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Investigation of polymerization parameters affecting dopamine selectivity of a polymeric membrane

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Summary

By means of electrochemical oxidative polymerization, poly (1,3-phenylenediamine) films on a gold electrode were prepared at a potential of 0.8 V. The permeation properties of polymeric films at the different thickness were investigated by cyclic and differential pulse voltammetry techniques. Voltammetric studies showed that polymeric film at the 1.2 mC thickness exhibited selective permeation for dopamine while rejecting ascorbic acid. Then, all the polymerization parameters affecting the permselective characteristics were systematically investigated and the optimal values were determined. Moreover, stability of polymeric membrane was examined. The results showed that polymeric membrane, owing to permselective character, could be used as a dopamine selective membrane.

Key words: permselective polymeric membrane; dopamine sensor

Introduction

Dopamine in central nervous systems coexists with ascorbic acid and its function is to regulate neural interactions by reducing permeability of gap junctions between adjacent neurons of the same type. A measure of this regulation is the concentration of dopamine released to the neurons. In electrochemical detection of dopamine, the presence of electroactive ascorbic acid in brain extracellular fluid reduces the sensitivity and selectivity of dopamine because its oxidation peak potential is close to that of dopamine (1). Therefore, it is very important to prepare dopamine selective polymeric membranes against ascorbic acid.

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Electrochemically prepared polymeric coatings are currently gaining considerable attention because of their novel electrochemical properties. In our previous papers, we have shown that conducting or non-conducting polymeric films such as polypyrrole, poly (*p*-phenylenediamine), polyphenols, poly (*o*-toluidine), polyindoline, polybenzidine, poly (3-methylthiophene) and polyaniline, can be successfully used for a variety of technological applications, such as an enzyme immobilization media (2-7), permselective membranes (8-10) and electrocatalysis (11-13).

Also, it has been reported that polymeric films such as nation and poly (*o*-toluidine) can be used as dopamine selective polymeric membranes (14,15).

We have previously reported the synthesis, electrochemical characterization and glucose sensor application of poly (1,3-phenylenediamine) film (16). In the present paper, we describe the electrochemical preparation, complete optimization of the polymerization parameters and voltammetric behavior of poly (1,3-phenylenediamine) film as a dopamine selective polymeric membrane.

Experimental

Materials

1,3-phenylenediamine as the monomer was purchased from Merck and used as received. All the other chemicals used such as dopamine hydrochloride, ascorbic acid and KCl were of analytical grade and purchased either from Sigma Chemical Company (St. Louis, MO, USA) or from E. Merck (Darmstadt, Germany). Aqueous solutions were prepared with doubly-distilled water. Ascorbic acid and dopamine solutions were prepared freshly for each experiment. Monomer solutions were purged by nitrogen gas for about 10 min before polymerization and polymerization solution was blanketed with the same gas during electropolymerization.

Apparatus

A BAS 100W (Bioanalytical Systems, Inc. West Lafeyette, IN, USA) electrochemical analyzer was used for polymerization, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) experiments. All electrochemical operations were made using a conventional three-electrode electrochemical cell consisting of a bare or polymer coated Au electrode (geometric area, 1. 98 mm^2) as working electrode, Ag/AgCl (BAS, MF-2063) as a reference electrode and a Pt wire coil auxiliary electrode. In the cyclic voltammetric experiments, the scan rate was 50 mV/s.

Preparation of Poly (1,3-phenylenediamine) Film

Prior to each polymerization, gold disc electrodes were polished with successively finer grades of diamond polishing compounds and aqueous alumina slurry (Johnson Matthey Catalog Comp., USA) down to 0.5 μm. Electropolymerization was carried out in deaerated aqueous solution containing 1,3-phenylenediamine as monomer and KCl as the supporting electrolyte. After the polymerization, the resulting polymeric films were rinsed with deionized water for the voltammetric measurements. Visual inspection revealed the formation of a thin and homogenous polymeric films of yellowish color on the electrode surface. For the optimization of the polymerization parameters, the DPV runs were performed in 0.1 M aqueous Na_2SO_4 (pH 6.0) containing 10 mM of dopamine or ascorbic acid.

Results and discussion

From the cyclic voltammograms obtained with a gold electrode (not shown), it was decided that monomer could be polymerized in the potential range of 0.6 - 1.0 V vs Ag / AgCl. As discussed in our previous work where Pt was employed as the working electrode (16), the decrease in the current magnitude with the subsequent scans is indicative of the formation of a non-electroactive polymeric film. On the other hand, it has been known that non-electroactive polymeric films can be used as permselective membranes. Thus, in the present work, we consider the use of the poly (1,3-phenylenediamine) film as a permselective membrane which would be selective for dopamine while preventing electroactive ascorbic acid permeation through film.

The effects of Polymerization Parameters on the Permselectivity Character

The Effects of Film Thickness and Electropolymerization Potential

Film thickness is one of the most important factors affecting the permselectivity characteristics of the resultant polymer. In order to determine the optimal film thickness, the polymeric films at desired thickness were prepared at a potential of 0.7 V by varying the charge consumed during the electropolymerization process. The values of other parameters were kept constant (monomer: 0.1 M and KCl: 0.1 M). Once the optimum value for the studied parameter was determined, the effect of the next parameter was studied at the optimal values of the already investigated parameters and at the constant values of these not yet studied. As depicted in Figure 1, from the responses to dopamine and ascorbic acid of the prepared polymer electrodes, it is seen that ascorbic acid current diminishes to zero for thickness larger than 1.0 mC and that current to dopamine rises to a maximum value at a thickness of 1.2 mC. Therefore, the optimal film thickness was chosen as 1.2 mC. Polymerization potential and concentrations of both monomer and electrolyte were optimized at this constant film thickness.

The polymerization potential dependence of polymer electrode at the optimal (constant) thickness was studied in the range of 0.6-1.0 V. Dopamine currents obtained at different potentials are presented in Figure 2. As can be seen, peak currents increased with increasing potential and reached to a maximum value at ca. 0.8 V, after which it decreased. Thus, optimal polymerization potential was found to be 0.8 V vs Ag / AgCl.

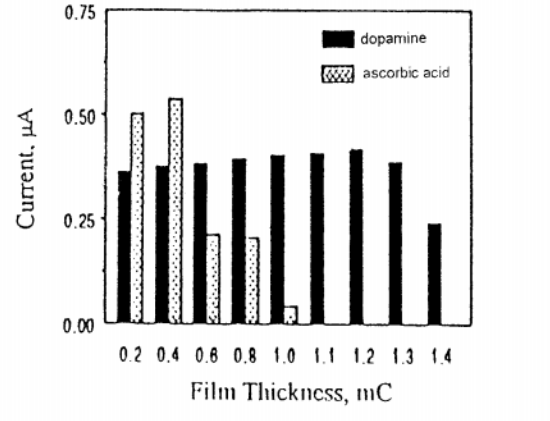

Figure 1. The effect of film thickness on the responses to dopamine and ascorbic acid.

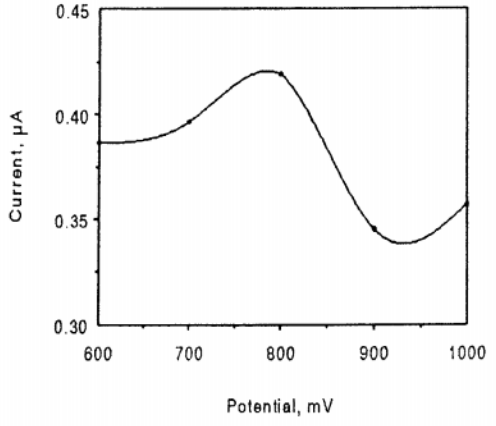

Figure 2. The effect of polymerization potential on the response to dopamine.

Effects of monomer and electrolyte concentrations

The effects of the monomer and electrolyte concentrations in electropolymerization solution on the peak currents of dopamine for polymer electrode at the optimal thickness were examined in the range of 0.05 to 0.25 M. As depicted in Figure 3 and 4, the optimal concentrations for monomer and electrolyte corresponding to maximum dopamine currents were found as 0.100 and 0.150 M, respectively. These optimal values were also suitable to enable a controllable film growth.

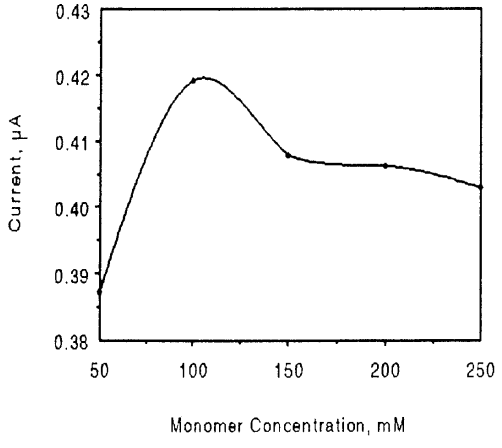

Figure 3. The effect of monomer concentration on the response to dopamine.

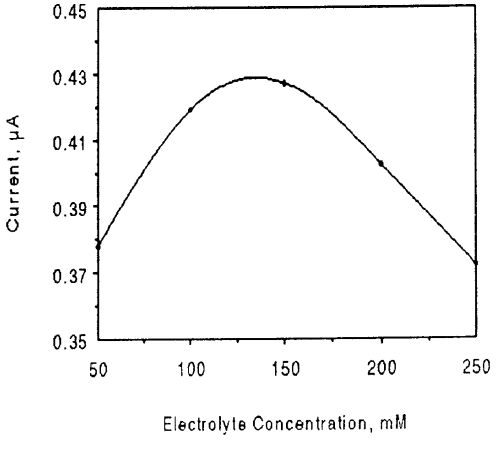

Figure 4. The effect of electrolyte concentration on the response to dopamine.

After optimization of the mentioned chemical and electrochemical variables, the optimal experimental conditions were as follows: polymerization potential; 0.8 V vs Ag/AgCl, film thickness; 1.2 mC, monomer concentration; 0.100 M and electrolyte concentration; 0.150 M. Therefore, polymer electrode prepared under the optimal conditions was used in voltammetric studies.

Voltammetric Behavior of the Optimized Polymer Electrode

The DPVs of the electroactive ascorbic acid and dopamine at the bare gold and optimized polymer electrodes are depicted in Figure 5 and 6, respectively.

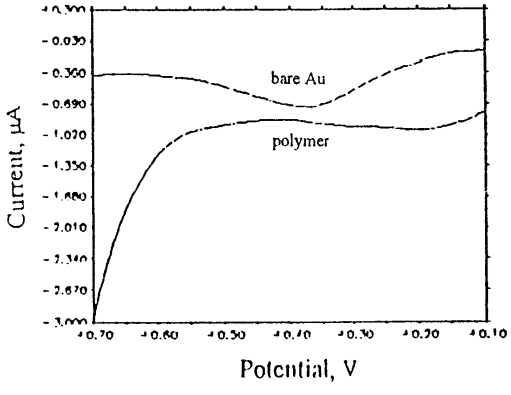

Figure 5. DPV of 10 mM ascorbic acid at the bare Au and polymer electrode.

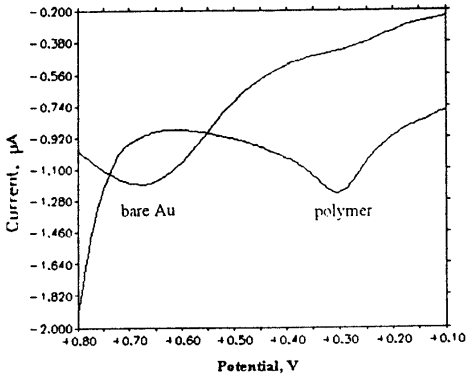

Figure 6. DPV of 10 mM dopamine at the bare Au and polymer electrode.

As can be easily seen in Figure 5, an oxidation peak (at ca. 0.40 V) observed at the bare electrode disappears at the polymer electrode. This difference on the voltammograms confirms that the optimized polymeric film suppresses ascorbic acid oxidation. On the other hand, it is clear in Figure 6 that the optimized polymeric film allows penetration of large amounts of dopamine. These permeation findings obtained with optimized polymer electrodes have also been supported by CV behaviors of ascorbic acid, dopamine and ascorbic acid plus dopamine mixture (not shown). These results show that the optimized polymeric film might be used as dopamine selective polymeric membrane in the presence of electroactive ascorbic acid.

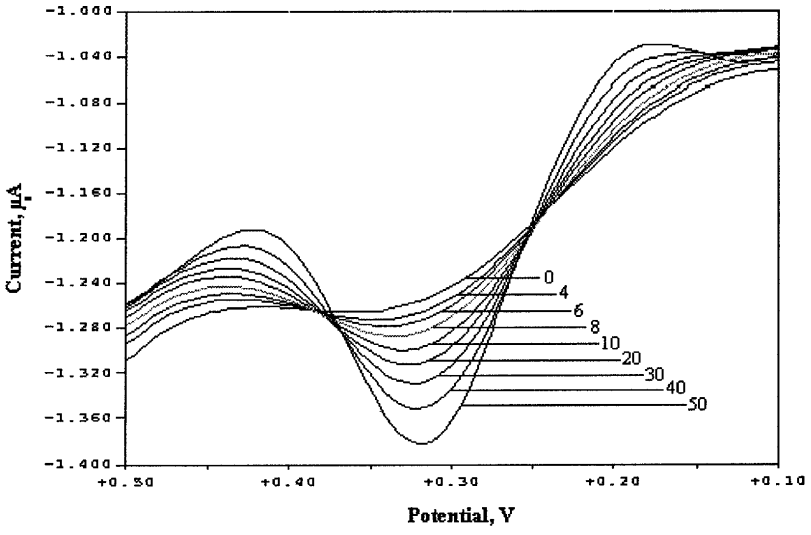

Figure 7. A series of DPVs of a mixture containing 10 mM ascorbic acid and increasing concentration of dopamine at the optimized polymer electrode.

It has been observed that dopamine peak current was unaffected from the varying concentrations of ascorbic acid (not shown). On the other hand, it has been known that ascorbic acid concentration in the extracelular fluid of the central nervous system is very high (100-500 μM), while the dopamine level is over 3 orders of magnitude smaller (17). Figure 7 shows DPVs obtained for increasing micromolar concentrations of dopamine in the presence of 10 mM ascorbic acid. From this figure, it is seen that the responses of the optimized polymer electrode to dopamine were linear in the range of 10-50 μM. Also, the limit of detection is anticipated as <5 μM. Stability of the optimized polymer electrode was tested by successfully running the same electrode in a dopamine plus ascorbic acid mixture (10 mM each). It was found that the stability of the optimized polymeric membrane was satisfactory because its response was almost unchanged for the successive runs.

As a result, we have demonstrated in the present paper that dopamine selective polymeric membrane can be easily prepared by electrochemical polymerization of the relevant monomer (one-step preparation). Cyclic and differential pulse voltammetric studies show that optimized polymeric membrane prevents ascorbic acid oxidation while allowing dopamine. From a practical point of view, these findings suggest that polymeric film can be used as dopamine selective polymeric membrane in the presence of electroactive ascorbic acid.

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