Preparation and Properties of Amperometric Uric Acid Sensor Based on Poly(2-aminophenol)

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ABSTRACT: Poly(2-aminophenol) films were electrochemically prepared on Pt electrodes at a constant potential from a deoxygenated aqueous solution of monomer dissolved in 0.1 M KCl. The uric acid selectivity of polymeric electrodes prepared at the different thicknesses was examined in the presence of ascorbic acid. The results showed that the polymeric film allows penetration of large amounts of uric acid while blocking the electrochemical activity of ascorbic acid in the potential region examined when compared with that on the bare Pt electrode. The regular and repetitive responses for uric acid were obtained even in the presence of the interfering substances such as ascorbic acid, cysteine, oxalic acid, lactose, sucrose, and urea. Moreover, the stability and the reversibility of the polymeric sensor were satisfactory. Therefore, it has been claimed that the polymeric electrode could be used as uric acid-selective membrane in the presence of the mentioned interfering species. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 406–410, 2011

Key words: electropolymerization; permselective polymer; uric acid; sensor

INTRODUCTION

It is known that uric acid is the waste product produced from the degradation of purine. In healthy human, uric acid is filtered from the blood by the kidneys and excreted into urine. The abnormal concentration of uric acid as a result of a number of kidney diseases causes the some diseases such as gout, hyperuricemia, and Lesch-Nyhan.¹ From the point of view of diagnosis and treatment of the mentioned diseases, accurate, sensitive and fast determination of uric acid is very important for the clinical chemistry.

Despite colorimetric, enzymatic and electrochemical methods have been used to detect the concentration of uric acid, the electrochemical methods have some advantages such as a higher selectivity, less costly and less time consuming than the other methods.^{2–4} In electrochemical method, the conducting/ non-conducting polymeric films have been used as sensor materials.^{5–13} One of the most important problems faced in the determination of uric acid is the presence of ascorbic acid, which is present with uric acid in biological fluids.^{14,15} Thus, an accurate analysis for uric acid becomes problem due to the fact that the oxidation peaks of the electroactive interferents are close to that of uric acid and fouling electrode surface of electroinactive interferents. In order to overcome the mentioned problem, conducting polymer electrodes have been used due to their electrocatalytic properties.^{16–20} On the other hand, in our previous papers, we have showed that chemically or electrochemically prepared non-conducting polymeric coatings could be successfully used as permselective membrane in dopamine or H_2O_2 sensor design.^{21–28} In the present article, our aim is to develop the permselective membrane to selectively determine uric acid in the presence of the interferents.

MATERIALS AND METHODS

Materials

2-aminophenol was used as received from Merck (Darmstad, Germany). All the other chemicals were of analytical grade and purchased either from Sigma Chemical Co. (St. Louis, MO) or Merck. Aqueous solutions were prepared with doubly distilled water. All the permselectivity studies were carried out in phosphate buffer saline (PBS, pH 7) solution. Ascorbic acid was prepared freshly for each measurement. The high purity of nitrogen gas was used for purg-ing/blanketing in electropolymerization.

Instrumentation

An electrochemical workstation (BAS 100B, Bioanalytical System, USA) equipped with a personal

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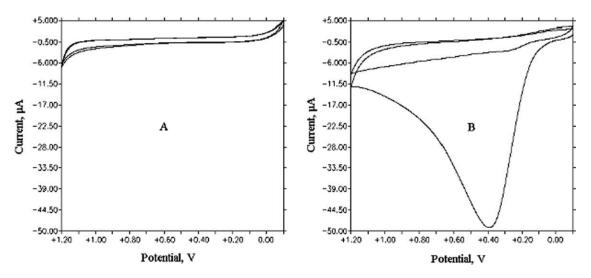


Figure 1 CVs of bare Pt electrode in the absence (A) and presence (B) of 2-aminophenol in 0.1 M KCl.

computer was used for electropolymerization, cyclic voltammetry (CV), and differential pulse voltammetry (DPV) experiments. All electrochemical studies were performed using a conventional three-electrode system consisting of a bare or polymer modified Pt working electrode (2 mm in diameter), a Ag/AgCl reference electrode, and a Pt wire coil auxiliary electrode. Before modifying, Pt working 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. All electrolysis and voltammetric experiments were made at room temperature. The DPV conditions: scan rate: 20 m Vs^{-1} , pulse amplitude: 50 mV, sample width: 17 ms, pulse width: 50 ms, pulse period: 200 ms, quiet time: 2 s.

Preparation of poly(2-aminophenol) films

Electropolymerization of 2-aminophenol was realized using a Pt working electrode at potential of 0.3 V in 0.1 M KCl solution containing 25 mM of the mentioned monomer. The monomer solution was deoxygenated by bubbling nitrogen for 10 min and maintained under nitrogen atmosphere during the electropolymerization.

After completion of polymerization, the modified electrodes were rinsed with distilled water for the subsequent voltammetric experiments.

RESULTS AND DISCUSSION

Figure 1(A,B) shows the cyclic voltammograms of the bare Pt electrode in the absence and presence of 2-aminophenol, respectively. As could be easily seen in Figure 1B, monomer started to oxidize at approximately 0.10 V and then peak current decreased quickly to almost the background level on the following potential sweeps.

This voltammogram is typical for electrochemically grown non-electroactive polymeric films and can be explained by blockage of the access of monomer to the electrode surface. The poly(2-aminophenol) is mainly a polymer of phenoxazine rings. It has been known that the films of the polymer formed in acidic media were electroconductive, but nonconductive in neutral and basic solutions.²⁹ The preparation and mechanism of the ladder-type polymer with phenoxazine rings by electropolymerization of *o*-aminophenol in aqueous medium have been studied in detail.³⁰

Although it was possible to polymerize the monomer at the higher potentials, electropolymerization was realized at a potential of 0.3 V to secure a controllable film formation at low electrolysis rate. Under these conditions, approximately 5±1 min was required for a passage of a 1.2 mC charge. Visual inspection showed the formation of thin, adherent, and homogenous-looking polymeric film with a brownish color.

Uric acid selectivity of poly(2-aminophenol) electrode

In order to examine permselectivity characteristics of the poly(2-aminophenol) films, the DPV technique was used due to its better peak resolution and current sensitivity than CV. The film thickness is one of the most important parameters affecting the permselectivity character of the polymers. By altering the amount of charge consumed during electropolymerization, it is possible to obtain poly(2-aminophenol) films at desired thicknesses.

The selectivity characteristics of uric acid and ascorbic acid at poly(2-aminophenol) electrodes were

Current, µA

-0.600

-1.140-

-1.680

-2.220

-2.760

- 3.300

- 3.840

-4.380

-4.920

-5.460

-6.000+

Figure 2 DPVs of ascorbic acid (1 mM) in PBS.

+0.60

Potential, V

+0.80

Polymer electrode

Bare electrode

+0.20

0.0

+0.40

systematically examined in the range of 0.5–2 mC. From the DPV results, it was observed that the regular and repetitive responses could be obtained at 1.2 mC. Then, the effect of the monomer concentration in the electropolymerization medium was investigated in the range of 10–30 mM. The maximal response for uric acid was obtained with the electrode coated in an electropolymerization solution containing 25 mM of 2-aminophenol. Therefore, poly(2-aminophenol) films at the thickness of 1.2 mC prepared in the presence of 25 mM monomer were used for the subsequent DPV measurements.

Figures 2 and 3 represent DPV behaviors of ascorbic acid and uric acid at the bare and poly(2-aminophenol) electrodes.

Based on the above DPV results, the direct oxidation of ascorbic acid on the bare electrode is appeared at ca. 300 mV. When compared with that of the bare electrode, it is clear that this oxidation

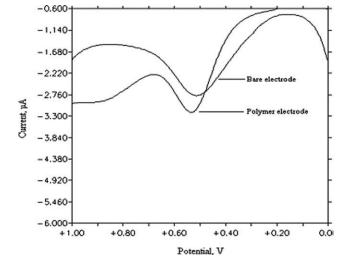


Figure 3 DPVs of uric acid (0.5 mM) in PBS.

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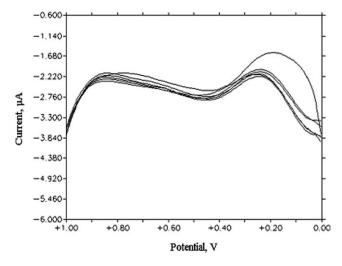


Figure 4 DPVs of the polymer electrode in increasing concentration of ascorbic acid (1–1.5 mM) in PBS (pH 7).

peak was suppressed on the polymer electrode (Fig. 2). On the other hand, Figure 3 showed that the polymer electrode had good electro-oxidation for uric acid. This voltammetric behavior reflects that interference of ascorbic acid was completely eliminated with polymeric membrane.

In order to confirm above the results, the voltammetric behavior of the polymer electrode was also examined in various ascorbic acid concentrations. As expected and depicted in Figure 4, no response was observed in increasing concentration of ascorbic acid.

The permselectivity behavior of the polymer electrode to uric acid was also investigated in the presence of interferents such as ascorbic acid, cysteine, oxalic acid, lactose, sucrose, and urea. Figure 5

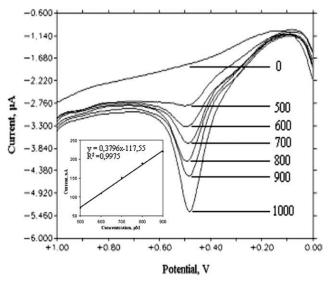


Figure 5 DPVs of the polymer electrode in increasing concentration of uric acid in the presence of interfering substances (concentration of uric acid: $500-1000 \mu$ M; interferents: cysteine, oxalic acid = 2 mM; ascorbic acid, lactose, sucrose, urea = 1 mM).

shows DPVs obtained for increasing concentration of uric acid in the presence of the mentioned interfering species and the corresponding calibration curve for the uric acid peak currents. While the concentration of uric acid is zero, no response was observed in the presence of the relevant interferents. This behavior of the polymer electrode is critical for permselective membranes. From this figure, it is also seen that peak currents increase linearly with increasing uric acid concentration even in the presence of the mentioned interferents. The amperometric peak current is linearly dependent on the concentration of uric acid in the range of 0.5–0.9 mM with correlation coefficients of 0.9975.

The stability and reversibility of uric acid sensor

The stability of sensor was examined for 0.5 mM uric acid (Fig. 6). Each bar shows the average of the results obtained from four independent experiments performed in every 3 days. The polymeric sensor was stored in PBS at room temperature when not in use. After the each uric acid test, the permeation of ascorbic acid through the polymeric film was also checked. The results showed that polymeric sensor was responded to uric acid along the two months under the defined storage conditions. Also, no response for ascorbic acid was observed. From these findings, it should be noted that the polymeric membrane was not deteriorated.

Moreover, the stable voltammograms obtained from the successive measurements (40 runs) showed that the polymeric film gave good reproducible responses during the repeated DPVs (Fig. 7).

CONCLUSIONS

By using the proposed polymer-modified electrode, it is possible to selectively determine uric acid in the presence of the interfering substances. When comparing with the literature, it was found that the polymeric electrode had some important advantages. These are as follows:

• The electrochemical polymeric sensor has been developed in the one-step procedure (easy preparation).

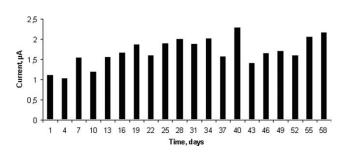


Figure 6 The stability of uric acid sensor.

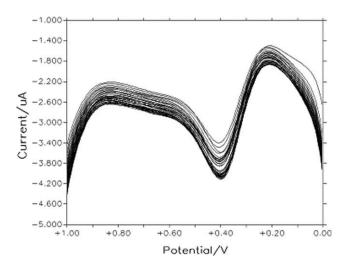


Figure 7 The reversibility of uric acid sensor.

- The period of preparation is short (only 5 min).
- The unwanted responses from ascorbic acid which is the most important interferent have been completely eliminated.
- It should also be noted that the polymeric membrane responses to uric acid over a broad range of interference. Moreover, it has been shown that the sensor response increased linearly with increasing concentration of uric acid even in the presence of the mentioned interfering species.
- The amperometric sensor has high *R*-value (0.9975).
- The stability and reversibility of the polymeric sensor are satisfactory.

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