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RESEARCH ARTICLE

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Electrosynthesis of polyaniline in ionic liquid and its electrocatalytic properties

Abstract Ionic liquid like 1-butyl-3-methyl- imidazolium tetrafluorobrate ([BMIM]BF_4) has been used as solvent and electrolyte for the electropolymerization of aniline at glassy carbon electrode by cyclic voltammetry. Electrode modified with polyaniline (PAn) has obvious electrochemical activity in ionic liquid and acid solution (pH 0–4), and has significant electrocatalytic activity for redox reaction of catechol and hydroquione.

Keywords polyaniline, ionic liquid, cyclic voltammetry, electrocatalytic, catechol, hydroquione

1 Introduction

Conductive polymers are new kinds of materials with particular electric-conduction mechanism and electro-chromic. They would be widely applied in the research of chemical modified electrodes, storage batteries, light-emitting diodes, fixation enzymes and so on. Among a lager number of conductive polymers, polyaniline is one of the most valuable because of its anti-oxidation, excellent stability, unique doping and benign electrochemical reversibility, and easily obtainable raw material for its simple synthesis method. The electrochemical preparation and research of polyaniline are commonly used in the synthesis of conductive polymers.

Ionic liquid [1], a liquid state salt at low temperature, generally consist of organic cations and inorganic anions. They are non-volatile and non-flammable. They also have high thermal stability, chemical stability and wider electrochemistry window. Ionic liquid have been far-ranging as organic synthesis-separate process and electrochemical research. Nowadays, ionic liquids also have been applied on peculiar media for electropolymerizations. The electrochemical synthesis of conductive polymers such as polypyrrole [2–4], polythiophene [5,6], and polyaniline [7] in ionic media have been reported in some research papers. In addition, chloroaluminate ionic liquids are intractable materials and their preparation and application must be in conditions without water and oxygen. However, polyaniline is currently prepared in acidic solutions. In this paper, the electropolymerization of aniline was firstly carried out in ionic liquid [BMIM]BF_4 at normal temperature and pressure. Furthermore, it was found that the polyaniline-modified GC electrode had significant electrocatalytic activity for redox reaction of catechol and hydroquinone.

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2 Experiments

2.1 Instruments and reagents

CHI600 electrochemical work station was from Shanghai Chenhua Ltd. Saturated calomel electrodes (232 Model) were from Shanghai Precision Scientific Instrument Company Ltd. The employed glassy carbon (GC) electrode had an area of 0.074 cm^2. The platinum spiral electrode was prepared prior to use.

Aniline was distilled prior to use, a straw yellow liquid was obtained between 182℃ and 184℃. Potassium phthalate, H_2SO_4, catechol and hydroquinone were all analytical grade. Deionized water was used.

2.2 Experimental methods

Electrode pretreatment: Prior to use, the working electrode

was mechanically polished to a mirror finish, first with extremely fine sandpaper and then with 0.05 mm alumina powder. The polished surfaces were rinsed with nitric acid, acetone and water respectively in an ultrasonic bath.

A conventional three-electrode system was employed for the measurements of the cyclic voltammetry in a one- compartment cell. The working electrode was a glassy carbon, the reference electrode was a saturated calomel electrode and the counter electrode was platinum spiral wire. Ionic liquid [BMIM]BF_4 was synthesized according to the literature [8], distilled before use at 70℃.

3 Results and discussion

3.1 Electrochemical behavior of aniline

As can be seen in Fig. 1, in [BMIM]BF_4, the more concentration of aniline monomer, the higher oxidation potential and the biger current. However there was no oxidation peak (Fig. 1A) in ionic liquid without aniline. The doping peak current minished and there was no obvious film on electrode when aniline concentration was less than 0.1 mol/L, and the electrochemical properties of the polymer film electrode were favorable in potassium acid phthalate solutions (pH=4), and vice versa. This is because aniline concentration was too low, so that the monomer was oxizied to cation and to produced diphenyl aniline [9] by trail-trail dimerization. After oxidation, no good conjugate structure. The polymer film degraded during the growth of the film. The rate of degradation was bigger than that of the film growth, so there was no evident film besides only low-polymers. When the concentration of monomer was more than 0.1 mol/L, head-trail dimerization occurred and the doping peak current increased because of good conjugate structure formation. It shows that the polymer film had less reversibility when the concentration of aniline monomer was augmented in acidic solution.

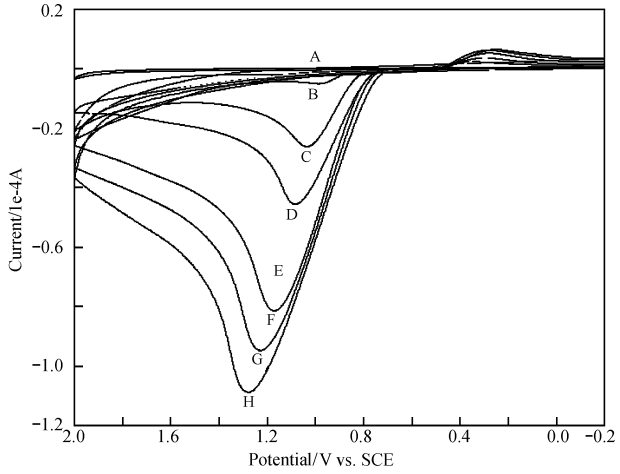

Fig. 1 Cyclic voltammograms of pure [BMIM]BF_4 (A) and aniline of various concentration on GC electrode in [BMIM]BF_4, Scan rate: 100 mV·s^{-1}, temperature: 25°C (B, C, D, E, F, G, H: 0.01, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 respectively)

3.2 Electrochemical polymerization of aniline

In Fig. 2, the oxidation peak of aniline was about 1.30 V in [BMIM]BF_4, compared with in acidic aqueous solution, oxidation potential of monomer increased, which was related to viscidity of ionic liquid. The more viscidity of ionic liquid, the higher the current at oxidative peak. Along with the reaction, the oxidation potential of monomer graduated away while the film on the electrode became thick, which was the self-catalysis of aniline. A pair of redox peak was observed at 0.15 V and 0.60 V, relative to doping and dedoping of H^+ respectively. With the polymerization of aniline, the current of redox peak increased. So the doping of H^+ increased the electricity, which indicated that polyaniline film modified electrode had electrochemical activity through doping.

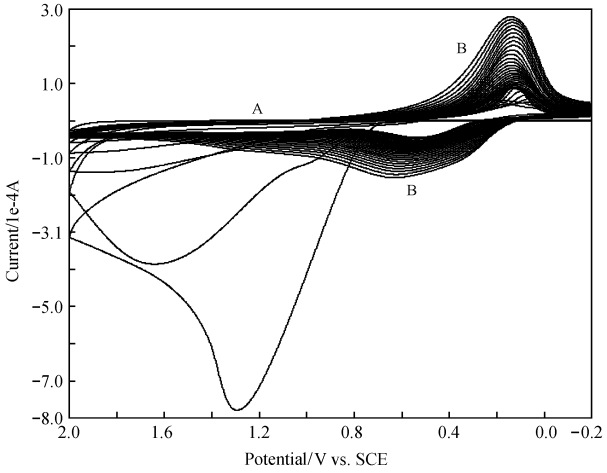

Fig. 2 Cyclic voltammograms on GC electrode in [BMIM]BF_4 in the absence of aniline (B) in the presence of aniline (0.5 mol/L), Scan rate: 100 mV·s^{-1}, temperature:25°C

3.3 Electrochemical behavior of polyaniline

It is illustrated in Fig.3 that a pair of oxidation–reduction peak of the polyaniline film modified electrode in pure ionic liquid. Peak current increased at first and then decreased. During the increasing of peak current at E_{pa}=0.70 V, E_{pc}=0.00 V, H^+ and BF_4^- taked into polymer film. The peak current increased and the oxidation peak potential was unchanged obviously. The reduction peak potential shifted to 0.5 V. To a certain extent, the inleakage of H^+ and BF_4^- became difficult, so the peak current decreased and the oxidation potential shifted to 1.2 V positively and reduction peak shifted to 0.40 V negatively.

In addition, polyaniline film modified electrode had no response in litmusless and alkalescence solution, but had preferable electrochemical response in pH=0–4 acidic solution. When the acidity was stronger (pH<2), there were pairs of peak (Fig. 4), which conformed with polyaniline film prepared in acidic solution [10]. When the acidity was

weaker (pH>2), the response of a pair of peak appear in acidic solution. That was because the doping process was related to acidity. The doping H^+ was sufficient in the strong acidic solution.

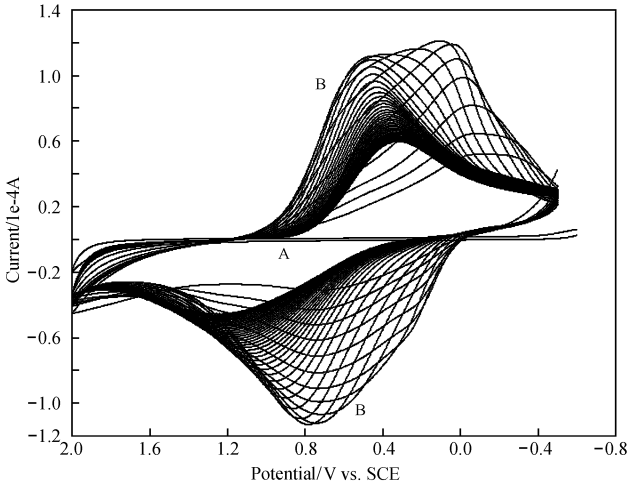

Fig. 3 Cyclic voltammograms in $[BMIM]BF_4$ on (A) GC electrode (B) GC electrode modified by polyaniline, Scan rate: 100 $mV \cdot s^{-1}$, temperature: 25℃

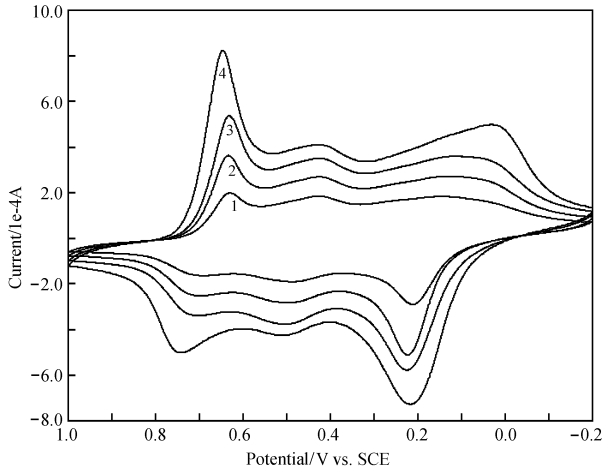

Fig. 4 Cyclic voltammograms on GC electrode modified by polyaniline in H_2SO_4 aqueous solution (pH=0) at scan rates of 10, 30, 50, 100 $mV \cdot s^{-1}$ respectively, temperature: 25℃

When acidity was feeble (pH>2), there was a pair of response of peak in acidic solutions (Fig. 5). Both anodic and cathodic peak currents were proportion to the square root of the potential sweep rate (Fig. 6A, B). This indicated that the charge-transfer processes within the film were diffusion-controlled, and the modified electrode had good repeatable response in acidic solutions.

3.4 Electrocatalysis behavior of polyaniline

Electropolymerization of aniline on the GC electrode was carried out in the solution of the ionic liquid $[BMIM]BF_4$ with monomer aniline concerntration 0.5 mol/L to form a polyaniline film modified electrode. It was shown in Fig. 7 and 8 that on the polyaniline film-modified electrode, cyclic voltammograms of 0.01 mol/L hydroquinone and catechol in H_2SO_4 aqueous solution (pH=0).

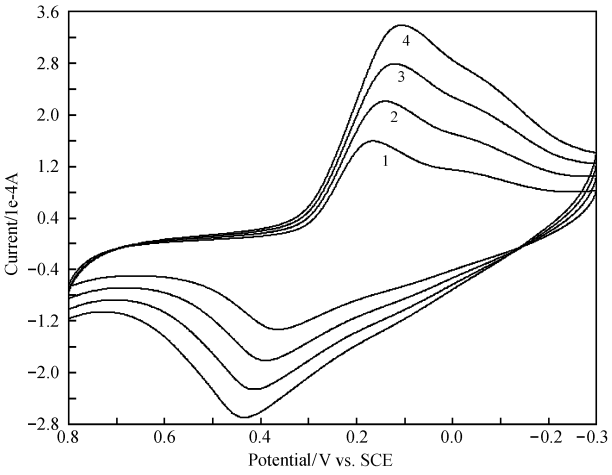

Fig. 5 Cyclic voltammograms on GC electrode modified by polyaniline in buffer solution (pH=4) at scan rates of 20, 30, 40, 50 $mV \cdot s^{-1}$ respectively, temperature: 25°C

In Fig. 7, the cyclic voltammograms of hydroquinone on GC electrode is shown, the oxidation peak potential was 0.581V, the reduction peak potential was 0.250V, ΔE=0.331V; while on the polyaniline film-modified electrode the oxidative peak potential was 0.568 V and the reductive peak potential was 0.341 V, $\triangle E$=0.227 V. The difference between the oxidation peak potential and reduction

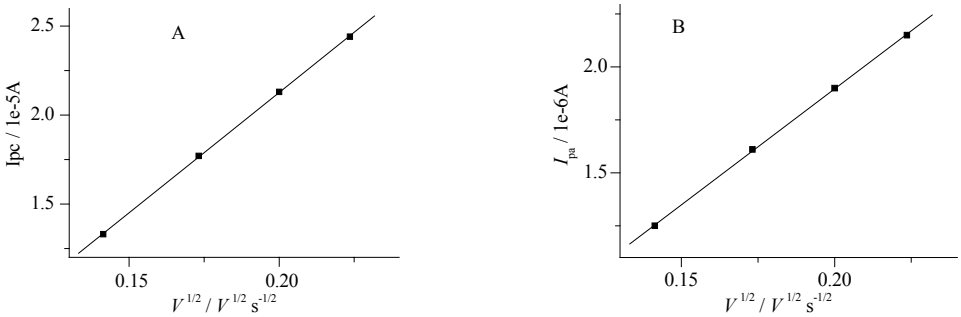

Fig. 6 (A) $I_{pc} \sim V^{1/2}$ (B) $I_{pa} \sim V^{1/2}$ curves of GC electrode modified by polyaniline in buffer solution (pH 4)

peak potential on the polyaniline film-modified electrode was less than on GC electrode, but the oxidation–reduction peak current was opposite. In chemical constituent and function groups, the catechol is similar to hydroquinone two hydroxyls and one benzene ring, but their different structure, their cyclic voltammograms were different. The electric charge density on hydroxyls on benzene ring in diphenols is biggest for hydroquinone, second for catechol and least for resorcinol. The more the electric charge density on hydroxyls, the easily the hydroxyls are oxidized, therefore the anodic peak potential of hydroquinone was less than that of catechol. On the contrary, when the oxidation product was deoxidized, the reduction peak potential of catechol was bigger than that of hydroquinone, which was approved by the cyclic voltammograms in Fig. 7 and 8.

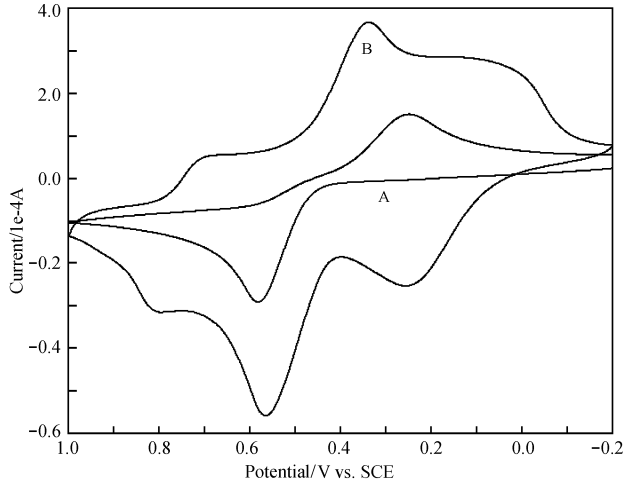

Fig. 7 Cyclic voltammograms of 0.01 mol/L hydroquione on (A) GC electrode (B) GC electrode modified by polyaniline in H_2SO_4 aqueous solution(pH=0), Scan rate:100 mV·s^{-1}, temperature: 25°C

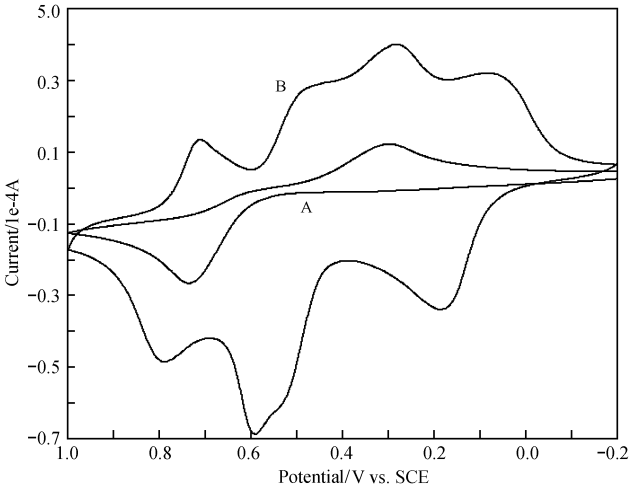

Fig. 8 Cyclic voltammograms of 0.01 mol/L catechol on (A) GC electrode (B) GC electrode modified by polyaniline in H_2SO_4 aqueous (pH=0), Scan rate:100 mV·s^{-1}, temperature: 25°C

Figure 8 also indicated cyclic voltammograms of 0.01mol/L catechol on GC electrode in H_2SO_4 aqueous solution (pH=0). The oxidation peak potential was 0.736V, the reduction peak potential was 0.297 V, ΔE=0.439V. For polyaniline film-modified electrode, the oxidation peak potential on GC electrode was 0.590V, the reductiong peak potential was 0.280 V, ΔE=0.310V, so the peak potential difference on GC electrode was less than on polyaniline film-modified electrode, and the current of oxidation- reduction peak was opposite. From Figs. 7 and 8, other peaks besides the response peaks of catechol and hydroquinone. Polyaniline film-modified electrode participated in the redox process of these two diphenols during its doping of H^+.

In the electrocatalytical oxidation of the two diphenols, the hydrogen bonds between PAn and polyphenol compounds were formed, so that the hydroxyl bond in polyphenols was weak and the concerned electrons could be transferd easily through N···H-O or $\mathrm{N}\cdots\mathrm{H}^{+}-\mathrm{O}$ bonds. At one time, the porous structure of the film augmented the interface between polyphenol compounds or oxidation outcome and the polyaniline film-modified electrode, which resulted in the improvment of adsorption properties and catalysis of PAn film on electrode. Thus the catalytic process was a synergic reaction including electric charge transfer catalysis and chemical catalysis [11], therefore polyphenol compounds could participate easily in the oxidation-reduction reaction

4 Conclusions

Aniline has been electropolymerized in the ionic liquid [BMIM]BF_4. The polyaniline film modified electrode has perfect electrochemical responses in acidic solutions (pH=0–4). The charge-transfer processes within the polyaniline film was controlled by diffusion in potassium phthalate solutions (pH=4). The polyaniline film has perfect catalysis to catechol and hydroquinone. The polyaniline film prepared in ionic liquid has perfect electrochemical response, which can be applied to catalyze other oxidation-reduction reactions. The concerned properties of the polyaniline film are being researched further.

References

1. Shi Jiahua, Sun Xun, Yang Chunhe, Gao Qingyu, Li Yongfang, Advance in Research of Room Ionic Liquids, Huaxue Tongbao (in Chinese), 2002, 4: 243–250
2. Pickup P. G., Osteryoung R. A., Electrochemical polymerization of pyrrole and electrochemistry of polypyrrole films in ambient temperature molten salts., J. Am. Chem. Soc.,1984, 106: 2294–2299
3. Pickup P. G., Osteryoung R. A., Charging and discharging rate studies of polypyrrole films in aluminum chloride:1-methyl-(3-ethyl)imidazolium chloride molten salts and in acetonitrile, J. Electroanal. Chem.,1985, 195(2): 271–288
4. Sekiguchi K., Atobe M., Fuchigami T., Electropolymerization of pyrrole in 1-ethylimidazolium trifluoromethanesulfonate room temperature ionic liquid, Electrochem. Commun., 2002, 4:

881–885
5. Janiszewska L., Osteryoung R. A., Electrochemistry of polythiophene and polybithiophene films in ambient temperature molten salts, J. Electrochem. Soc., 1987, 134(11): 2787–2794
6. Shi J. H., Sun X., Yang C. H., et al. Electrochemical Synthesis of Polythiophene in an Ionic Liquid. Chin. Chem. Lett., 2002, 13(4): 306–307
7. Koura N., Ejiri H., Takeishi K., Polyaniline secondary cells with ambient temperature molten salt electrolytes. J. Electrochem. Soc., 1993, 140(3): 602–605
8. Suarez P. A. Z., Dullius J. E., Einloft S., et al. The use of new ionic liquids in two-phase catalytic hydrogenation reaction by rhodium complexes. Polyhedron, 1996, 15(7): 1217–1219
9. Dong Shaojun, Che Gangli, Xie Yuanwu. Chemical modified. Beijing: Scinence Publish company (in Chinese), 2003: 347–362
10. Noufi R., Nozik A. J., White J., et al. Enhanced stability of photoelectrogenerated polyaniline films. J. Electrochem. Soc., 1982, 129(10): 2261–2265
11. Diaz A. F., Kanazawa K. K., Gardin G. P., Electrochemical polymerization of pyrrole., J. Chem. Soc. Chem. Commun., 1979, 14: 635–636