

Preparation of Polyaniline Modified Electrode in Novel Ionic Liquid and its Application in Ion Chromatography

Ren Dandan, Jingang Xu, Xi Lingling*, and Zhu Yan

Department of Chemistry, Zhejiang University, Hangzhou 310028, P.R. China

Abstract

In this work, a promising electrochemical detector has been fabricated by immersing a glass carbon electrode (GCE) in aniline containing novel ionic liquid and scanning between -1.0 and 1.0 V for 40 cycles, and was used in ion chromatography (IC) system. The morphology of the modified electrode surface was characterized by scanning electron microscope (SEM). The polyaniline (PANI) film showed excellent electrocatalytic activity than bare GCE and provided enhanced selectivity and stability for the detection of ascorbic acid (AA). Separated by IC with phosphate buffer solution (pH = 5.2) as eluent, AA could be determined by the PANI/GCE successfully at the working potential of 0.3 V. The retention time of AA was approximately 5.75 min, and the peak shape of AA was satisfactory. The calibration curve of AA was linear ($r > 0.99$), in the range between 0.05 mg/L and 1000 mg/L and the detection limit was 23.41 μ g/L ($S/N = 3$). The proposed method was successfully applied in the detection of AA in four beverage samples. The recoveries of AA in these samples were from 92.32% to 110.57%.

Introduction

An electroanalytical technique using electrochemical sensors for the detection of redox active chemicals has received considerable interest due to its advantages in simplicity, high sensitivity, and wide dynamic range. For example, Nafion cation-exchange membrane could exchange and enrich the neurotransmitter dopamine without the interference of ascorbic acid (AA) and uric acid (1). A crown ether-modified electrode could be used for the trace analysis of Tl^+ , Ag^+ , and Pb^{2+} by coordination on the surface (2), and an enzyme electrode combined with the chemically-modified electrode with the specificity of the enzyme, it has shown wide application in the area of electrochemical biosensors (3). Recently, the sol-gel technique (4), electrodeposition (5), and self-assembly (6) to immobilize various organic and inorganic electron transfer mediators on electrode surface to prepare CME have been reported.

Conducting polymer-modified electrodes has been more attractive because it possesses several advantages in efficient electrocatalysis, sensitivity, selectivity, and a low-detection limit

for the detection of biomolecules (7). Electrochemically generated modified electrodes with conducting polymers such as polypyrrole (8–12), polyaniline (PANI) (13–16), poly (3-methylthiophene) (17–20), and polythiadiazole (21–22) etc. have been reported. Of all the electrically conductive polymers, PANI has become one of the most extensively studied conducting polymers, due to its high polymerization yield, high conductivity, and redox reversibility (13–16). Experiments showed that PANI synthesized in protonic acid solution would lose its conductivity in pH > 4 environment. This restricted its application in bioelectrochemistry, which required a neutral pH environment. To improve the chemical and physical properties of PANI, acidic groups have been introduced into PANI chains to form the doped PANI, which can maintain its electrochemical activity in neutral or basic solutions (21–25).

In this work, a promising electrochemical detector has been fabricated by immersing a glass carbon electrode (GCE) in 5 mL aniline containing 1.2 g 1-methylimidazolium trifluoroacetate and scanned between -1.0 and 1.0 V for 40 cycles at the rate of 0.05 V/s, and it was used in an ion chromatography (IC) system. Ionic liquid doped into the PANI chains improved its buffer capacity and porosity, which shifted the local pH, and also helped to improve proton transfer or charge transfer. The morphology of the modified electrode surface was characterized by a scanning electron microscope. The size of the film polymerized in neat 1-methylimidazolium trifluoroacetate were densely ordered spherical structures containing many arms, which could adhere more strongly to the surface of GCE than the PANI grains performed in inorganic proton acid solution. The PANI film showed excellent electrocatalytic activity in comparison with the bare GCE and provided enhanced selectivity and stability for the detection of certain types of redox active chemicals, such as AA, hydrogen peroxide, cysteine and so on. Taking AA as a model compound, separated by IC, AA could be determined by the PANI-GCE successfully.

Experimental

Reagents and apparatus

1-Methylimidazolium trifluoroacetate was prepared accordingly: 0.20 mol 1-methylimidazole and 10 mL water were added to a 100 mL three-necked round-bottomed flask. The mixture was cooled to -20°C under stirring. Then, 0.2 mol trifluoroacetic

*Author to whom correspondence should be addressed: email xilingling@yahoo.com.

acid was added drop-wise into the flask. The reaction mixture was stirred for an additional period of 3 h at room temperature. Then, water was removed under a vacuum (ca. 5.0 mm Hg) at 70°C for approximately 2 h. The yellowish viscous liquid was obtained and stored in a desiccator.

Aniline, cupric sulfate, and sodium perchlorate were purchased from Shanghai Shenxiang Chemical Reagent Co. Ltd. (Shanghai, China). AA was purchased from Sigma-aldrich (St. Louis, MO) and used as received. Citric acid was purchased from the First of Shanghai Reagent Factory (Shanghai, China). All other chemicals were of analytical grade. They were used as received without further purification. The phosphate buffer solutions (PBS) at different pHs were prepared using Na_2HPO_4 and NaH_2PO_4 . Citric acid at a different pH was prepared by adding a few drops of sodium hydroxide solution into a 2 mmol/L citric acid solution. Double-distilled water was used throughout the experiments. AA-standard solutions were prepared directly before use. All experiments were carried out at ambient temperature.

Electrochemical experiments were performed by a CHI832A Electrochemical Work Station (Chenhua, Shanghai, China). The workstation was controlled by CHI832 software. A conventional three-electrode system was used, which has platinum wire as the counter electrode, Ag–AgCl electrode as the reference electrode, and glass carbon disk electrode as the working electrode. A Hitachi Scientific Instruments (Tokyo, Japan) model S-4700H scanning electron microscope was used for surface image measurements. All pH measurements were performed with a Suntex model SP-701 pH meter (Jiangsu, China). The chromatographic separation was performed by Dionex ICS1500 (Sunnyvale, CA) and Dionex ED-40 electrochemical detector using TOSOH TSKgel Super IC-AZ separation column (150 mm \times 4.6 mm, i.d., Japan), Dionex IonPac AS9-HC column (250 mm \times 4 mm, i.d.), Dionex IonPac AS11 column (250 mm \times 4 mm, i.d.), Dionex IonPac AS16 column (250 mm \times 4 mm, i.d.). The workstation was controlled by Dionex Chromeleon Vision 6.8.

Electrode modification

Before modification, the GCE was polished with alumina powder (0.05 μm) on a polishing cloth, and ultrasonically rinsed thoroughly with perchloric acid (18%, w/w), ethanol and double distilled water in turn. After that, it was treated with cyclic voltammetry scanning in the range from -1.0 to 1.0 V at the rate of 0.1 V/s in 0.1 M H_2SO_4 until a stable cyclic voltammogram for a clean GCE was obtained. The PANI film modified GCE was prepared by immersing the GCE in 5 mL aniline containing 1.2 g 1-methylimidazolium trifluoroacetate and scanning between -1.0 and 1.0 V for 40 cycles at the rate of 0.05 V/s. The PANI–GCE was obtained by rinsing with distilled water and air drying for 1 h.

Chromatographic condition

Using TSKgel Super IC-AZ ion exchange column as an analytical column, PBS of pH 5.2 as eluent at a flow rate of 0.8 mL/min, AA could be determined by PANI/GCE at the applied potential of 0.3 V.

Sample treatment

Four beverage samples were examined for estimation of AA. All the samples were further diluted so that the matrix could not

damage the chromatography column, and the concentration of AA was in the linear range. The samples were then spiked with an appropriate amount of AA for experiments.

Results and Discussion

Characterization of PANI–GCE

Figure 1 shows cyclic voltammograms in the course of polymerization of aniline for 40 potential scan cycles in 1-methylimidazolium trifluoroacetate. A broad oxidation peak was observed at approximately $+0.1$ V and a reverse cathodic peak was seen at approximately -0.3 V. The peaks current increases with increasing the cycle number. It shows that the PANI film is growing on the GCE surface. On the extended scanning, the film color changes from yellow to greenish black, and finally a black polymer film is obtained.

The morphology of the PANI–GCE surface was characterized by the SEM technique. As shown in Figure 2, the PANI film was distributed uniformly on the surface of the electrode. The size of the film polymerized in neat 1-methylimidazolium trifluoroacetate was densely ordered spherical structures containing many arms, which can adhere more strongly to the surface of the GCE than the PANI grains performed in the inorganic proton acid solution.

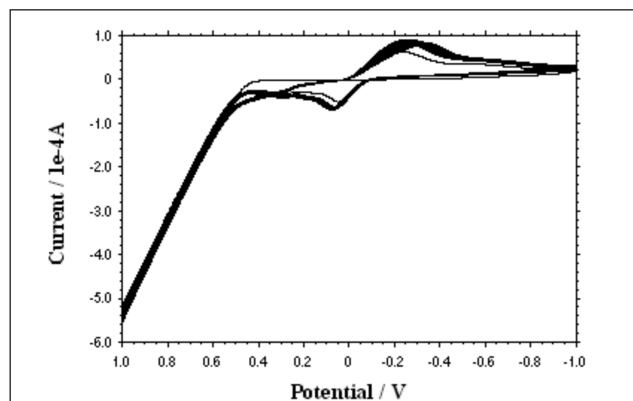


Figure 1. Cyclic voltammograms in the course of polymerization of aniline for 40 potential scan cycles in neat 1-methylimidazolium trifluoroacetate. Scan rate: 0.05 V/s.

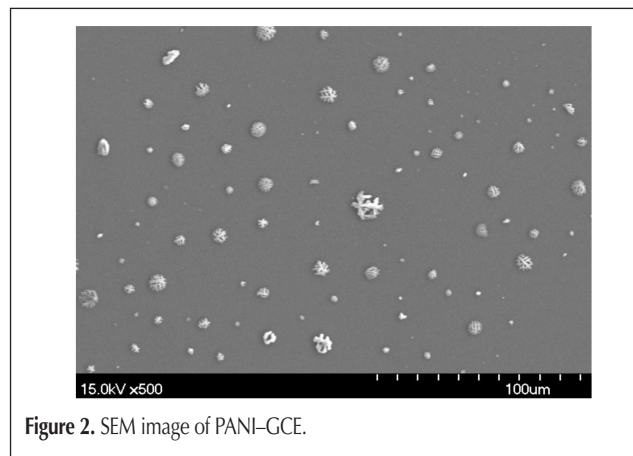


Figure 2. SEM image of PANI–GCE.

Figure 3 shows the Cyclic voltammograms of the PANI-GCE in a 0.1 mol/L PBS (pH 7.0) at different scan rates. The peak current increased as the scan rate (ν) increased, while the peak potential was practically insensitive to the change of scan rates, and the peak separation (ΔE_p) was very small. With the tested scan rate range (0.005–0.35 V/s), the peak current i_{pa} varied linearly with ν as can be obtained. This indicates that the electroactivity of the PANI film in 0.1 mol/L PBS was similar to that of the surface-attached electroactive sites (26). It was also similar to other conductive polymer modified electrodes. Moreover, the electroactivity of PANI films in neutral solutions were quite stable, in the potential range -1.0 to 1.0 V at 0.05 V/s; against repetitive 20 potential scan cycles, the films did not suffer from degradation. From this fact, it can be stated that the polymers showed reversible redox activity and highly mechanic stability in a neutral pH.

Electrocatalytic oxidation of AA

To investigate the electrocatalytic activity of the PANI-GCE, electrochemical catalytic oxidation of AA was investigated by cyclic voltammetry. Figure 4 shows the oxidation process of cyclic voltammograms at the PANI-GCE in the absence of AA and the presence of 0.5 mmol/L AA. The modified GCE gave significantly increased peak currents at approximately 0.3 V versus

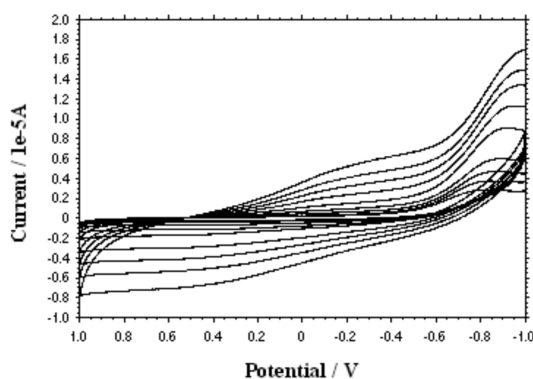


Figure 3. CVs of PANI-GC electrode in 0.1 M PBS at various scan rates. The scan rates from inner to outer are 0.005, 0.01, 0.02, 0.04, 0.08, 0.16, 0.25, and 0.35 V/s, respectively.

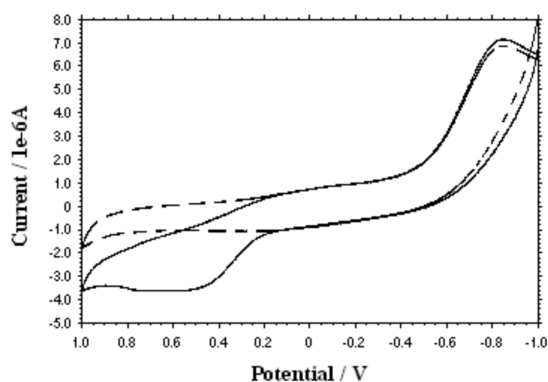


Figure 4. CVs of IL-PANI-GCE in (broken line) pH 5.2 PBS blank and (real line) 10 ppm AA solution. potential range: -1.0 – 1.0 V, scan rate: 50 mV/s.

Ag–AgCl and a fast electron transfer process to AA. At the condition of faintly acid, IL-PANI had good catalytic activity to the oxidation of AA. Moreover, the signal-to-noise (S/N) value of 10 mg/L AA on IL-PANI-GCE was ten times of that on a bare GCE by direct current amperometric detection.

The effect of different scan rates on the electrocatalytic properties of PANI-GCE towards AA oxidation have been studied. The electrocatalytic peak current increased as the potential scan rate increased. This clear shift of the peak potential occurred as expected for irreversible electrochemical reactions and a kinetic limitation in the reaction between the redox sites of PANI and AA.

The effect of column, eluent and applied potential

Using this PANI-GCE in an IC system, five types of eluents: phthalic acid (pH 5.2), citric acid (pH 6.5), citric acid (pH 5.2), PBS (pH 6.5), and PBS (pH 5.2) were examined. The influence of the pH of the mobile phase was examined using a buffer solution with pH 6.5 and 5.2. In the weak acid solution, the S/N of electrocatalytic was larger than in the nearly-neutral solution. The influence of different mobile phases were investigated, among phthalic acid, citric acid, and PBS, only PBS showed a satisfactory result in the separation of AA. Using pH 5.2 PBS as eluent, the peak shape of AA was satisfactory, with a retention time of approximately 5.75 min.

Figure 5 illustrates the changing of value of S/N of PANI-GCE for AA oxidation in the potential range from 0.1 to 0.5 V. The more positive potential applied, the higher was the catalytic activity. However, the catalytic ability decreased when the applied potential was higher than 0.3 V, the value of S/N would be increased and the selectivity of the electrode would be reduced. However, when the applied potential was higher than 0.3 V, the catalytic ability decreased, the value of S/N increased, and the selectivity of the electrode was reduced.

Using the optimized mobile phase previously described, four columns were examined: Dionex IonPac AS9-HC column (250 mm \times 4 mm, i.d.), Dionex IonPac AS11 column (250 mm \times 4 mm, i.d.), Dionex IonPac AS16 column (250 mm \times 4 mm, i.d.), TOSOH TSKgel SuperIC-AZ column (150 mm \times 4.6 mm, i.d.). The latter gave clearly better overall resolution and was the only column that allowed the separation of AA.

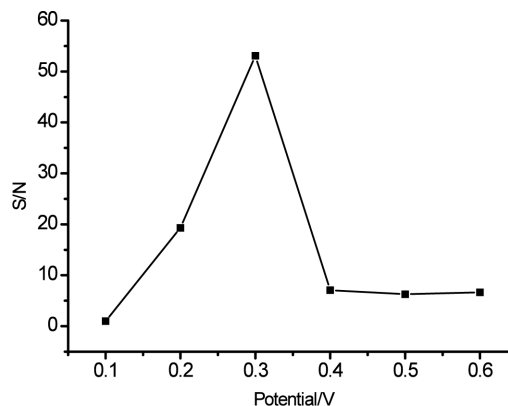


Figure 5. Effect of the applied potential.

Application in IC

Using the optimized chromatographic condition previously described, taking PBS of pH 5.2 as eluent at the applied potential of 0.3 V and the flow rate of 0.8 mL/min, AA could be determined successfully. Figure 6 shows a typical chromatogram of 1 mg/L AA. The retention time of AA was approximately 5.75 min, and the peak shape of AA was satisfactory. The calibration curve of AA was linear ($r > 0.99$) in the range between 0.05 mg/L and 1000 mg/L, and the detection limit was 23.41 $\mu\text{g/L}$ ($S/N = 3$).

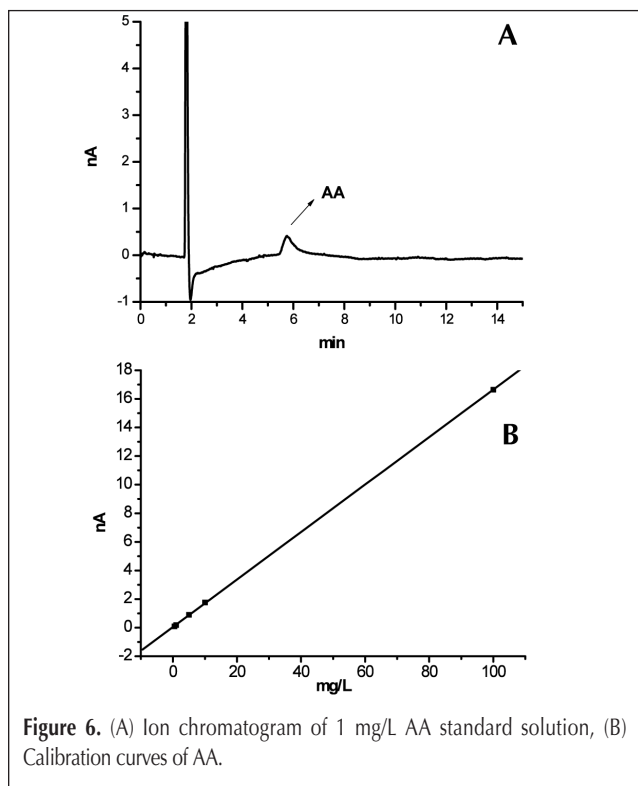


Figure 6. (A) Ion chromatogram of 1 mg/L AA standard solution, (B) Calibration curves of AA.

Samples	AA (mg/L)	RSD (%) ($n = 6$)	Recovery (%)
Fruit drink	428.30	3.50	92.32–104.24
Energy drink	56.94	0.99	94.80–110.57
Black tea	88.37	3.80	95.45–96.42
Red wine	N.D.	–	–

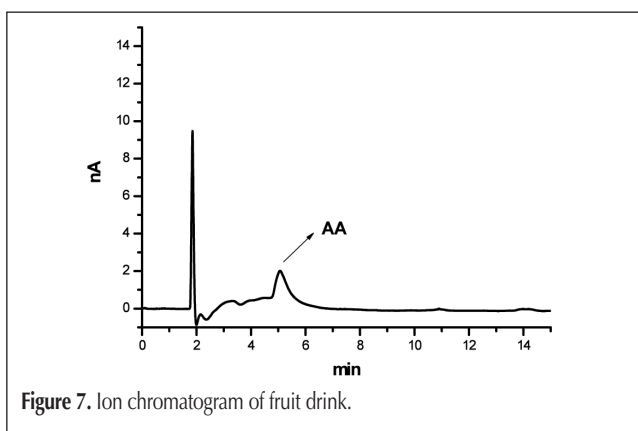


Figure 7. Ion chromatogram of fruit drink.

The proposed method described herein was successfully applied in the detection of AA in four beverages. Figure 7 shows the chromatogram of a fruit drink. The relative standard deviation (RSD) of the retention time was 0.13%, the RSD of the peak area was 0.99%. The recoveries of AA in these samples were from 92.32% to 110.57% (Table I); the recoveries and RSDs were acceptable, showing that the proposed method could be used efficiently for the determination of AA in beverages or other real samples.

Conclusion

The PANI-GCE could be easily carried out using cyclic voltammetry. The PANI-GCE modified electrode exhibits a good electrochemical activity in a faintly acid and neutral solution. This electroactive PANI film doped with ionic liquid could act as stable mediators for the catalytic oxidation of AA. Using it for detection with IC, the determination of AA was carried out at a less positive constant potential. The electrode exhibited a rapid current response and a high sensitivity. Moreover, the linear calibration curve was achieved in a wide concentration range from 0.05 to 1000 mg/L. The proposed method described herein was successfully applied in the detection of AA in four beverages. The recoveries and RSDs were acceptable, showing the method could be used efficiently for the determination of AA in real samples.

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