Figure 3 shows that the response to hydrogen peroxide increased with increasing film thickness and reached to a maximum at ca. 10 mC, after which it decreased.

Immediately after the above optimization work, the response behavior of polymer electrodes having optimal film thickness was examined toward electroactive interferents. Figure 4 depicts that no currents were observed on the polymer electrode with ascorbic and oxalic acids that are normally electroactive at the bare platinum at 0.7 V.

Optimization of Monomer and Electrolyte Concentrations and pH of Measuring Medium

The effects on the response of the hydrogen peroxide of concentrations of monomer and electrolyte used in electropolymerization stage were studied. First, the monomer concentration was varied over a range of 25-125 mM at a constant concentration of KCl (0.1M).

For each electrode, a 10-mC charge was consumed, and as expected, the electrolysis period was decreased with increasing monomer concentrations. The highest amperometric response corresponding to 1 mM of hydrogen peroxide was obtained with the polymer electrode coated in a solution containing 100 mM of the monomer.

Keeping the monomer concentration constant at 100 mM, the effect of the electrolyte concentration was investigated in a similar manner and optimal electrolyte concentration was found as 150 mM. The effects of both monomer and electrolyte concentrations are displayed in Figure 5.

The dependence of the hydrogen peroxide response on the pH of the PBS medium of the poly(*o*-toluidine) electrode was tested over a

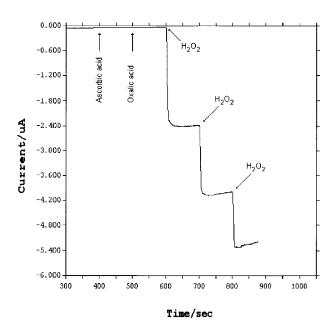


Figure 6 Permselectivity of the optimized poly(o-to-luidine) electrode. Each injection corresponds to 1 mM of the substance indicated.

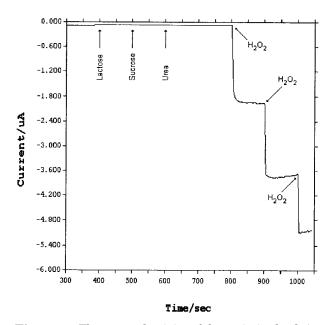


Figure 7 The permselectivity of the optimized poly(o-toluidine) electrode. Each injection corresponds to 1 m*M* of the substance indicated.

range of 5–9 pH. For polymer electrodes coated under the optimal conditions, the highest amperometric response for 1 mM of hydrogen peroxide was observed at pH 8.

Permselectivity of Poly(*o*-toluidine)-coated Electrode

It was mentioned above that a poly(*o*-toluidine) film-coated electrode prevented the permeation of the electroactive substances through the polymeric film. To confirm the permselectivity of the optimized poly(*o*-toluidine)-coated electrodes, the amperometric responses to the electroactive ascorbic acid, oxalic acid, and hydrogen peroxide are presented in Figure 6. As expected, perfect responses for hydrogen peroxide injections were seen while observing no current for the interferents.

Moreover, the fouling of the electrode surfaces, either bare or coated, is a severe problem in sensor applications. The poly(*o*-toluidine)-coated electrode responded to hydrogen peroxide even in the presence of nonelectroactive substances such as lactose, sucrose, and urea, as shown in Figure 7.

CONCLUSIONS

In brief, our results demonstrate that poly(*o*-toluidine) polymer film can be easily synthe-

sized by electropolymerization of the corresponding monomer in an aqueous solution on Pt electrode surfaces and that polymeric films prepared in this one-step procedure are extremely efficient in preventing the permeation of the mentioned electroactive and nonelectroactive interfering substances while allowing hydrogen peroxide passage through the film. Finally, we believe that this permselective poly(o-toluidine)-coated polymer film electrode can be used as an inner/protective membrane in hydrogen peroxide-based amperometric biosensor construction.

This work was supported by the Scientific and Technical Research Council of Turkey (TÜBİTAK) (Grant No. KTÇAG-DPT-6).

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